SUMMARY
Air oxidation treatment at 100-260°C was applied to modify the properties of the so called Soluble, a clean extract having a potential as precursor of carbon fiber, obtained by the degradative solvent extraction of rice straw. At around 160 °C oxygen started to react with the functional groups of Soluble, which prevented the evaporation of smaller molecular weight compounds of Soluble. The changes in the functional groups during the oxidation were investigated by an in-situ FTIR technique. The melting point of Soluble was found to increase after the air oxidation. The oxidation reactions of the functional groups were judged to play the important role on the modification of Soluble.

1. Introduction
We have recently presented a degradative solvent extraction method for producing high quality extracts having similar properties from several types of low-rank coals and biomasses\(^1\). The extract which was called Soluble showed unique properties such as high carbon content (higher than 80 %), low oxygen content (lower than 10 %), free from moisture and ash. In addition, Soluble melted completely at less than 100 °C, which suggested that Soluble can be utilized not only as a high quality fuel but also as a raw material of advanced carbonaceous material such as carbon fiber. However, Soluble must be reformulated beforehand to be used as the raw material of carbon fiber. In this study the pretreatment called air oxidation (air blowing) at low temperature was used to reform Soluble. The changes in physical and chemical properties during the oxidation were investigated in detail in reference to a treatment in a N\(_2\) stream (N\(_2\) purge method).

2. Experimental
The oxidation pretreatment of Soluble was performed by using TGA (TGA50, Shimadzu). On each run, around 15 mg of sample was heated at the heating rate of 5 °C/min in an air stream of 100 ml/min. Gas formation rates were estimated by analyzing the exit gas stream on a micro GC analyzer (CP4900, VARIAN). To analyze the sample on the way of oxidation, the oxidation was terminated at 100, 120, ..., and 260 °C by changing the gas stream from air to N\(_2\). The samples collected were then characterized by CHN analysis (JM10, J-Science), TGA, and thermomechanical analysis (TMA50, Shimadzu). The treatment using the N\(_2\) purge method was also performed in the same manner for comparison purpose.

The changes of functional groups of the Soluble during the pretreatment were also investigated by using the in-situ FTIR technique. All IR spectra were measured at 4 cm\(^{-1}\) resolutions on a FTIR spectrometer (JEOL, JIR-WIN-SPEC50) with a microscope (JEOL, MAV 204). Neat Soluble sample of around 0.5 mg was heated up from room temperature to 260 °C at the rate of 5 °C/min under air and nitrogen stream of 20 ml/min. The temperature was held constant at 20 °C interval for 4 min and the diffuse reflectance spectra were collected by the acquisition of 150 scans.

3. Results and Discussion
Fig. 1 shows the changes in weight, gas formation rates and oxygen content of Soluble during the air oxidation and the N\(_2\) purge. The weight started to decrease at around 150 °C by both treatments, and very interestingly the weight change during the air oxidation was smaller than that during the N\(_2\) purge. Water formation started at around 150 °C during the air oxidation, but no gas formation was observed. The oxygen content started to increase at around 160 °C during the air oxidation, but no significant change was observed during the N\(_2\) purge.
Fig. 2. In situ FTIR spectra of Soluble during oxidation in air.

Fig. 3. Change in the amount of the functional groups of Soluble during air oxidation.

formation was detected below 220 °C during the N<sub>2</sub> purge. Since the weight change below 220 °C during the N<sub>2</sub> purge is due to the evaporation of small molecular weight compounds, the air oxidation is judged to have prevented the evaporation of such small molecular weight compounds by some reactions between oxygen and the small molecular weight compounds before they are evaporated.

Fig. 2 shows the in-situ FTIR spectra during the air oxidation of Soluble. The relative changes of the amount of functional groups of Soluble estimated by the multipeak-fitting of the in-situ FTIR spectra are shown in Fig. 3. With the progress of oxidation, formation of oxygen functional groups by consuming OH+COOH groups (3000-3700 cm<sup>-1</sup>) and aliphatic CH groups (2738, 2855, 2925 and 2960 cm<sup>-1</sup>) was clearly observed. Decrease in the amount of OH+COOH groups over 140 °C was well associated with the water formation profile shown in Fig. 1. At around 160 °C the increase of carbonyl groups (1700 cm<sup>-1</sup>) started. A small increase in the aldehyde groups (1740 cm<sup>-1</sup>), which will be formed by the oxidation of aliphatic groups, were also observed at around 160 °C. Significant increase of ester groups (1760 cm<sup>-1</sup>) appeared 180 °C. Formation of anhydride groups (1800 cm<sup>-1</sup>) was clearly observed at around 200 °C, which will be formed by consuming aldehyde groups and carboxylic groups. These changes in oxygen functional groups of Soluble molecules are expected to have contributed to suppress the evaporation of small molecular weight compounds.

Fig. 4 shows the TMA curves of Soluble treated by the air oxidation at elevated temperatures. It was found that the Soluble treated at higher temperature showed higher melting temperature. These results also confirmed that the molecular weight increased by the air oxidation.

4. Conclusions
The air oxidation treatment at low temperature was found to be effective to modify Soluble. The air oxidation prevented the evaporation of smaller molecular weight compounds of Soluble by the oxidation of functional groups of Soluble. During oxidation treatment, formation of carbonyl groups and aldehyde groups started at around 160 °C. Then the formation of ester groups started at 180 °C. The significant increase of anhydride was found at 200 °C, which could be due to the consumption of aldehyde groups and carboxylic groups. The increase of oxidation temperature resulted in the increase of the melting temperature Soluble. These results also suggested the significant change of Soluble structure by the air oxidation at low temperatures.

5. Acknowledgments
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6. References