Changes in degraded peat land characteristic using FTIR-spectroscopy

E Maftu'ah¹, A Fahmi¹ and A Hayati

¹Indonesian Swampland Agriculture Research Institute (ISARI)
Jl. Kebun Karet, Loktabat, Banjarbaru, South Kalimatan, INDONESIA
Lambung Mangkurat University, South Kalimantan, INDONESIA

Email: eni_balittra@yahoo.com

Abstract. Degraded peatlands can be detected laboratory analysis and field appearance. Peatlands degradation is characterized by a very reduced water holding capacity which is caused by peat fire or over drain. The capacity of peat to hold water is closely related to their functional groups. Analysis using Fourier Transfrom Infrared (FTIR) Spectroscopy enable to determine the functional groups of peat. The research was aimed to study peatland degradation based on functional group changes through FTIR analysis. The samples of peat soil were taken from burned peatland, agricultural peatland and natural peat in Kalampangan, Central Kalimantan. The hydrophobic properties of the functional group are indicated as lignin, carboxylic or phenolic groups, fat, wax or lipids, while the hydrophilic functional group is indicated as protein and cellulose. Degraded peat have the hydrophobic group of 56.20%, while in natural peatlands was around 29%. Hydrophilic functional group on burned peatlands was 34.5-43%, natural peatland was 60-70% and agricultural peatland was 66%. Functional group analysis using FTIR can be used to detect the level of peatland degradation, through a significant increase in hydrophobic groups.

1. Introduction
Tropical peatlands are important natural resources and have considerable effects on regional and global environments [1]. Peatlands have two main functions, the production function as a cultivation area, and the environmental function as a conservation and restoration area. Both of these functions are closely related so integrated and harmonized management methods are needed to avoid peatland and environmental degradation. The use of peatland for agriculture are still a controversy since the land clearing and peat management are contrary to the peat characteristic. Inaccurate management of peatlands induce biophysical land degradation (subsidence and irreversible drying), land fires, green house gas emissions, and decreased soil fertility [2].

Degradation is a condition where the functional capacity of peat is reduced; in general, is caused by human activities. Degraded peatlands can be detected by 2 (two) ways; (1) laboratory analysis, and (2) field appearance. Degraded peatlands are characterized by changes in physical properties, biology, and chemistry which cause a decrease in the ecological function of the peat which in turn endanger the environmental and social economic development. Peat land degradation in terms of decreasing its function as a growing media of plants, characterized by one properties or combination of several properties i.e; hydrophobic, increased in soil acidity, decreased in total organic carbon (TOC) and total organic N [3]. Land degradation peat is often caused by land drainage. Over drainage of peatland caused
irreversible drying and peat oxidation [4], so that peat was not able to store water and peat become dry. This matter increasing peat susceptibility to fire [5], and significantly released CO$_2$ into the atmosphere [6], especially in extreme El lino conditions [7, 8].

Degraded peat characteristics indicated by irreversible drying conditions that are dependent on water content, ash content and peat component such as lignin, cellulose, hemicellulose, total acidity, COOH group and OH-phenolics [9]. According to [10] hydrophobic character of peat soil is caused by (1) the presence of humic acid which naturally hydrophobic since their particles are covered by wax, (2) the presence of non-polar groups such as ethyl, methyl and temporary aromatic compounds and hydrophobic aromatic compounds cause decrease of hydrophillic group (3) absorption of compounds hydrophobic such as oil, fat, and fractions N-organic on the surface of the humic fraction. Data about soil hydrophobicity can help to evaluate the soil quality parameters as well as the soil fertility [11]. Fourier Transform Infrared Spectroscopy analysis can show the direct information of functional group in the soil organic matter [12], detect the presence of the peat functional groups [13]. This study aims to determine the changes in the characteristics of degraded peat soil through FTIR analysis.

2. Materials and Methods

2.1. Site description
The research was carried out on tropical peatland at the village of Kalampangan, Sebagau District, Palangkaraya Municipality from May 2017 to September 2017. The coordinates of the research location was at -2°17’31. 114°1’51”, -2°17’32 114°1’51, and -2°17’3 114°1’13’. The samples were taken from 1) peatlands area on which Galam tress (Melaleuca leucadendra) and Kalakai scrub (Stenochlaena palustris) were grown naturally; and 2) Degraded peatlands cause by fire and become an abandoned area. As a control, soil samples on agricultural peatland which have been used for agriculture for 10 years were taken (Fig 1).

![Figure 1. Sampling area include a. peat land, b. degraded peat land, c. agricultural peatland](image)

2.2. Data measurement and analysis
All peat soil samples were taken from 0-30 cm depth. At each location, the soil sample was taken from as much as 5 sampling points, then the samples mixed and become a composited sample. Soil chemical properties were analyzed included H$_2$O pH, KCl pH, organic C, total N, total P, total K, CEC, available P, exchanged of K, Ca, Mg, and Na, as well as humic acid, fulvic acid and total acidity. Peat soil samples were also analyzed by FTIR to determine the functional groups.

3. Result and Discussion
The results showed the difference between degraded peatlands and natural peatlands for both the chemical analysis and the results of FTIR analysis. Degraded peatlands at the study site were caused by peat clearing, and the land was not utilized so that it became idle land and overgrown with shrubs. Degraded peatlands characterized by physical appearance, including abandoned and overgrown shrubs.
Criteria for determining degraded peatlands can be proposed to (1) land cover conditions, (2) the characteristic of peatlands and environmental conditions, (3) soil hydrological, physical and biological conditions, (4) legislation [14]. According to [15] degraded peatlands can be identified directly through field sightings from land cover. Peatlands can be categorized as degraded if there is land cover in the form of shrubs, and open land, former mining. Indicators of peatland are categorized as degraded, among others: (1) tree felling, (2) logging roads, (3) fire scars, (4) dry/inundated land conditions, and (5) ex-mining [15].

3.1. Chemical peat soil characteristic

Some chemical characteristics of peatlands soil samples were differ (Table 1). The chemical characteristic different between all 3 soil samples. The significant difference was in pH, total nitrogen, Ex Aluminum, organic C, available P, water content and fulvic acid, total P, total K whereas CEC, and humic acid levels were not a significant difference.

| Soil properties          | Degreded peat lands | Agricultural peatlands | Natural peatland |
|--------------------------|---------------------|------------------------|-----------------|
| H₂O pH                   | 3.62                | 4.70                   | 3.75            |
| KCl pH                   | 3.13                | 3.60                   | 3.20            |
| EC (mS/cm)               | 0.059               | 0.037                  | 0.047           |
| Organic C (%)            | 48.54               | 47.83                  | 54.83           |
| Total N (%)              | 0.915               | 0.823                  | 1.523           |
| Available K (cmol+/kg)   | 0.780               | 0.493                  | 0.93            |
| Exchangable Na (cmol+/kg)| 0.234               | 0.260                  | 0.260           |
| Exchangable Ca (cmol+/kg)| 4.294               | 5.705                  | 4.705           |
| Exchangable Mg (cmol+/kg)| 2.586               | 3.744                  | 2.442           |
| CEC (cmol+/kg)           | 135.77              | 146.82                 | 146.82          |
| Exchangable Al (cmol+/kg)| 15.494              | 7.841                  | 8.481           |
| Exchangable H (cmol+/kg) | 3.099               | 1.568                  | 2.688           |
| Total P (mg/100g)        | 36.533              | 40.984                 | 47.984          |
| Total K (mg/100g)        | 1.543               | 3.940                  | 2.407           |
| Available P (ppm)        | 47.046              | 214.416                | 84.186          |
| Water contents (%)       | 87.36               | 292.04                 | 289.94          |
| Humic acid               | 47.10               | 45.23                  | 49.23           |
| Fulvic acid              | 2.48                | 9.55                   | 6.55            |
| Total acidity            | 520                 | 480                    | 505             |

In degraded peatlands, soil acidity (pH H₂O) is classified as very acid, 3.62, whereas in agricultural 4.70. The acidity of natural peatland was 3.75, very acid. The organic C of natural peatlands is highest because plant roots contribute to organic matter in soil; low decomposition taken place in natural peatland and might maintain high organic matter. In peat cultivated for agriculture, total N level was markedly decreased.

Available P levels of agricultural peatland were higher than that of degraded peatlands. The availability of oxygen in agricultural peatland was higher and affects the decomposition and mineralization of organic P. The activity of aerobic-heterotrophic microorganisms in agricultural peatland was for intensive decomposition and mineralization. The decomposition of peat will be more intensive in the better-aerated layer because respiration by aerobics becomes more intensive. According to [16] and [17], the decomposition of peat will be more intensive in the better-aerated layer because respiration by aerobics becomes more intensive. The amount of P available in peat material is also determined by the level of decomposition [18]. Peat with an advanced decomposition level has the
ability to store P higher than peat with a low decomposition level. This is related to the amount of colloid in peat with a higher decomposition rate compared to peat decomposition level is low.

Availability of potassium on all locations was almost similar, ranging from 0.49-0.95 cmol(+)/kg^{-1}. The content and availability of K in peatland was vary depending on the level of decomposition and mineralization of peat. [19] stated that the availability of potassium in Central Kalimantan peat soils ranging from 0.29 - 1.13 cmol(+)/kg^{-1}. Most of peatland was deficient in K, since potassium has a monovalent charge which is bound weakly by peat and is quickly lost from the root area [20].

The soil total acidity showed significant different. The source of acidity of the peat in studied area was dominated by ion H^+ and Al^{3+}. The source of H ion was the dissociation of organic acids which are in peat usually dominated by fulvic and humic acid. Organic acids make a real contribution to the low pH of peat soil. Decomposed organic matter has a reactive group include carboxylates (-COOH) and phenolics (C_6H_4OH) which dominate the exchange complex. organic acids that are strong enough to dissociate and produce large amounts of ions. The cause of acidity is also due to the presence of Al ions.

Soil water content at the study site also showed a significant difference. In degraded peatlands there was a significant decrease in water content, reaching more than 3 times compared to natural peatlands and agricultural land. Water content in degraded peatlands was 89% while at natural peatlands it reached 289% and at intensive agricultural land, it reached 292%.

Cation exchange capacity (CEC) and humic acid were relatively similar at the study site. This is due to the high content of lignin and carboxylate in peatlands. CEC values in peatlands are caused by negative pH-dependent charges from humic acid, which are mostly derived from carboxylic and phenolic groups. The carboxylate group contributes to the CEC as much as 10-30%, and the biggest contributor to the CEC was the lignin fraction derivative which depends on the load of 64 -74% [21].

3.2. FTIR analysis

The results of FTIR analysis of composite peat material taken from 0 - 30 cm depth of degraded agricultural and natural peatland were shown in Figures 2 and Table 1. The number of carriers of hydrophobic properties was at the peak of 1265 cm^{-1} indicated as lignin, other carboxylic acids, esters or aromatics (Fig 2). The hydrophobic properties of the functional group were demonstrated at the wavelength 800 - 880 cm^{-1} and 1211 cm^{-1} which indicated as lignin, carboxylic or phenolic groups (1435 cm^{-1}), other lignin or aromatics (1620 cm^{-1}), fat, wax or lipids (2800 - 2924 cm^{-1}), while the hydrophilic functional group is indicated at a wavelength of 1381 cm^{-1} (protein) and 3410-3749 cm^{-1} (cellulose). The hydrophobic group of degraded peat was about 56.20%, while in natural peat was around 29% (Table 2). Hydrophilic functional group on degraded peatlands was due to the fire was 34.5 - 43%, while at natural and agricultural peat was 60-70% and 66% respectively.
Figure 2. Fourier Transform Infra-Red (FTIR) analysis results from peat materials at the study sites

Table 2. Wave numbers, functional groups, the area of FTIR analysis and character

| Wave numbers (cm⁻¹) | Functional group | Characterization/Reference | Total area (%) |
|---------------------|------------------|-----------------------------|----------------|
|                     |                  |                             | P-1  | P-2  | P-3  |
| <900                |                  |                             | 8.87 | 23.53| 5.73 |
| 1126                | C-O chain of phenolic OH, aryl methyl ethers | Lignin [22] | 12.26 | 11.06| 14.76 |
| 1435-1589           | The symmetrical circuit of COO-, N-H deformation and circuit C = N | Protein [23] | 6.42 | 0.16 |      |
| 1620                | The C = O circuit of the quinone, or C = O of the conjugated H-ketone bond, the C = C aromatic circuit, the -H bond at C = O | Lignin or other aromatic groups, aromatic or aliphatic carboxylic acids [24] | 14.40 | 35.60| 12.91 |
| 2800-2924           | symetric CH₂     | Fat, wax, lipids [24]      | 1.82 | 9.60 |      |
| 3410                | H Group Hidroxy, carboxyl and phenolic groups, primary amino group | Cellulose [24] | 70.14 | 34.50| 66.70 |

Note: P-1=natural peatland, P-2=degraded peatland, P-3= agricultural peatland
Hydrophobicity is a condition where peat soil surface cannot absorb water. This hydrophobicity is caused by a decrease in total acidity, carboxyl groups and levels of hydroxy-phenolics [25]. The ability of peat soil to absorb water is closely related to the reduction availability of carboxylic and OH-phenolics [26]. The characteristics of peat are closely correlated to irreversible drying include water and ash content, as well as peat functional groups such as lignin, cellulose, hemicellulose, total acidity, COOH group, and OH-phenolics. According to [27] hydrophobic character on peat soil cused by (1) humic acid particles which are covered by wax, (2) non-polar groups such as ethyl, methyl and temporary aromatic compounds that are hydrophobic and reduced in hydrophillic carboxylic and hydroxyl, (3) absorption of hydrophobic compounds such as oil, fat, and fractions N-organic on the surface of the humic fraction. Soil moisture content played an important role to define peat as hydrophilic and hydrophobic [28].

4. Conclusion
The level of degradation of peatlands can be determined from the presence of hydrophobic groups and compounds. Fourier Tansform Infrared Spectroscopy analysis can detect both hydrophobic and hydrophilic functional groups of peat. The hydrophobic properties of the functional group are indicated at the wavelength of 800 - 880 cm\(^{-1}\) and 1211 cm\(^{-1}\) which indicated as lignin, carboxylic or phenolic groups (1435 cm\(^{-1}\)), wavelength of 1620 cm\(^{-1}\) which indicated as other lignin or aromatics, wavelength of 2800 - 2924 cm\(^{-1}\) which indicated as fat, wax or lipids, while the hydrophilic functional group is indicated at a wavelength of 1381 cm\(^{-1}\) which indicated as protein and 3410-3749 cm\(^{-1}\) which indicated as cellulose. The content of hydrophobic group in degraded and natural peat 56.20\%, and 29% respectively. Hydrophilic functional group on degraded peatlands due to fire was 34.5 - 43%, while at natural peatland between 60-70% and agricultural peatland about 66%. Hydrophobicity can help to evaluate the soil quality parameters as well as the peat soil characteristic. Functional group analysis using FTIR can be used to detect the level of peatland degradation, through a significant increase in hydrophobic groups.

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