Analysis of FTIR spectroscopic data to observe hydrophilic and hydrophobic levels of peat in hemic and sapric maturity

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Abstract. Naturally, peat soils are hydrophilic, which means they have high water holding capacity. However, due to land conversion, wildfires and land clearing, natural condition of peat soils is disturbed so they become hydrophobic. Under hydrophobic condition, peat loses its water-loving character; this is irreversible because in anaerobic conditions, peat compounds will be degraded, which causes carboxylate and phenolic functional groups not functioning. It is characterized by peat buoyancy of peat when wet. To observe hydrophilic and hydrophobic peat characters when the limit for this change is reached, FTIR spectrum was observed. This study aimed to observe composition of hydrophilic and hydrophobic peat functional groups through FTIR spectrum. Observations were made on peat soils originating from Padang Island and Tebing Tinggi, Riau with hemic and sapric maturity levels. Results showed that FTIR spectrum of hydrophilic hemic and sapric maturity levels had a wider area of hydroxyl group and carboxylate ions than hydrophobic peats. Width of the area was due to high humidity. The level of peat maturity does not affect the change in peat functional groups.

1. Introduction

The world consists of 400 million ha peatlands or about 3% of the Earth's landmass. Peatlands are formed from piles of plant remains, such as grass, moss, trees and animal bodies that have accumulated and decayed over thousands of years. The process of tropical peat formation in Indonesia is estimated to have occurred since 6,800-4,200 years ago [1]. Peat has many functions, one of which is the ability to hold water (hydrophilic), so that it serves as a source of water [2].

Based on its maturity level, peat is classified into three types, namely fibric, hemic, and sapric. Different peat maturity causes variation in the ability to retain and hold water. Under natural conditions, fibric peat has a water holding capacity of 4.5 – 20 times of its dry weight. Meanwhile, hemic peat has a water holding to 4.5 – 8.5 times and sapric peat has a water holding to < 450% of its dry weight [3]. High ability of water holding capacity of peat soils is caused by very high content of peat organic matters (>70%) and large porosity (>80%) [4]. Sapric peats can hold higher amount of water than fibric peats, but sapric absorbs less water than fibric [5]. Fibric peats contain higher OH-phenolic groups [6, 7] and higher cellulose as a hydrophilic component [8].

Cultivation activities and construction of drainage systems have changed the function of peatlands. In 2009, around one-third of global wetland areas had been lost [9] and this loss continues at a rate of 1% per year. The decline in tropical peatland areas is much faster (20% per year) [10]. Due to the use of...
peatlands with no attention to conservation rules, peat can be irreversibly dried. It causes hydrophilic property of peat to change to hydrophobic; that is unable to hold water as before.

Hydrophobic character is influenced by humic acid in the form of waxy membrane and the presence of nonpolar groups such as ethyl, methyl, and aromatic compounds [11]. According to Nugroho and Widodo [5], peat soils decrease in porosity if they run into continuous drying. Porosity is related to the level of peat decomposition. Porosity of fibric peat was about 88%, while sapric had around 82.60% [12]. Once porosity decreases, peats lose their ability to hold irreversible water. According to Valat et al. [11] on woody peat types, the nature of hydrophobic is characterized by large contact angle between solids and liquids compared to sphagnum peat types, and the wrinkle is irreversible. Furthermore, Masganti et al. [13] reported that hydrophobicity of sapric peats appeared when it was dried for 7 hours 30 minutes at a moisture level of 54.89%. Hydrophobicity arises due to the decrease in total acidity, carboxyl groups and phenolic hydroxyl content.

To determine hydrophilic and hydrophobic characters with hemic and sapric maturity levels, especially the limit for the change in properties is reached, Fourier Transform Infrared (FTIR) spectrum was observed. This allowed further understanding of composition of functional groups. This study aimed to observe this composition among hydrophilic and hydrophobic peat functional groups at hemic and sapric maturity levels.

2. Methodology
Peat soil samples were collected from two locations on Padang Island and Tebing Tinggi, Riau Islands. Peat soils, with hemic and sapric maturity levels, were taken with a peat auger and were evaluated on-site manually based on their color and structure. Hemic peat is generally brown, while sapric peat is usually dark brown to black. Leftovers in hand determines peat’s maturity levels; hemic keeps about 50%, while sapric mostly (more than two thirds) oozes out the soil. Hydrophilic samples were peat soils taken as their original condition. Hydrophobic samples were ± 5-day air-dried peat samples.

Soil samples were analyzed in the soil laboratory of the Faculty of Agriculture, Gadjah Mada University, Yogyakarta. Peat samples were formed into pellets and were analyzed for their constituent groups using an FTIR spectrophotometer. Observations were carried out at wavenumbers of 500-4000 cm\(^{-1}\). Results of the analysis were interpreted according to Flaig et al. [14].

3. Results and discussion

3.1. Results
Soil moisture content and pH of observed peats are presented in Table 1. Moisture content of hydrophilic hemic was higher than of hydrophobic hemic. Similar condition applied to sapric peat. Meanwhile, pH showed insignificant difference. Similar acidity was observed in sapric and hemic peats, either in hydrophilic or hydrophobic conditions.

| Peat Maturity       | Moisture content (%) | pH H\(_2\)O |
|---------------------|----------------------|-------------|
| Hydrophilic hemic   | 505.19a              | 3.51a       |
| Hydrophobic hemic   | 118.01c              | 3.61a       |
| Hydrophilic sapric  | 335.46b              | 3.54a       |
| Hydrophobic sapric  | 87.49c               | 3.51a       |

Note: Numbers followed by the same letter in the same column show that there is no significant difference according to DMRT 5%.

Infrared spectrogram of hemic peat under hydrophilic conditions (Figure 1) showed a different graph from the one of hydrophobic hemic peat (Figure 2).
Analysis of hydrophilic hemic peat (Table 2) showed that aliphatic groups were distributed at two peaks of 3448.72 cm\(^{-1}\) and 2924.09 cm\(^{-1}\). The OH group at the peak of 3448.72 cm\(^{-1}\) indicates the presence of hydrogen bonds, OH groups and free OH. These functional groups act as carriers of hydrophilic properties. Figure 1 suggests that this cluster had the largest percentage of area, which was 40%. Hydrophilic character is also brought by COOH group in the form of a carboxylate salt at a peak of 1381 cm\(^{-1}\) and carboxylate ions at a peak of 2854 cm\(^{-1}\) and a C-H aliphatic group at a peak of 2924 cm\(^{-1}\). Carriers of hydrophobic properties are ester, ether, and phenol (1280 cm\(^{-1}\) peak) with an area of 2.11% and the C=C group, in the form of cyclic and benzene, at a peak of 1635 cm\(^{-1}\) with an area of 8.04%.

Table 2. Structure of hydrophilic hemic peat functional groups

| No. | Peak    | Functional Group                          | Area (%) |
|-----|---------|-------------------------------------------|----------|
| 1   | 1126,43 | C-O group alcohol, phenol                 | 3.77     |
| 2   | 1157,29 | C-O group alcohol, phenol                 | 0.44     |
| 3   | 1280,73 | C-O group of ester, ether, phenol         | 2.11     |
| 4   | 1381,03 | CH\(_3\) bending, salt of carboxylic acid | 2.23     |
| 5   | 1458,18 | CH\(_3\) bending group, salt of carboxylic acid | 0.83 |
| 6   | 1635,64 | C=O group amide group, ketone             | 8.04     |
| 7   | 2337,72 | Carboxyl ion                              | 13.58    |
| 8   | 2854,65 | CH\(_2\) symmetry of fat, wax, lipid      | 14.86    |
| 9   | 2924,09 | C-H, C-H\(_2\), C-H\(_3\) aliphatic groups | 2.58 |
| 10  | 3448,72 | OH group, free OH, H-aliphatic            | 40.06    |
Figure 2. Results of Hydrophobic hemic peat FTIR spectroscopy

When peat dries and becomes hydrophobic, there is a decrease in peaks and area of hydrophilic carrier groups (Table 3). The OH group, free OH and H-aliphatic were found at 3425.58 cm\(^{-1}\) with an area of 28.91%. Meanwhile, there was an increase in the peak and area of the group which brought hydrophobic properties.

Table 3. Structure of hydrophobic hemic peat functional groups

| No. | Peak   | Functional Group                        | Area (%) |
|-----|--------|-----------------------------------------|----------|
| 1   | 1064.71| C-O group, alcohol, phenol              | 4.04     |
| 2   | 1165.00| C-O group, alcohol, phenol              | 1.08     |
| 3   | 1273.02| C-O group, ester, ether, phenol         | 4.46     |
| 4   | 1381.03| CH\(_3\) bending, salt of carboxylic acid| 1.57     |
| 5   | 1635.64| C=O group amide group, ketone           | 9.81     |
| 6   | 2337.72| Carboxyl ion                            | 11.10    |
| 7   | 2854.65| Symmetric C-H\(_2\), carboxylate ion    | 13.67    |
| 8   | 2924.09| Aliphatic group, C-H, C-H\(_2\), C-H\(_3\)| 3.96     |
| 9   | 3425.58| OH group, free OH, H-aliphatic          | 28.91    |
Figure 3. Results of Hydrophilic sapric peat FTIR spectroscopy

FTIR analysis of hydrophilic sapric peat (Table 4) showed two peaks of aliphatic groups, namely at the peaks of 2924.09 cm\(^{-1}\) and 3448.72 cm\(^{-1}\). The peak of 3448.72 cm\(^{-1}\) indicates free OH and OH groups. OH group is the carrier of hydrophilic properties and the largest percentage of area was 42.38%. COOH group in the form of a carboxylate salt was found at the peak of 1318.03 cm\(^{-1}\), while carboxylate ions at the peak of 2846 cm\(^{-1}\), and aliphatic C-H group at the peak of 2924 cm\(^{-1}\). Meanwhile, hydrophobic group in peat was discovered at the peak of 1273.02 cm\(^{-1}\) and C=C group, in the form of cyclic and benzene, at the peak of 1635 cm\(^{-1}\).

Table 4. Structure of hydrophilic sapric peat functional groups

| No. | Peak      | Functional Group                      | Area (%) |
|-----|-----------|----------------------------------------|----------|
| 1   | 1080,14   | C-O group, alcohol, phenol             | 3.36     |
| 2   | 1126,43   | C-O group, alcohol, phenol             | 0.81     |
| 3   | 1157,29   | C-O group, alcohol, phenol             | 0.81     |
| 4   | 1273,02   | C-O group, ester, ether, phenol        | 2.51     |
| 5   | 1381,03   | CH\(_3\) bending, salt of carboxylic acid | 2.07     |
| 6   | 1458,18   | Unclassified                           | 0.89     |
| 7   | 1519,91   | CH\(_3\) bending, acid from carboxylic | 0.88     |
| 8   | 1635,64   | C=O group amide group, ketone          | 7.57     |
| 9   | 2337,72   | C=O group amide group, ketone          | 13.49    |
| 10  | 2846,93   | Symmetric C-H\(_2\), carboxylate ion   | 14.52    |
| 11  | 2924,09   | Aliphatic group, C-H, C-H\(_2\), C-H\(_3\) | 2.91     |
| 12  | 3448,72   | OH group, free OH, H-aliphatic         | 42.38    |

Observations on hydrophobic sapric peat (Table 5) showed that there are two peaks of aliphatic groups, at the peaks of 2924.09 cm\(^{-1}\) and 3425.58 cm\(^{-1}\). Peak of 3425.58 cm\(^{-1}\) indicates OH groups, free OH, carriers of hydrophilic properties. However, there was a decrease in the percentage of hydrophobic sapric peat area at the peak of 3425.58 cm\(^{-1}\) previously from more than 40% to 32.79% due to water
retention. Hydrophobic groups at the peak of 1064 cm\(^{-1}\), 1219.01 cm\(^{-1}\), 1257 cm\(^{-1}\) experienced an increase in area of 6.88%, 1.69%, 3.6%, respectively.

3.2. Discussion
Changes in moisture content cause air absorption in pore space of peat particles, further causing acidity to increase (as seen from decreasing pH in Table 1). Lowering moisture content and oxidation process allow peat organic matter to develop a complex transformation, which rising hydrophobic carriers. This can be seen from observations of FTIR (Figures 1-4).

Observations of hydrophilic hemic and sapric peat soils using FTIR spectrogram (Figures 1 and 3) indicated that there was a wide area of OH groups and carboxylate ions compared to the area of OH groups and carboxylate ions in hydrophobic peat (Figures 2 and 4). The width of the area was due to wet peat samples (field conditions); meanwhile, in hydrophobic peat, absorption area of the OH group and carboxylate ions has decreased. Depletion in the area of the OH group was due to dried peat samples so
that the OH area decreased, causing hydrophobic groups to rise. This is in line with results of Utami et al. [15] which stated that the area of OH group on hydrophobic peat decreases, while C-O group on hydrophobic peat increases. The reduction in the area of OH group was due to water pores being filled with air. According to Lambert [16], drying peat soils caused polar groups to become exposed; and due to flexibility of organic structure, some of proton donors (such as OH groups) and proton acceptors (such as C=O groups) pair each other. C-O groups of esters, ethers, phenols carrying hydrophobic properties increased in hemic and sapric hydrophobic peat. This finding suits the outcome of Siregar et al. [17] where dried, mashed and shaken peat soils destroyed its structure, allowing -COOH and -OH -phenonal functional groups malfunctioned.

4. Conclusion

Investigating peaks and area of functional groups carrying hydrophilic nature with hemic and sapric maturity levels, this research found OH group, free OH, and -COOH groups at the peak of 3448.72 with an area of 40.06% and 42.38%, respectively. Meanwhile, when it turned into hydrophobic, the area of functional group decreased to 28.91% and 32.79%, respectively. The decrease in the area of functional group carrying hydrophilic nature was followed by the increase in the area of carrier for hydrophobic character. In hydrophilic conditions, functional groups carrying hydrophobic properties (ester, ether, and phenol) of hemic peat were at the peak of 1280.73 with an area of 2.11%; while sapric was at the peak of 1273.02 with an area of 2.51%. Under hydrophobic conditions, functional groups carrying hydrophobic properties of hemic peat increased in area to 4.46% and sapric peat to 3.6%.

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