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# Hydrothermal Treatment of Hokkaido Peat – An Application of FTIR and $^{13}\text{C}$ NMR Spectroscopy on Examining of Artificial Coalification Process and Development

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## 1. Introduction

There have been great changes in attitude toward the use of peat as an energy source since World War II (WEC, 2001). In Japan, peatland covers over 2500 km<sup>2</sup> and accounts for a total energy resource of approximately 1.99 GJ.10<sup>10</sup> (Spedding, 1988). Peatland in Japan is widely distributed throughout Hokkaido, which is the northernmost area of the country's four main islands. Although peatland also exists in other regions, its distribution is extremely localized. Peatland is distributed over an area of approximately 2000 km<sup>2</sup> in Hokkaido (Noto, 1991), which is equivalent to approximately 6% of the flat area on this island. Peatland is also widespread in the northeastern part of Sapporo, which is the largest city in Hokkaido. Peatland in Japan is often lacustrine peat, which is formed when lakes and marshes become filled with dead plants from their surrounding areas and are then transformed into land. This type of peat is characterized by the spongy formation of plant fiber. In the peatland of Hokkaido, peat usually accumulates to a thickness of three to five meters on the ground surface, while the soft clay layer underlying the peat is often over 20 meters thick. In some areas, a sand layer exists between the peat and the clay layers.

One approach to study artificial coalification process is dewatering and conversion by hydrothermal treatment. Hydrothermal treatment of peat has been studied recently by the authors (Mursito et al., 2010; Mursito et al., 2010). In this method, raw peat is directly transformed without pretreatment or drying, which leads to greatly reduced costs. However, few studies have been conducted to evaluate the hydrothermal treatment of raw peat by means of all coalification process. Despite this lack of study, experiments imitating coalification by subjecting materials to heating with high pressure water were reported first by Bergius in 1913, who termed the method hydrothermal carbonization.

The conversion of cold climate peat into liquid fuel has been studied and conducted in Germany, Canada, Sweden, Finland, Iceland and Israel (Björnbom et al., 1986). Although there has been much less interest in peat liquefaction than coal liquefaction, a large number of batch autoclave studies have evaluated the use of cold climate peat as the raw material for the formation of liquid fuel. The conversion of peat to liquid fuel in Sweden produced an organic product similar to very heavy oil after raw peat was treated with CO under high pressures and temperatures (Björnbom et al., 1981). In Canada, the conversion of peat to gas and liquid employed CO and/or H<sub>2</sub> and water (Cavalier & Chornet, 1977).

Hydrothermal treatment of Hokkaido cold climate peat has also been investigated. However, it is still necessary to evaluate the liquid and gas products formed during the process to facilitate its energy and chemical utilization. The aim of this chapter is to characterize and determine the effectiveness of hydrothermal treatment for upgrading and dewatering processes on the solid products of Hokkaido cold climate peat as well as to determine its artificial coalification process by applying of FTIR and <sup>13</sup>C NMR spectroscopy. A fundamental study of the effects of processed temperature on the products of hydrothermal treatment of cold climate peat is also described in this Chapter.

## 2. Experimental

### 2.1 Materials

Raw cold climate peat samples were obtained from peatland areas owned by the Takahashi Peat Moss Company, Hokkaido, Japan. The site is located in a peat mining area that consists of about 40 ha that already contained an open and systematic drainage system. The peat mining method used at the site is the cut and block and dry method, and the peat moss products are primarily used for agriculture and gardening. The peat in the study area is approximately 5–10 m thick and the water level is about 50 cm. Prior to World War II, about 1200 ha of peatland in this area were owned by the Japan Oil-Petroleum Company, which converted the harvested peat into oil. The typical properties of the peat from this mining site are shown in Table 1.

### 2.2 Apparatus and experimental procedure

All experiments were conducted in a 0.5 L batch-type reactor (Taiatsu Techno MA22) that was equipped with an automatic temperature controller and had a maximum pressure of 30 MPa and a maximum temperature of 400°C (Fig. 1) (Mursito et al., 2010). The raw peat samples were introduced to the reactor without any pretreatment except for milling. The amount of the raw peat added to the reactor was 300 g, which corresponded to 40 g of moisture-free peat. The reactor was pressurized with N<sub>2</sub> to 2.0 MPa at ambient temperature, after which the raw peat was agitated at 200 rpm while the reaction temperature was automatically adjusted from 150°C to 380°C at an average heating rate of 6.6°C/min. Under supercritical conditions (380°C), the charge was 230 g and the initial pressure was 0.1 MPa. After the desired reaction time of 30 min, the reactor was cooled immediately.

After cooling, the gas products were released through a gasometer (Shinagawa DC-1) and their volume was determined by collection into a gas micro syringe (ITO MS-GANX00). The evolved gas composition was then determined by gas chromatography (GC) using a GC equipped with a thermal conductivity detector (Shimadzu GC-4C) using Molecular Sieve 5A

Properties	Raw	Treated temperatures (°C)							
		150°C	200°C	250°C	270°C	300°C	330°C	350°C	380°C
Proximate analysis									
(wt%)									
Moisture (a.r)	86.9	-	-	-	-	-	-	-	-
Equilibrium									
Moisture (X) (a.r)	13.3	12.3	12.8	5.6	5.3	4.8	3.2	3.0	2.4
Volatile Matter (d.a.f)	68.1	67.5	65.0	56.4	52.8	48.4	45.4	44.0	37.2
Fixed Carbon (d.a.f)	31.9	32.5	35.0	43.6	47.2	51.6	54.6	56.0	62.8
Ash (d.b)	4.4	12.8	9.1	8.3	7.1	6.0	7.4	7.5	8.2
Ultimate analysis									
(wt%) (d.a.f)									
C	54.7	57.6	59.6	67.0	68.0	72.2	74.3	75.2	79.1
H	5.7	5.8	5.7	5.5	5.4	5.5	5.5	5.4	5.4
N	1.1	2.2	1.7	1.7	1.6	1.6	1.7	1.7	1.7
O (diff.)	38.0	33.8	32.3	25.1	24.3	20.0	17.9	17.2	13.3
S	0.5	0.7	0.6	0.6	0.6	0.6	0.5	0.5	0.5
Yield of solid products									
(Y) (wt%) (d.b)	-	77.7	77.6	65.3	65.2	61.2	53.9	50.4	48.3
Calorific value (CV)									
(kJ.kg <sup>-1</sup> ) (d.b)	21,527	20508	22427	25008	25836	27985	28299	29296	30047
Effective calorific value									
(ECV) (kJ.kg <sup>-1</sup> )	17307	16727	18263	22436	23268	25457	26242	27264	28233

d.b = dry basis; a.r = as received basis; d.a.f = dry ash free basis; diff. = differences

Table 1. Proximate and ultimate analysis, yield of solid products and calorific value of Takahashi peat moss and hydrothermally upgraded peat.

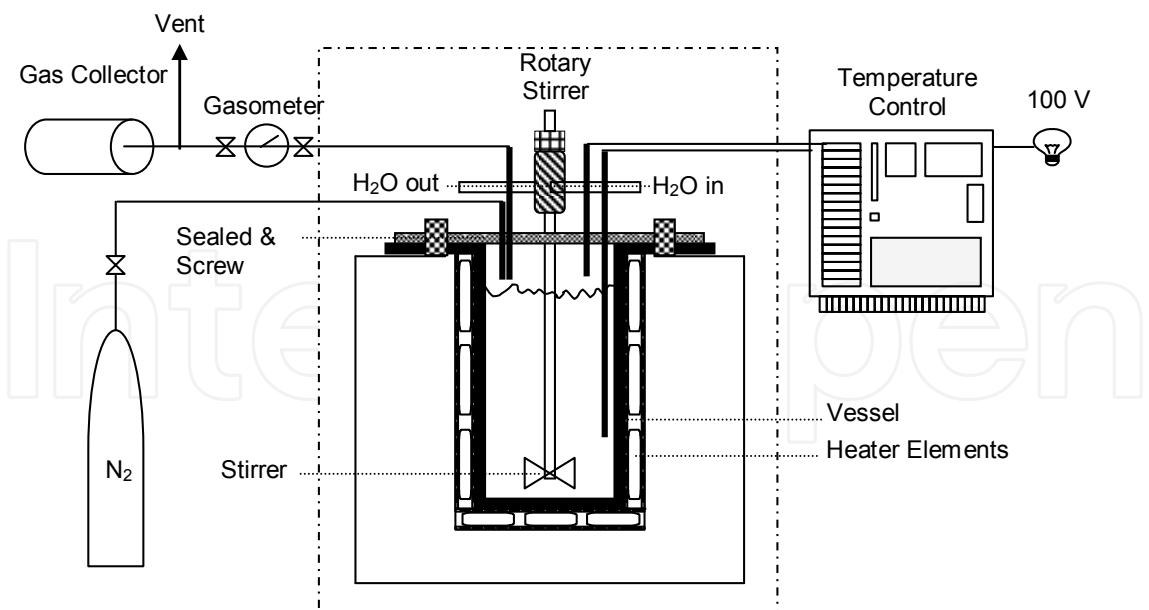


Fig. 1. Schematic figures of hydrothermal batch type reactors.

and Porapak Q columns. The column temperature was set at 60° C and argon was applied as the carrier gas at a rate of 30 mL/min. The results were recorded using a Shimadzu C-R8A Chromatopac data processor. The results of GC analysis are discussed elsewhere. The solid

and liquid phases were then collected from the reactor and separated by filtration (ADVANTEC 5C) using a water aspirator. The total moisture content of the filtered solid products was then determined using a moisture content analyzer (Sartorius MA 150).

### 2.3 Analysis

The liquid product was filtered through a sheet of Advantec 0.45  $\mu\text{m}$  pore size membrane filter prior to analysis. After dilution by a factor of 1000 using ultra-pure water, the total organic carbon (TOC) content and total inorganic carbon (TIC) content of the liquid product was determined using a Shimadzu TOC-5000A VCSH TOC analyzer. The organic compounds in the liquid product were identified and quantified by GC-MS (Agilent 6890N and JEOL Jms-Q1000GC (A)) using a J&W Scientific methyl silicon capillary column measuring 0.32 mm  $\times$  60 m. The split ratio was 99 and the column temperature was maintained at 40° C for 3 minutes, followed by an increase of 15 °C/min. to 250° C, which was maintained for 10 minutes. The composition of the sugar compounds in the liquid products was determined by high-performance liquid chromatography (HPLC) using a JASCO RI-2031 refractive index detector and Shodex KS-811, with 2 mM  $\text{HClO}_4$  applied at 0.7 mL/min. as the eluent. The results of liquid products content analysis are discussed elsewhere.

The elemental composition of the raw peat and solid product was determined using an elemental analyzer (Yanaco CHN Corder MT-5 and MT-6). Additionally, proximate analysis (based on JIS M 8812) total sulfur analysis (based on JIS M 8819) and calorific analysis (based on JIS M 8814) were conducted separately. The gross calorific value (CV) was measured using the bomb calorimetric method and the effective calorific value (ECV) of the sample at a constant pressure was determined based on JIS M 8814, which is followed by ISO 1928. The equilibrium moisture content of the dried solid product was further analyzed while maintaining their moisture contents according to JIS M 8811. Briefly, an aliquot of the sample was placed inside a desiccator containing saturated salt solution and then measured rapidly using a moisture content analyzer (Sartorius MA 150).

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. The cross polarization/magic angle spinning (CP/MAS)  $^{13}\text{C}$  NMR spectrum of raw peat and the solid product was measured using a solid state spectrometer (JEOL CMX-300). The measurement conditions were as follows: spinning speed in excess of 12 kHz, contact time of 2 ms, pulse repetition time of 7 s and scan number of 10,000. Chemical shifts are in ppm referenced to hexamethylbenzene. The curve fitting analysis of the spectrum was conducted using the Grams/AI 32 Ver. 8.0 software (Galactic Industries Corp., USA).

### 2.4 Sequential extraction of peat bitumen, plant constituents and humic substances

After drying at room temperature, the raw peat was milled and sieved through an 80-mesh screen, after which the plant constituents (hemicelluloses, cellulose and lignin), peat bitumen, humic substances (humic acid (HA), fulvic acid (FA) and humin (Hm)) and other insoluble contents were fractionated using methods that have been previously described. Briefly, the peat bitumen (benzene/ethanol-soluble) was extracted in a Soxhlet apparatus for

8 hours with a mixture of benzene and ethanol (4:1 vol./vol.). The bitumen-free peat was then extracted in ultra-pure water at 100° C for 5 hours to obtain the water-soluble materials. Next, the samples were dried at room temperature, after which the residual peat was sequentially extracted with 2% HCl at 100 °C for 5 hours to obtain the hemicelluloses. The samples were then incubated in 72% H<sub>2</sub>SO<sub>4</sub> at room temperature for 4 hours, after which the concentration of H<sub>2</sub>SO<sub>4</sub> was adjusted to 4% by the addition of ultra-pure water and the samples were heated at 100 °C for 3 hours to obtain the cellulose.

The residual peat was then correlated with the humic substances, lignin and other insoluble compounds. To accomplish this, the humic substances were removed by acid and alkali extraction. Briefly, the air-dried peat was washed twice with 0.01 M HCl and then treated with NaOH at pH 13.5 for 48 hours, which gave a supernatant fraction (humic and fulvic acids), and a fraction that contained the humin and other insolubles. All fractions were separated by filtration and centrifugation.

3. Results and discussion

3.1 Sequential extraction of raw peat and solid products

The liquid content of the raw peat was 86.9 wt.%, which corresponded to the moisture content, and the products increased from 87.3 wt.% to 89.4 wt.% as the temperature increased. As the temperature increased, the gas products content increased from 1.6 wt.% to 4.8 wt.%. The increase in the liquid and gas products in response to increasing temperature suggest that dewatering and decomposition occurred during the process. Takahashi peat that contained most of the organic constituents of the original plant materials were least decomposed and peatification occurred shortly. The amounts and concentration of plant constituents, peat bitumen (benzene/ethanol soluble) and humic substances in Takahashi moss peat are described in Table 2.

Humic substances, insoluble fractions and lignin	(wt.%) dry-base
Humic and fulvic acids (HA and FA)	0.9
Humin (Hm), insoluble fractions and lignin	4.2
Carbohydrates	
Hemicelluloses	30.7
Cellulose	40.7
Extracted peat bitumen (benzene/ethanol soluble)	9.0
Water soluble compounds	14.5

Table 2. Humic substances, plant constituents and bitumen of Takahashi moss peat.

Extracted peat bitumen can be formed during natural decomposition and accounted for 9.0 wt.% of the raw peat, suggesting that the extracted materials correspond to the wax like hydrophobic formations. The hemicellulose and cellulose content was 30.7 wt.% and 40.7 wt.%, respectively. The high levels of carbohydrate indicate that the plant constituents still remained and were decomposed during peatification. The materials from which Takahashi moss peat is formed consist of cattails and reed grass (in Japanese, gama and ashi, which differ greatly from the raw materials that lead to the formation of tropical peat. This difference may explain why Takahashi peat differs from Pontianak peat. The water soluble



content of the raw peat was 14.5 wt.%. The total humic substances, lignin and other insoluble fractions comprised 5.1 wt.% of the raw peat, of which HA and FA comprised 0.9 wt.%.

Figure 2 shows the effect of the processing temperature on the contents of peat bitumen, water soluble compounds and carbohydrates in the solid products. All other compounds consisted of char and other insoluble materials. The peat bitumen content in the solid products ranged from 4.7 to 26.0 wt.%, which suggests that peat bitumen formed in solid products formed in response to hydrothermal treatment. The peat bitumen decreased at low temperatures (150°C to 250°C), then increased slightly at 250°C and continued to increase with increasing temperature. Under supercritical conditions, the peat bitumen decreased slightly when compared to the peat bitumen content at 350°C, which may have been due to the intensive decomposition of organics in raw peat during the formation of gaseous and liquid products as a result of the supercritical reaction. The water soluble content accounted for 14.5 wt.% of the raw peat and 6.2 wt.% of the product formed at 380°C, indicating that this fraction decreased with increasing temperature. Both carbohydrates (hemicellulose and cellulose) decreased with increasing temperature and were no longer present in products formed at 300°C and above. Hydrothermal dewatering was highly affected by the decomposition of carbohydrates at 150°C to 270°C, suggesting that organics containing polysaccharides will be obtained in the liquid products.

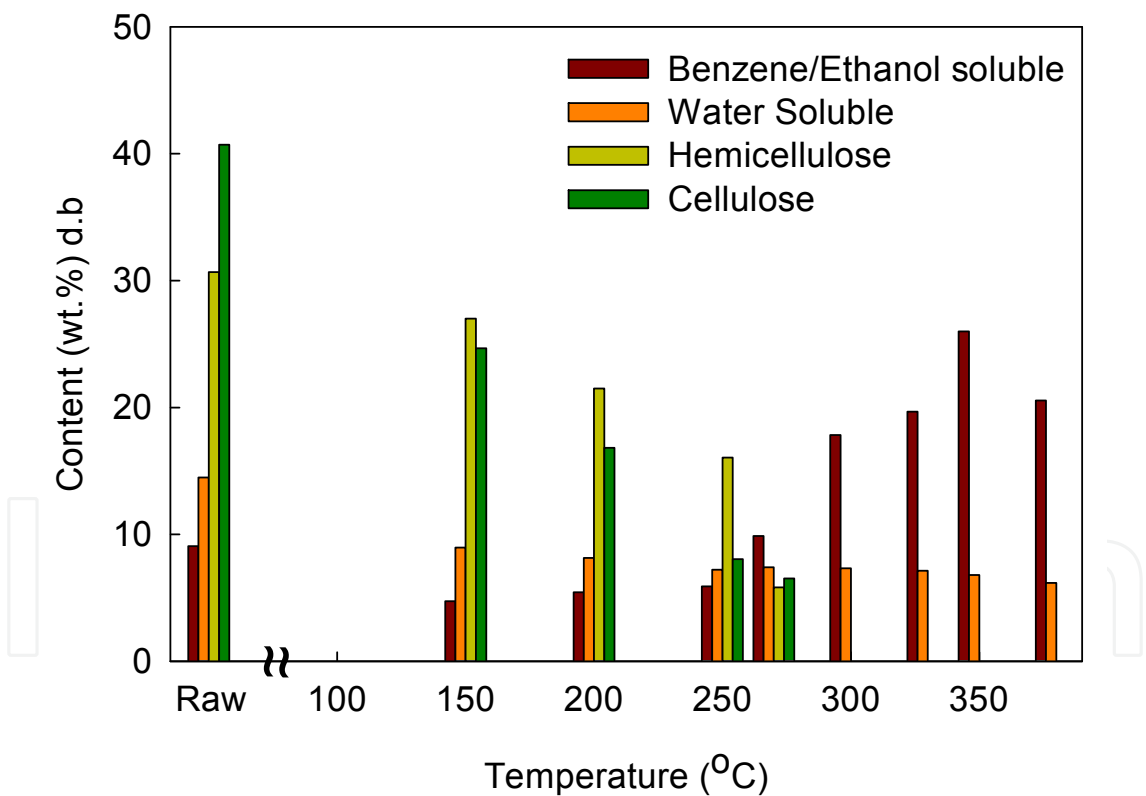


Fig. 2. The effect of temperature on the concentration of peat bitumen (benzene/ ethanol soluble), water soluble compounds and carbohydrates in solid products

3.2 Properties of solid products

Table 1 show the effects of temperature on the yield and moisture contents of solid products, respectively. The yield decreased as the temperature increased. Specifically, the maximum

solid product yield was 77.7 wt.% at the lower temperature of 150°C, while the minimum yield was 48.3 wt.% at the supercritical temperature (380°C). The decrease in the yield of the solid product was due to the extensive thermal decomposition of the raw material into liquid and gaseous products. Dewatering also occurred during the decomposition reaction. Indeed, the minimum moisture content of the filtered solid products was 20.9 wt.% when the reaction was conducted at 380°C, while the maximum moisture content of 47.9 wt.% was obtained at 150°C. Moreover, the equilibrium moisture content of the solid products obtained at 380°C was 2.4 wt.%, while it was 13.3 wt.% at 150°C. As the temperature increased, the equilibrium moisture content of the solid products decreased when the products were maintained at a constant humidity (77–79%), indicating that the product may be hydrophobic when subjected to high temperatures. In general, the use of higher temperatures for the hydrothermal treatment of raw peat improves the dewaterability of the solid product; therefore, solid products produced at higher temperatures have better resistance against moisture adsorption when they are maintained at high humidity.

Lower equilibrium moisture contents resulted in the solid products having higher calorific values. In addition, the effective calorific value of peat fuel decreased as the level of moisture increased. The gross calorific value (CV) determined by the bomb calorimetric method and the effective calorific value (ECV) of the samples are shown in Table 1. The ECV was calculated using the equation as described on (JIS M 8814) :

$$\text{ECV} = [\text{CV} - 212.2 \times \text{H} - 0.8 \times (\text{O} + \text{N})] \times (1 - 0.01 \text{X}) - 24.43 \text{X} \quad (1)$$

where ECV is the effective calorific value, which is the net calorific value at a constant pressure of the equilibrium moisture content sample in kJ/kg, CV is the gross calorific value at a constant volume of the dry sample in kJ/kg, H, O and N are the hydrogen, oxygen and nitrogen contents of the dry sample in mass percentage, respectively, X is the moisture content in mass percentage for which the ECV is desired.

In the present study, CV increased from 20,508 kJ/kg in the 150°C product to 30,047 kJ/kg in the 380°C product, while the ECV of the 150°C product was 16,727 kJ/kg and that of the 380°C product was 28,233 kJ/kg. However, the yield decreased as the temperature increased.

In addition, the fixed carbon content increased from 31.9 wt.% to 62.8 wt.%, and the volatile matter decreased from 68.1 wt.% to 37.2 wt.% as the temperature increased. The ash content of the raw peat and solid products also increased from 4.4 wt.% and 8.2 wt.%. All of the solid products had lower levels of volatile material than the raw peat. Moreover, the chemical variations in the C, H, N and O contents of the solid products following the hydrothermal reaction of peat at different temperatures were also very interesting. Hydrothermal treatment decomposed the raw peat, which resulted in the oxygen content decreasing from 38.0 wt.% to 13.3 wt.% as the temperature increased. These findings suggest that oxygen loss corresponds to dewatering and the decreased yield of solid product. There was also a significant correlation between oxygen loss and the calorific value. The extensive removal of oxygen-rich compounds from the raw peat resulted in a solid product with a low oxygen content and a high calorific value. Additionally, the carbon content of the solid products increased from 54.7 wt.% to 79.1 wt.%. Moreover, the hydrogen content decreased slightly while the nitrogen content increased slightly in response to increased temperature. The sulfur content was relatively stable (0.5 wt.% to 0.7 wt.%), regardless of treatment.



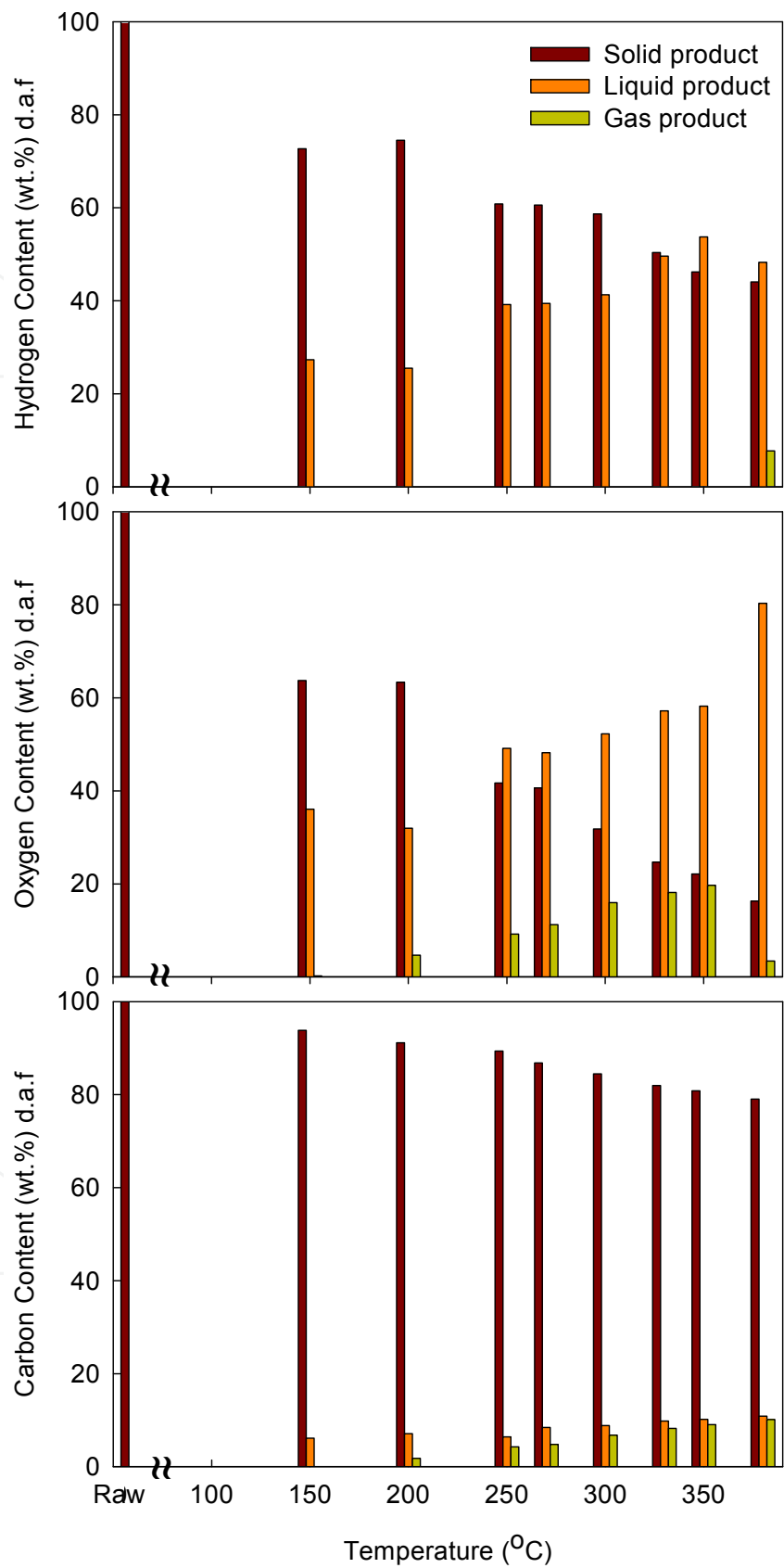


Fig. 3. The effect of temperature on the conversion of C, H and O of raw peat into solid, liquid and gas products.

The carbon, hydrogen and oxygen contents of solid, liquid and gas products calculated based on analysis of the product are shown in Fig. 3. Conversion of the carbon in raw peat into solid, liquid and gas products was relatively slower than conversion of the hydrogen and oxygen. The oxygen and hydrogen content in the liquid product increased rapidly because the decomposition of peat increased suddenly, as shown in the yield of the solid products.

### 3.3 Coalification properties of solid products

Figure 4 shows a plot of the coalification band of the cold climate peat and hydrothermally upgraded and coalified solid products. As the temperature of the hydrothermal treatment increased, the atomic H/C and O/C ratio of the solid products decreased. These results indicate that hydrothermally upgraded solid 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. Heat and pressure causes a disruption of the colloidal nature of peat during hydrothermal treatment (Cavalier & Chornet, 1977; Lau et al., 1987), which results in the solid products having a low equilibrium moisture content. Extensive losses of oxygen also led to decreases in the equilibrium moisture content of the solid products. Moreover, oxygen from the peat could be removed by reduction (loss of oxygen) and dehydration reactions. Dehydration followed decarboxylation, while reduction followed by dehydrogenation (Kalkreuth & Chornet, 1982; Van Krevelen, 1950) of the solid products began at the same temperature (150°C). Hydrothermal dewatering causes dehydration, reduction and decarboxylation of the product to liquid and gas; therefore, decarboxylation

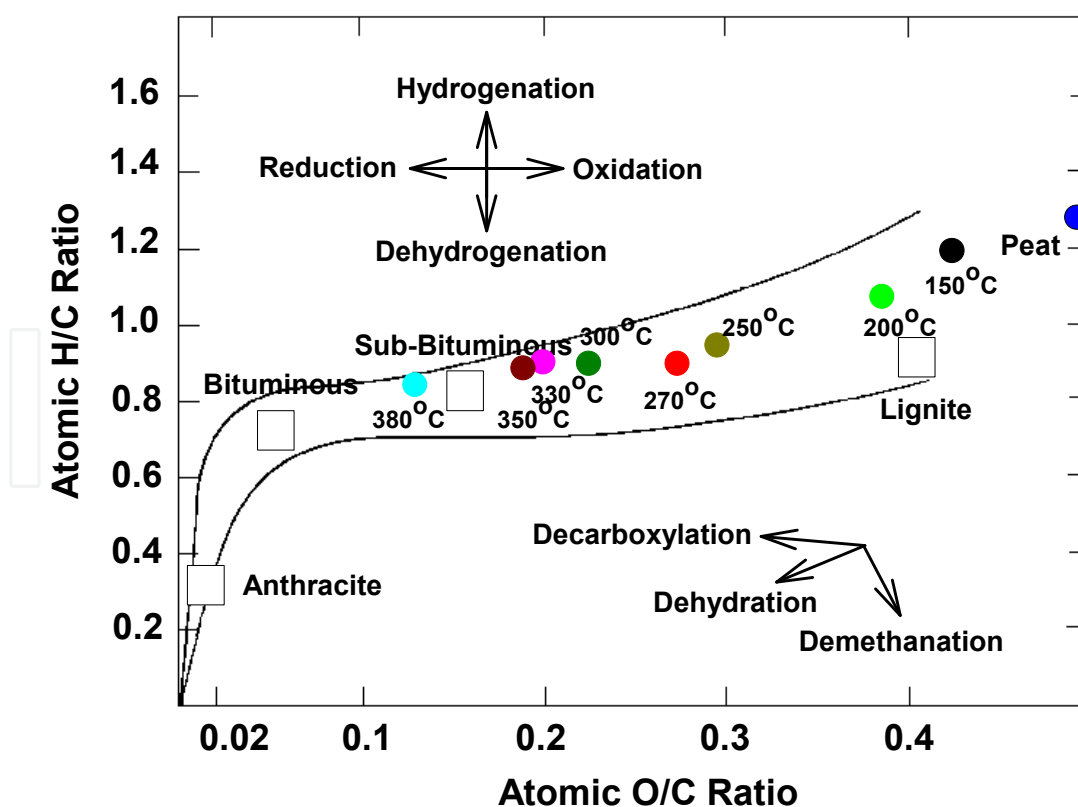


Fig. 4. Coalification band representing raw moss peat and hydrothermally coalified solid products.

by hydrothermal treatment of raw tropical peat can produce organic soluble materials that contain carboxylic groups in the wastewater as well as gaseous products. Moreover, disruption of colloidal forms of peat by hydrothermal treatment can lead to extensive dehydration and possibly increase the number of organic soluble materials in wastewater.

3.4 FTIR results of solid products

Figure 5 shows the FTIR spectra of the raw peat and solid products. Assignments of the peaks in each spectrum of the main functional groups were conducted using the JASCO IR

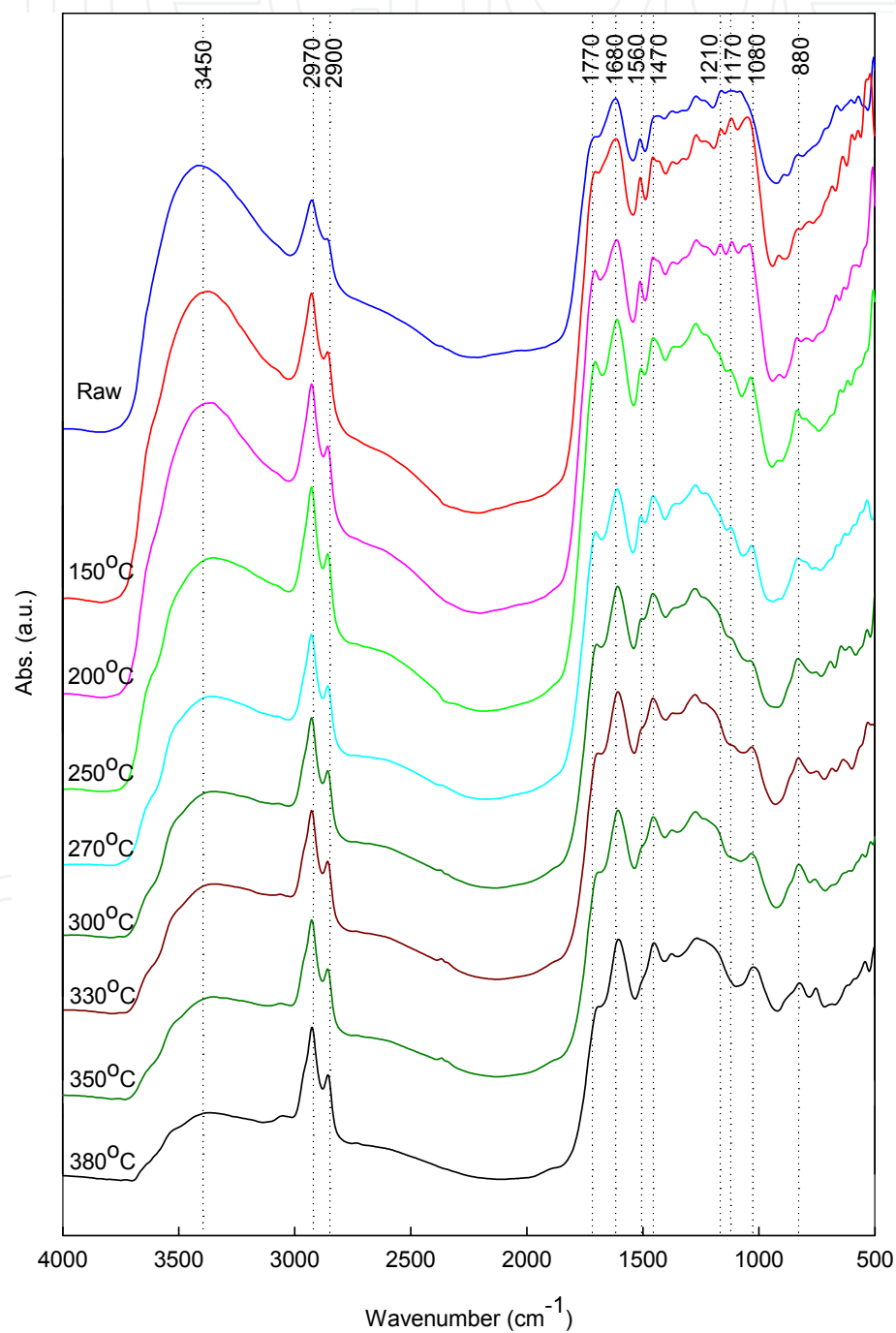
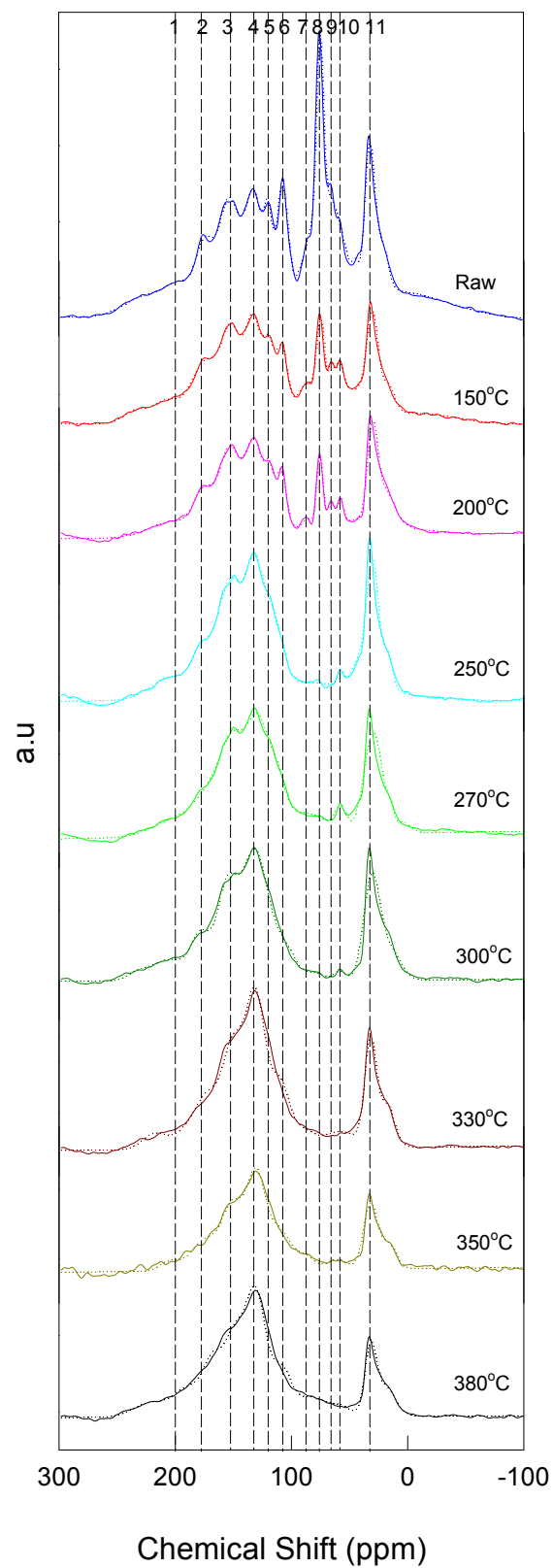


Fig. 5. FTIR spectra of raw peat and solid products produced at all processing temperatures.

Mentor Pro 6.5 software and several publications (Kalkreuth & Chornet, 1982; Van Krevelen, 1950; Orem et al., 1996; Painter et al., 1981; Ibarra & Juan, 1985; Ibarra et al., 1996; Xuguang, 2005). Examination in a range of  $3500\text{--}3300\text{ cm}^{-1}$  zone revealed a progressive lowering in relative peak intensity in  $\text{--OH}$  stretching mode of the solid products at  $380^\circ\text{C}$ . This peak is somewhat diminished in relative intensity, probably due to the dewatering of raw peat during hydrothermal treatment and the loss of hydroxyl-functionalized carbohydrates (Kalkreuth & Chornet, 1982). The spectrum in a range of  $3000\text{--}2800\text{ cm}^{-1}$  showed existence of  $\text{--CH}_x$  stretching mode in an aliphatic carbon. In addition, significant changes can also be observed in a range of  $1800\text{--}1100\text{ cm}^{-1}$ . The carbonyl  $\text{C=O}$  stretching vibration mode of carboxylic acid at  $1770\text{ cm}^{-1}$  was observed initially but the signal was almost completely disappeared with treatment at  $350\text{--}380^\circ\text{C}$ . The relative intensity of the ketone carboxyl band  $\text{C=O}$  groups was clearly observed at  $1680\text{ cm}^{-1}$  and shifted slightly at higher temperatures. A peak at  $1470\text{--}1511\text{ cm}^{-1}$  assigned to the stretching vibration mode of  $\text{C=C}$  in aromatic ring carbons (Kalkreuth & Chornet, 1982), was gradually sharpened in relative intensity with increase in temperature. Peak assigned to the bending vibration mode of  $\text{C--O--R}$  in ethers were observed at  $1080\text{ cm}^{-1}$ , and with increasing temperature, were no longer present at  $270^\circ\text{C}$ . Peak assigned to the bending vibration mode of  $\text{--C--H}$  in aromatics was also observed at  $900\text{--}700\text{ cm}^{-1}$  during the hydrothermal process at all temperatures. Peak assigned to aromatic nuclei  $\text{CH}$  at  $880\text{ cm}^{-1}$  tended to sharpen in its relative intensity with temperature. Dehydration and decarboxylation were also affected, with lowering in relative intensity of  $\text{OH}$  stretch bonding and carboxyl groups being observed in response to treatment. The relative peak intensity of the aromatic ring carbons was sharply observed due to the thermal decomposition that occurred during treatment, and this greatly affected the other carbon functional groups.

### 3.5 $^{13}\text{C}$ NMR results of solid products

The  $^{13}\text{C}$  NMR spectra of the carbon-functional groups of raw peat and hydrothermally treated solid products produced at different treated temperature are shown in Fig. 6. Determination and assignment of the peak area distribution of carbon-functional groups was based on several publications (Orem et al., 1996; Hammond et al., 1985; Freitas et al., 1999; Yoshida et al., 1987; Yoshida et al., 2002). The strongest peak in the  $^{13}\text{C}$  NMR spectrum was at  $74\text{--}76\text{ ppm}$ , which corresponds to methoxyl carbons ( $\text{OCH}_3$ ) may have been related to the presence of carbohydrate carbons (i.e., hemicelluloses, cellulose). These were confirmed on Section 3.1 that the major components of Hokkaido peat are hemicelluloses and cellulose for about 71.4 wt.%. Secondly, the peaks at  $30\text{--}32\text{ ppm}$  in raw peat containing aliphatic carbons ( $\text{CH}_x$  ( $\text{CH}_2$  and  $\text{CH}_3$ )), which was likely due to the occurrence of humic acids and related substances (i.e., humic substances). Peat contains the most important organic fraction in nature, humic substances, which are composed of humic acid (HA), fulvic acid (FA) and humin (Hm) (Cavalier & Chornet, 1977). Lignin, cellulose and hemicellulose decreased as the humification of peat increased. In addition, the peak areas of the aliphatic carbons ( $\text{CH}_x$ ) decreased progressively as the temperature increased. The spectrum of raw peat contained a peak area at  $56\text{--}59\text{ ppm}$  and  $64\text{--}65\text{ ppm}$ , which may have been due to ether carbons in lignin and cellulose in the  $^{13}\text{C}$  NMR spectrum. These results suggest that most organic constituents in the original plant material were least biodegraded, decomposed during peatification. These peaks decreased with increasing temperature and the ether carbon peak was nearly completely gone at  $330^\circ\text{C}$ . The area at  $74\text{--}76\text{ ppm}$ , which



1: C=O; 2: COOH; 3: Ar-O; 4: Ar-C; 5: Ar-H; 6, 7, 8, 9 and 10: methoxyl carbons OCH<sub>3</sub>; 11: aliphatic carbons CH<sub>x</sub> (CH<sub>2</sub> and CH<sub>3</sub>)

Fig. 6. <sup>13</sup>C NMR spectra of raw peat and solid products produced at all processing temperatures.



corresponds to methoxyl carbons (OCH<sub>3</sub>) may have been related to the presence of carbohydrate carbons. This peak area decreased with increasing temperature, eventually decreasing to almost undetectable limits. These findings indicate that carbohydrate carbons were decomposed easily by hydrothermal treatment. The peak representative of aromatic carbons bound to the hydrogen (Ar-H), aromatic non-oxygenated carbon (Ar-C) and aromatic oxygenated carbon (Ar-O) were observed at the area of 100–106 ppm, 127–130 ppm and 151–155 ppm respectively. Furthermore, increasing the temperature of the hydrothermal treatment resulted in an increase in relative area intensity of the aromatic carbons. Finally, the peak area of carboxyl carbons (COOH) in the region of 171–180 ppm and carbonyl carbon (C=O) peaks at 195–200 ppm were observed in the spectrum of raw peat.

#### 4. Conclusion

In this Chapter, the effectiveness of hydrothermal upgrading and dewatering of Hokkaido cold climate peat was evaluated at temperatures ranging from 150°C to 380°C, a maximum final pressure of 25.1 MPa and a residence time of 30 minutes. The hydrothermally dewatered peat fuel product had a significantly higher ECV than raw peat, with the raw peat having an ECV of 17,307 kJ/kg and the products having ECV values ranging from 16,727 kJ/kg to 28,233 kJ/kg. Hydrothermal dewatering may also have impacted the extensive dehydration process by causing a significant loss in the oxygen content. Additionally, the carbon content of the solid products increased from 54.7 wt.% to 79.1 wt.% as the temperature increased. The hydrothermally upgraded peat fuel also had an equilibrium moisture content that ranged from 2.4 wt.% to 13.3 wt.%. A significant loss of oxygen could result in the formation of solid products with low equilibrium moisture.

An application of FTIR and <sup>13</sup>C NMR spectroscopy on hydrothermal coalification could determine the decomposition of organic compounds in peat at different treated temperature. Increasing the temperature of the hydrothermal treatment resulted in an increase in relative area intensity of the aromatic carbons bound to the hydrogen (Ar-H), aromatic non-oxygenated carbon (Ar-C) and aromatic oxygenated carbon (Ar-O). These mean and also correspond to the increasing of aromaticity as well as coalification degree.

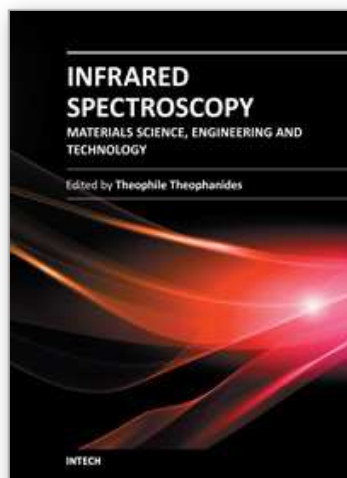
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