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The Effects of Fire on Organic Functional Groups of Peat in Relation to Water Content

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ABSTRACT

The aim of this research was to study the decline of organic functional group through the process of burning in peat. In addition, this study was also to examine the relationship between water content in peat and organic functional group after combustion (burning). Peat drying was conducted in an oven at a temperature of 75°C with the interval of 0, 1, 2, 3, 4, 5 and 6 hours. Each time interval had three replicates within two sets of experiments so that the total number of samples were 42 (experimental units). Variables measured were moisture content, total acidity, COOH groups, and OH-phenolate. The relationship between the water content with total acidity, COOH groups and OH-phenolate were determined by the equation y = bx + a. The results showed that the relationship between the water content with organic functional group was linear. While the relationship between peat water content with organic functional group after burning was irregular, although water levels through the process of burning have been greatly reduced.

Keywords: Burning peat, organic functional groups, water content

INTRODUCTION

Forest fires in Indonesia are not only regional catastrophic events, but also a global one which affect neighboring countries. In addition, the burning will cause global warming due to gases such as CO_2 emitted into the atmospheres (Adinugroho *et al*. 2005; Dise 2009).

Wildfires are not just happening on dry land, but also in wetlands, including peatlands. Peat fires occur naturally or by human negligence. Naturally it is usually due to the heat generated by rocks and other objects that can store and dissipate heat so it can burn twigs and dried leaves spontaneously. In addition, the friction between the dry twigs by wind also generate sparks (Kurnain 2004). One of human induced factors is the opening of peatlands by making channels or ditches on a large scale so that the peat loss its water content (Adinugroho *et al*. 2005; Baisley 2012, Waddington *et al*. 2014). As a result, peat will dry and very easy to catch fires (Baisley 2012; Wichtmann *et al*. 2013).

Haris (1998) stated that excessive drying will likely damage the bonding structure of water and peat colloids. This situation means that at irreversible drying phase, the structure of the physical bonding between water and organic colloids has been damaged. Intensive drying of the peat will accelerate the maturation process of the material to make the peat surface lose the ability to bind water (hydrophobic) so at high temperatures peat becomes flammable (Suryadi *et al.* 2003). Moreover, Nugroho (2002) stated peat drying was limiting the capacity of burning in line with Suryadi *et al.* (2005).

A description of chemical bonds in water after peat fires is the last hope in assessing a material's ability to absorb water. The presence or absence of water can be predicted through the alteration on chemical properties (total acidity, COOH groups and OH-phenolate) from peat fires. Haris (1998) concluded that the drying of peat did not change the chemical properties of peat soil, although the water content had been mostly reduced. The total acidity and OH-phenolate tended to have positive correlations with peat water content, but the COOH groups did not have any significant relationships.

Therefore, it is crucial to know how far the influence of burning on organic functional group of peat. Moreover, it is also important to know the relationship between peat water content and its organic functional group after the burning process.

The objective of the research was to determine effect of fire on organic functional group such as total acidity, COOH groups, and OH-phenolate and their relationships. These parameters play an important role in water re-absorption. This research was using pristine peat soil in order to know the moisture content prior to burning process, so that they can be related to the decline of organic functional group.

MATERIALS AND METHODS

Sampling Preparation

This research was a causal-comparative one, which focuses on the changes in the physico-chemical properties of peat as a result of drying and burning. Samples were taken by hand at a depth of 0-60 cm for a preliminary analysis such as ash content (%), bulk density (g cm^{-3}), and field water content (%). These analyses provided an overview of the maturity level of peat.

Then, peat was sieved with a 2 mm siever and then analyzed for water content (%), total acidity (me g^{-1}), COOH group (me g^{-1}), and OH-phenolate (me g^{-1}). The determination of peat water content by a gravimetric method which was based on water loss by weighing 5 g of peat into several aluminum cups and kept them in the oven at 75 °C with intervals of 0, 1, 2, 3, 4, 5, and 6 hours. Once finished, samples were kept in desiccators for cooling and further analyses.

Experimental Setup

The first set of experiment had 21 samples which were randomly chosen and grouped into seven experimental group of treatments. In every aluminum cup, 2 g of wet peat was weighted and put into an oven of 105° C for 12 hours. Once the drying was completed, all samples were kept in desiccators for cooling and further steps of experiment.

The second set of experiments (another 21 samples) were also treated as the first set but it would undergo combustion process. Burning process was conducted by adding 10 mL of ethanol 95% to each sample cup. Sample then was burned by stirring with a porcelain spoon to make the burning even. Sample cup was clamped during stirring. The burning process was completed when the fire extinguished itself.

Water content was determined by the formula:

$$\%\,\text{WCP} = \frac{\text{WWP} - \text{WODP}}{\text{WODP}} \times 100\%$$

where: WCP = water content of peat; WWP = weight of wet peat; and WODP = weight of oven dried peat.

Determination of total acidity using the method of Schnitzer (1972) by adding two g of peat into 100 mL Erlenmeyer with 20 mL of 0.2 *N* $Ba(OH)_2$. The air inside Erlenmeyer was replaced with N_2 gas and closed tightly. The mixture was shaked for 24 hours, then titrated with 0.5 *N* HCl while N_2 gas flew inside up to pH 8.4 (using pH electrode). Total acidity was calculated using the following equation:

$$\text{total acidity}\left(\frac{\text{me}}{\text{peat gram}}\right) = \frac{(\text{Vb-Vs}) \text{ x N}}{\text{peat gram}}$$

where: Vb = blank volume; Vs = sample volume; and *N* = normality HCl.

Carboxyl-group was determined with the Ca-acetate method (Stevenson 1994) by adding two g peat into a 100 mL Erlenmeyer with 10 mL of 1 *N* Ca $(CH_3COO)_2$. Forty mL of distilled water was added and shaked for 24 hours. Titration of the solution was obtained with 0.1 *N* NaOH up to pH 9.8 (using pH electrode). Acetate-group was calculated using the following equation:

$$\text{COOH group}\left(\frac{\text{me}}{\text{peat gram}}\right) = \frac{(\text{Vs-Vb}) \text{ x N}}{\text{peat gram}}$$

where: Vs = sample volume; Vb = blank volume; *N* = normality NaOH.

Functional group of OH-phenolate was determined using the difference between the total acidity with an equivalent amount of COOH groups. OH-phenolate was calculated using the following equation:

$$\text{OH} - \text{phenolat}\left(\frac{\text{me}}{\text{peat gram}}\right) = \text{Total acidity} - \text{COOH group}$$

Three replication was conducted to reduce the level of error. The scheme is described simply in Figure 1.

Data Analyses

Regression analyzes were conducted on each physical parameter (moisture content) and peat chemistry (total acidity, COOH groups and OH-phenolate) by using SigmaPlot (Jandel Scientific 2010). The relationship between the water content of peat with total acidity, COOH groups, and OH-phenolate due to the drying and burning was calculated with the equation below:

$$y = bx + a$$

where: a and b = constants, x = independent variables.

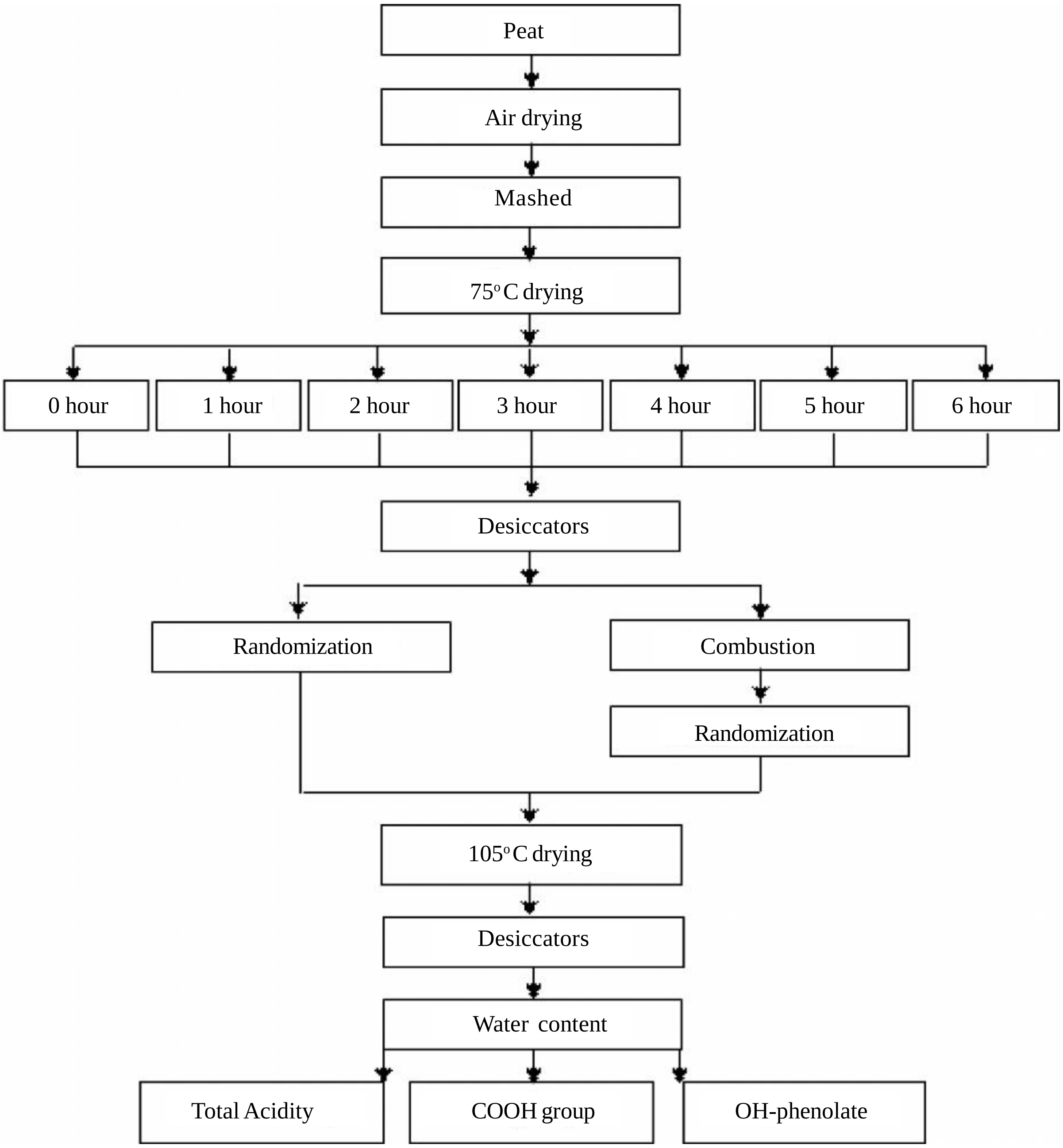

Figure 1. Trial scheme

RESULTS AND DISCUSSION

The results of field observations and preliminary analysis of the peat showed that the samples were hemic in maturity (Adinugroho *et al*. 2005), as presented in Table 1. Hemic peat ash content of 1.42%, means that the material losses after ignition was 98.58%. It also mean that soil samples can be classified as peat soils. Ash content on hemic peat was less than that of sapric, but larger than that of fibric. Peat which was partially decayed further has a greater ash content, because during the decomposition of peat C as CO_2 and CH_4 will be emitted into the air, so that the ratio of bases (mineral elements) with organic-C will be higher (Prasetyo 1996). Decomposition and moisture can also affect peat bulk density. Low bulk density of 0.19 g cm^{-3} shows that the rate of peat decomposition was at the level of medium. Saturated peat moisture content reflects the maturity of peat. Hemic peat water content was smaller than fibric peat water content,

Table 1. Initial properties of peat

Peat Property	Value
Ash content (%)	1.42
Bulk density ((g cm^{-3})	0.19
Saturated water content (%)	519.57

but higher than that of sapric peat. Saturated water content of peat also reflects the water holding capacity and it can be calculated based on the oven dry weight of 105°C (Noor 2001).

Water Content

The results showed that the declining trend of water content due to oven drying varied from 25.53 to 255.46%. Meanwhile, the average water content due to burning was lower than that of drying process. The average water content from burning peat also had a declining trend, ranged from 3.89 to 24.44%. The details of average moisture content due to the drying and burning can be seen in Table 2. Both drying and burning processes decreased peat water content. This suggest that the longer the drying process the weaker the resistance to drought. This condition will affect the physico-chemical properties of peat, especially water retention and chemical reactions. In other words, drying and burning processes causing total acidity, COOH groups, and OH-phenolate will not function properly to create hydrophilic behavior. Hence, there was a strong relationship between those parameters with peat irreversible drying (Utami *et al.* 2009)

Theoretically, Volarovich and Churaev (1968) in Haris (1998) classified the bond between water and peat into three major classifications, *i.e.* mechanical, capillary, and chemical bonding. Water in mechanical and capillary bonding can be removed by using pressure. They are related to the equivalent energy required to move a mass of water. However, to remove water in chemical bounding requires immense energy or even impossible. The equivalent energy required to remove water in chemical bonding is about 1 kJ mole^{-1} (0.24 kcal mole^{-1}), similar to a pressure of 5 × 107 pa (500 ATM). The above theory gives information about the very low content of water due to drying and burning processes when compared to current levels of natural water-saturated peat.

The low content of water is due to the physical stability of colloids which are affected by the process of drying and burning. The impacts on the physical stability of colloidal structures will cause the bonding between water and colloidal peat are disrupted. These changes negatively impact the initial hydrophilic to hydrophobic (Novriani and Rohim 2009). Decreased ability to absorb water from drying and burning is a result of the destruction of organic functional groups which also water binder groups.

Total Acidity

Determination of total acidity due to the drying and burning processes was performed using the method of Schnitzer (1972). The results showed that the average of total acidity due to the drying process was declined by time intervals, ranging from 2.34 to 4.74 me g^{-1} (Table 3). While the average total acidity from burning process had no regular relationships, probably due to the damage on total acidity properties of peat. The highest average total acidity from burning process was 2.32 me g^{-1}, while the lowest average was 1.98 me g^{-1} (Table 3). The relationship between water content and total acidity in samples with drying process tended to be linear (Figure 2), while in samples with burning process were irregular (Figure 3). This means that the decrease in water content due to drying process resulted in a decrease of the total acidity and fit the equation $y = 0.010x + 1.926$ ($R^2 = 0.982$). However, this decline was not found in samples with burning process.

COOH Group

Determination of COOH group was performed by Ca-acetate method (Stevenson 1994). The results showed that the drying process decreased COOH group by 2.17 to 1.51 me g^{-1}. Meanwhile, the burning process showed no pattern of relationship. The burning process showed a significant irregularity to

Table 2. Water content due to drying and burning processes

Treatment (hour)	Water content drying (%)	Water content due to burning (%)
0	255.46 ± 1.70	24.44 ± 3.90
1	215.66 ± 1.40	17.86 ± 4.81
2	201.34 ± 10.22	14.80 ± 2.07
3	175.54 ± 4.16	10.37 ± 0.62
4	146.07 ± 18.29	8.69 ± 2.93
5	115.85 ± 9.38	5.97 ± 0.24
6	25.53 ± 4.44	3.89 ± 0.98

Table 3. Total acidity due to drying and burning processes

Treatment (hour)	Water content drying (%)	Water content due to burning (%)
0	4.74 ± 0.09	2.32 ± 0.07
1	4.32 ± 0.04	2.20 ± 0.09
2	4.14 ± 0.13	2.14 ± 0.04
3	3.81 ± 0.06	2.41 ± 0.08
4	3.42 ± 0.26	2.02 ± 0.06
5	3.01 ± 0.12	1.98 ± 0.01
6	2.34 ± 0.08	2.42 ± 0.03

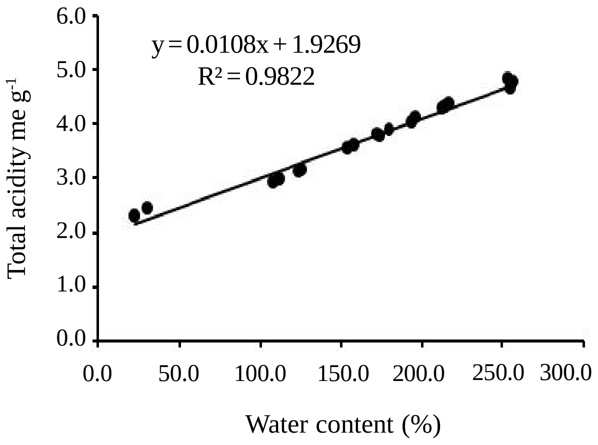

Figure 2. The relationship between peat water content and total acidity in samples with drying process.

the nature of the damage on COOH group. The lowest COOH groups in burning process was 0.36 me g^{-1}, while the highest was 0.99 me g^{-1}. The acetate group data for samples with the drying and burning processes are presented in Table 4. The relationship between water content and COOH group in samples with drying process is presented in Figure 4, while in burning process is presented in Figure 5. Figure 4 shows linear relationship and fit the equation y = 0.002x + 1.561. This means that the decrease in water content in samples with drying process tended to reduce COOH group. However, the pattern of this reduction was not found in samples with burning process.

OH-phenolate

Determination of OH-phenolate was performed by using the difference between the total acidity and equivalent amounts of COOH groups (Haris 1998). The results showed that OH-phenolate was declined due to drying process, varying from 0.83 to 2.97 me g^{-1}. Meanwhile, OH-phenolate showed no pattern of relationship in the burning process. In

Table 4. COOH groups due to drying and burning processes.

Treatment (hour)	Water content drying (%)	Water content due to burning (%)
0	1.77 ± 0.15	0.99 ± 0.03
1	2.11 ± 0.05	0.36 ± 0.10
2	2.17 ± 0.13	0.40 ± 0.06
3	2.07 ± 0.06	0.62 ± 0.08
4	1.93 ± 0.14	0.49 ± 0.14
5	1.76 ± 0.04	0.71 ± 0.16
6	1.51 ± 0.05	0.84 ± 0.15

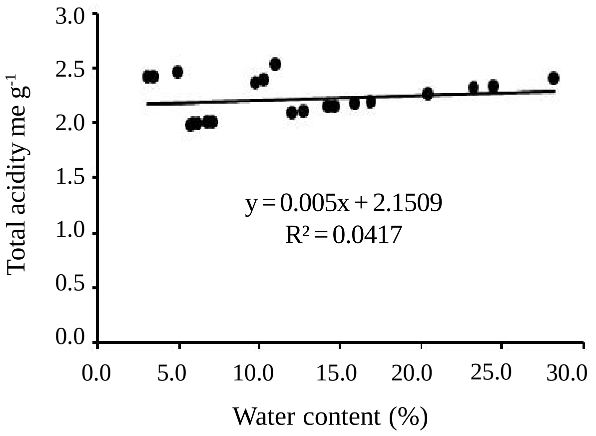

Figure 3. The relationship between peat water content and total acidity in samples with burning process.

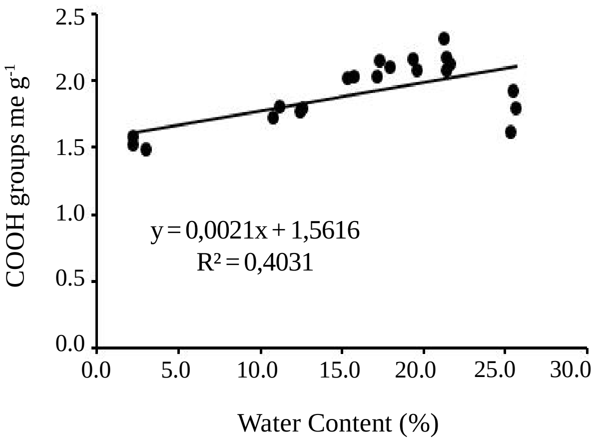

Figure 4. The relationship between peat water content and COOH group in samples with drying process.

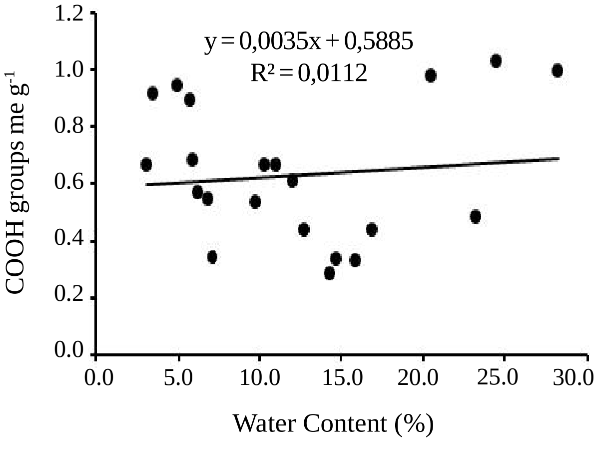

Figure 5. The relationship between peat water content and COOH group in samples with burning process.

other words, the burning peat samples had a significant irregularity to the OH-phenolate characteristics. The highest OH-phenolate in the burning process was 1.84 me g^{-1}, while the lowest was 1.27 me g^{-1}. The data of OH-phenolate for both drying and burning processes are presented in Table 5. Figure 6 shows the relationship between peat water content and OH-phenolate, which is linear in nature, $y = 0.008x + 0.365$ ($R^2 = 0.882$), limited, but peat soil can maintain chemical properties (Haris 1998).

The relationship between peat water content and organic functional group in samples with burning process was not performed as of drying process. However, it was predicted that burning process did not completely destroy the nature of the organic functional groups. Irregular relationship between those characteristics might be due to the partial decomposition of the organic compound structure during drying, but completely damaged in burning process. In addition, burning process in this research, and in nature to be specific, was not evenly distributed in changing the peat substrate. This might cause the moisture variability and differences in micro propagation of heat from the burning peat.

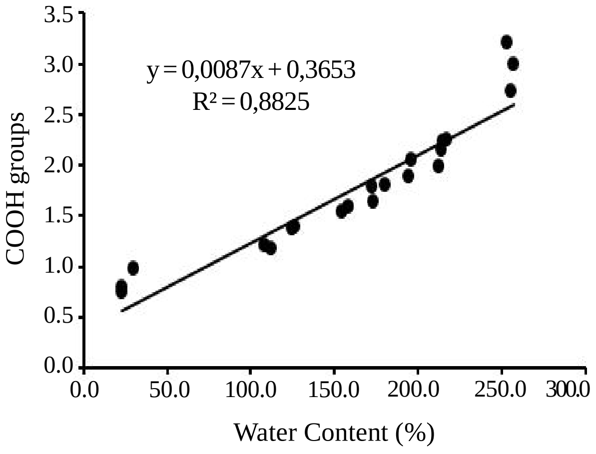

Figure 6. The relationship between peat water content and OH-phenolate in samples with drying process.

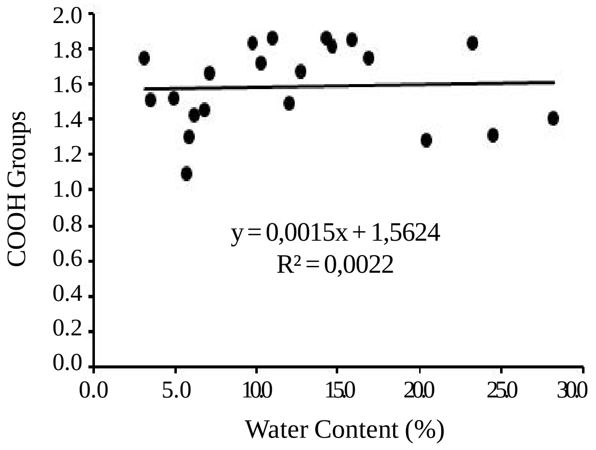

Figure 7. The relationship between peat water content and OH-phenolate in samples with burning process.

Table 5. OH-phenolate due to drying and burning processes.

Treatment (hour)	**Water content drying (%)**	**Water content due to burning (%)**
0	2.97 ± 0.24	1.33 ± 0.06
1	2.21 ± 0.06	1.84 ± 0.02
2	1.96 ± 0.08	1.73 ± 0.07
3	1.74 ± 0.09	1.80 ± 0.08
4	1.49 ± 0.12	1.53 ± 0.11
5	1.25 ± 0.11	1.27 ± 0.17
6	0.83 ± 0.12	1.58 ± 0.14

CONCLUSIONS

The declining trend of peat water content due to variations in oven time. Meanwhile, water content in the burning process were lower than that of drying process. The relationship between peat water content and organic functional group in samples with drying process was linear which meant that the decrease in water content causing the decrease in organic functional groups. The relationship between peat water content and organic functional group was not recorded in samples with burning process, even though the water contents had been reduced to the minimum. It is recommended to conduct the burning process with regulated furnace in order to burn the peat samples homogenously.

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