

Experimental Study on FT-IR Analysis of Chemical Species from Wooden Materials in Pre-combustion Condition

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Abstract

It is well known that a scorched odor is emitted from various materials of houses undergoing oxidative pyrolysis and/or combustion reactions. We focused on this change in quality of odor and intended to apply for fire detection in its early stage. The similarity odor index for aldehydes found the rise at the beginning of oxidative thermal decomposition. The electronic nose views the overall balance of odor molecules, but it can't separate the actual chemical components. In this report, therefore, in order to measure chemical species, gas at oxidative thermal decomposition was measured by FT-IR. The quality of odor in the collected gas was measured using electronic noses. In the experiment, the exhaust port of TG-DTA and the gas cell of FT-IR were connected (TG-DTA/FT-IR simultaneous measurement method). The gas emissions from TG-DTA was drawn continuously through a heated sampling line to the heater Gas Cell of the FT-IR. Thirteen kinds of wooden materials, consisting of six kinds of broad-leaved trees, six kinds of conifer trees and one kind of bamboo were used as the test samples. As a results of the wooden materials that a substance containing secondary alcohol, tertiary alcohol, and an aldehyde group was generated in the early stage of the oxidative thermal decomposition (from 200 °C to 300 °C). CO and CO₂ were generated from at 250 °C until the decomposition ended. It was also found from the measurement results obtained by the electronic noses that the similarity index for aldehydes rose from at approximately 230 °C. We found from these results that, in developing the technique of fire detection by odor, the fire can be detected in its early stage by focusing more attention on substances containing an aldehyde group than on CO and CO₂.

Keywords: Fire detection, FT-IR, odor, Wooden materials

Introduction

Fire detectors are ready for sensing a fire in an early stage and alerting residents, so as to start initial them to take actions of escape, evacuation and fire-fighting. In Japan, the installation of fire detectors is obligatory for fire prevention properties, such as residential houses, constructions and buildings of having a certain area, shops, and important cultural assets. Sensors detect fire automatically based on the temperature-rise, smoke, and flame-flicker that fire gives. However, it is not only signals on smoke and temperature-rise that are given by a fire, there is also a scorched odor that is peculiar to fires. Smelling of scorched odor that give the notice of situation unusual, and so the odor could be considered as one of important physical quantities as a fire sign. It was focused on this change in quality of odor and intended to apply for fire detection in its early stage [1]-[4]. To clarify the relation between the change in quality of odor and the temperature during oxidative pyrolysis and thermal degradation, the gas generated was collected in a sampling bag which was attached to the exhaust port of a TG-DTA system. The quality of odor in the collected gas was measured using electronic noses. As a result of the similarity index for aldehydes rose at beginning and during oxidative thermal decomposition. The electronic nose views the overall balance of odor molecules. However it does not separate the actual chemical components. In this report, therefore, in order to measure chemical species, gas at oxidative thermal decomposition was measured by FT-IR.

Experiment

1) Test samples

Thirteen kinds of wood, consisting of six kinds of broad-leaved trees (Chamaecyparis obtusa, Pine, Japanese Cedar, Hemlock, Acacia, Larch), and six kinds of conifer trees (Walnut, White birch, Kihada, Persimmon, Chestnut, Japanese Oak), and one kind of bamboo were used as the samples. These samples were crushed to fine pieces by a Wonder Blender (Osaka Chemical Co., Ltd. WB-1), and the crushed ones of its size of smaller than 200 meshes were employed in the test. In order to minimize the influence of water, the samples were dried at least 15 days in a desiccator containing silica gel in room temperature until there was no weight change.

2) Procedures

TG-DTA/FT-IR

In the experiment, the exhaust port of TG-DTA (Thermogravimetry-differential thermal analysis: Rigaku Corp. TG8120) and the gas cell of FT-IR (Fourier Transform Infrared Spectroscopy: JASCO Cop. FT-IR 4000) were connected (TG-DTA/FT-IR simultaneous measurement method). The gas emissions from TG-DTA was drawn continuously through a heated sampling line to the Gas Cell of the FT-IR. The

sampling line and the Gas Cell were heated and kept at about 140 °C [5]. The measurement conditions of the TG-DTA were set as follows: sample weight approximately 5 mg, aluminum pan, reference material Alumina, pure air (G3) atmosphere, gas flow rate of 300 ml/min, rate of temperature increase at 2 °C /min, and attained temperature of 550 °C. The cell volume was 0.5 L and the optical path of 2.7 m. The cell was fitted with NaCl windows. The nominal resolution was 8 cm⁻¹. The measurement conditions of the FT-IR were set as follows: measurement range of 1000~4000 cm⁻¹, sampling interval of 30 seconds, total measurement time of 5 hours.

Analysis of Odor

The gas generated during the oxidative thermal decomposition in a TG-DTA system was collected by an odor bag attached to the exhaust port of the system. The odor bag was replaced every 15 min of the gas at each time. In order to collect the odor gas released from the sample before thermal decomposition, atmospheric gas was allowed to flow in while the sample was in the place, and the gas was collected immediately after the start of measurement. The gas collected between 0 and 15 min was regarded as the sample for those of every 15 min. The collected gas was diluted by a factor of 5 to 20 with pure N₂ (G1), depending on the odor intensity, and measured using the electronic noses (Shimadzu Corp. FF-2A).

The electronic nose is a device that distinguishes between odor components based on the output balance of 10 types of metal oxide semiconductor sensors, and unlike devices such as GC-MS, does not detect the type of chemical substance. It is provided with nine types of standard gases as indices to judge the degree of similarity of odor components to these indices. Each index produces an analytical curve based on the response values from the sensor when measuring changes in the concentration of the standard gas [6].

Results and Discussion

Fig. 1 shows FT-IR spectra a) the Japanese cedar, b) the Japanese oak and c) the bamboo at the representation gases as the oxidative thermal decomposition. Changes among the spectra of all samples were observed at wavenumbers of 1120.44 cm⁻¹, 1182.15 cm⁻¹, 1725.98 cm⁻¹, 1787.96 cm⁻¹, 2817.49 cm⁻¹, 2177.24 cm⁻¹, and 2362.37 cm⁻¹. Regardless of wooden kinds such as coniferous trees, hardwood trees, bamboo, etc., it changed in all wooden materials as well. The functional groups at these wavenumbers are those of secondary alcohol (1120.44 cm⁻¹), tertiary alcohol (1182.15 cm⁻¹), ester (1725.98 cm⁻¹), alkene (1787.96 cm⁻¹), aldehyde (2817.49 cm⁻¹), CO (2177.24 cm⁻¹), and CO₂ (2362.37 cm⁻¹). Thus, we focused attention on these chemical species. Fig. 2 shows relations between transmittance and temperature at these wavenumbers.

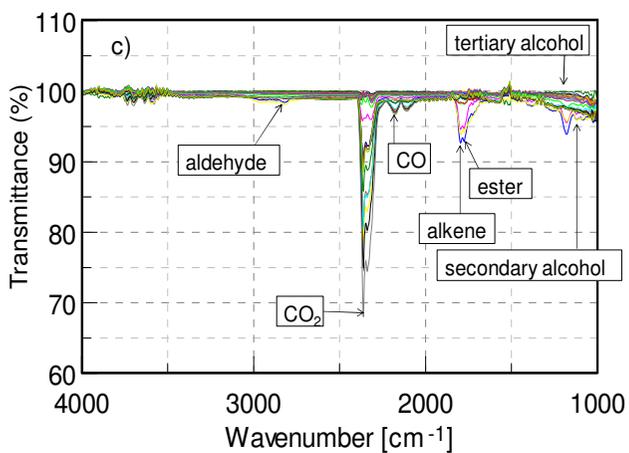
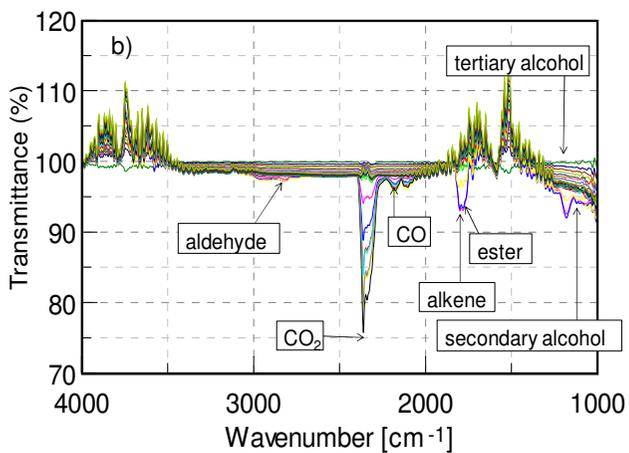
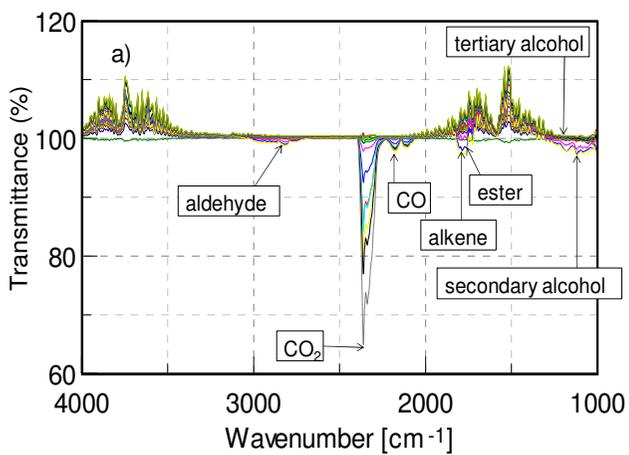


Fig. 1. FT-IR spectra of a) Japanese cedar, b) Japanese oak, and c) bamboo, respectively.

Fig. 2 shows a) the TG-DTA, b) the transmittance and temperature of the chemical species (FT-IR), and c) the odor measurement results for the Japanese cedar. From the TG-DTA measurement results, a weight reduction due to evaporation of water in the samples was observed at temperatures up to approximately 100 °C.

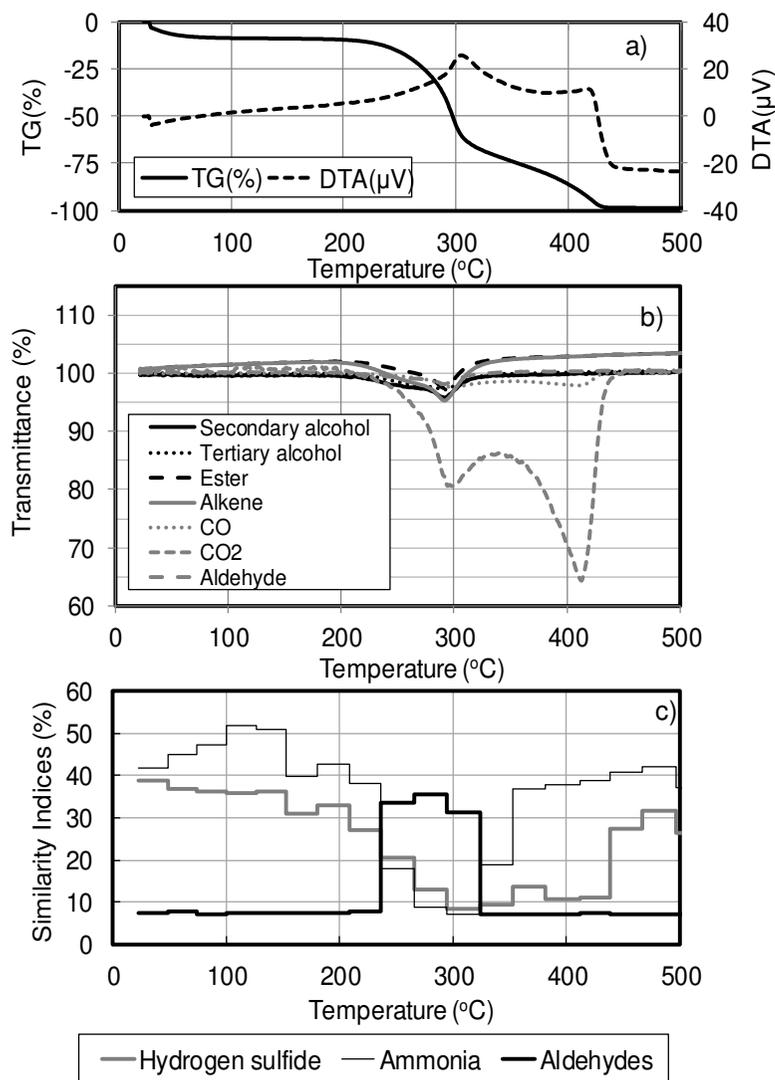


Fig. 2. Measurement results of Japanese cedar
a) TG-DTA diagram, b) FT-IR, and c) Odor similarity.

Then, a weight reduction due to the oxidative thermal decomposition was observed at around 200 °C and above. At approximately 300 °C, the first stage exothermic peak was observed, which is considered to be

due to the combustion of cellulose and hemicellulose contained in wooden materials. From the FT-IR measurement results shown in b), detection peaks of aldehyde, alcohols, ester, alkene, CO, and aldehyde were observed at temperatures below 300 °C that is the exothermic peak temperature of the TG-DTA. As for CO₂, we found from the odor measurement results shown in c) that the similarity indices for ammonia and hydrogen sulfide dropped and the similarity index for aldehydes rose as the active oxidative thermal decomposition progressed.

Fig. 3 shows temperature ranges in which the chemical species of the Japanese cedar were detected. Secondary alcohol, aldehyde, and tertiary alcohol began being detected in this order from approximately 200 °C. CO and CO₂ were detected in the range of approximately 250 °C to 450 °C. Through comparison with the TG-DTA measurement results shown in Fig. 2 a), it was assigned found that secondary alcohol, tertiary alcohol, and aldehyde were generated in the early stage of the oxidative thermal decomposition, in which the weight began decreasing at approximately 200 °C. We found from these results that the early stage of the oxidative thermal decomposition of the wooden materials can be detected by detecting secondary alcohol, tertiary alcohol, and aldehyde. The odor measurement results were obtained using the nine types of standard gases specified in the Japanese Offensive Odor Control Law. However, the standard gases do not include alcohols. That is why only the similarity index for aldehydes rose.

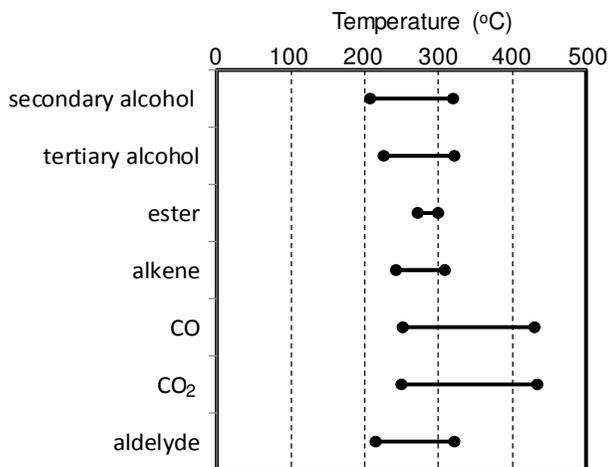


Fig. 3. Temperature ranges in which chemical species of Japanese cedar were detected.

Fig. 4 shows temperature ranges of the samples in which aldehyde was detected as measurement results of the odor and the FT-IR. The similarity index for aldehydes rose in the range of approximately 230 °C to 350 °C according to the odor measurement, and the substance containing an aldehyde group was detected by the FT-IR in the

temperature range of 200 °C to 320 °C. These results show that aldehyde was detected by both the odor and FT-IR measurements in the substantially same temperature range. Hence, it was found likely that the electronic noses also detect the substance containing an aldehyde group. Through the comparison with the measurement results of the TG-DTA shown in Fig. 2 a), it was also found that the substance containing an aldehyde group was generated by the thermal decomposition of cellulose and hemicellulose contained in the wooden materials in this temperature range.

During fire, not only wood-based polymers burn, but also synthetic polymers and hydrocarbon-based flammable liquids are involved in the combustion. Existing researches have shown that the combustion of the synthetic polymers increases the similarity index for aldehydes. However, the hydrocarbon-based flammable liquids do not generate aldehyde-based substances. However, measurements by the electronic noses have clarified that combustion of kerosene increases the similarity index for hydrocarbons. Thus, types of burning materials can be identified by selecting several standard gases in advance.

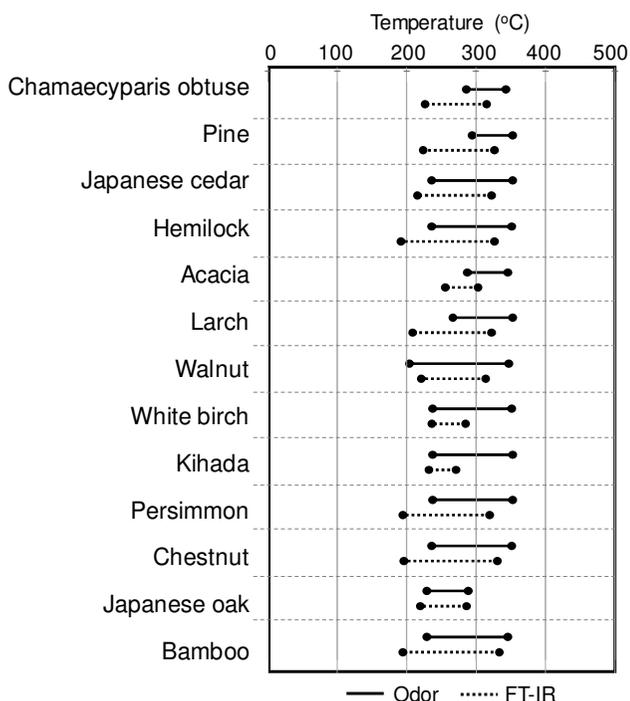


Fig. 4. Temperature ranges of samples in each of which the similarity index for aldehydes was detected by the electronic nose and temperature ranges of the samples in each of which a substance containing an aldehyde group was detected by the FT-IR.

Conclusion

We found from the TG-DTA / FT-IR simultaneous measurement results of the wooden materials that a substance containing secondary alcohol, tertiary alcohol, and an aldehyde group was generated in the early stage of the oxidative thermal decomposition (from 200 °C to 300 °C). CO and CO₂ were generated from at around 250 °C until the decomposition ended. We also found from the measurement results obtained by the electronic noses that the similarity index for aldehydes rose from at approximately 230 °C. We found from these results that, in developing the technique of fire detection by odor, the fire can be detected in its early stage by focusing more attention on substances containing an aldehyde group than on CO and CO₂. Since the electronic nose uses the oxide semiconductor sensors, we found that the oxide semiconductor sensors are effective for detecting aldehyde-based substances.

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References

- [1] O. Sugawa, K. Kamiya and Y. Oka, *Evaluation on Odor Intensity and Quality from Plastic and Wood Materials in Pre-combustion Condition*, 15th International Conference on Automatic Fire Detection, Vol.15, pp.21-28 (2014).
- [2] K. Kamiya, O. Sugawa, T. Imamura and Y. Oka, *Experimental Study on Odor Intensity and Quality from Wood Materials in Oxidative pyrolysis*, *Bulletin of Japan Association for Fire Science and Engineering*, Vol.63, No. 2 ,pp.25-35 (2013). (in Japanese)
- [3] Kyoko Kamiya, Osami Sugawa, Hiroki Kanai, Tomohiko Imamura and Yasushi Oka, *Evaluation on Odor Intensity and Quality from Wood in Pre-combustion Condition*, Proceedings of Asia Pacific Symposium on Safety 2011, pp.344-347 (2011).
- [4] D. Kohla, A. Eberheim, P. Schieberle, *Detection mechanisms of smoke compounds on homogenous semiconductor sensor films*, *Thin Solid Films*, 290, pp.1-6, (2005).
- [5] ISO 19702, Toxicity testing of fire effluents – Guidance for analysis of gases and vapours in fire effluent using FTIR gas analysis (2006).
- [6] J. Kita, Y. Aoyama, M. Kinoshita, H. Nakano, H. Akamaru, *Technical Digest of the 17th Sensor Symposium*, pp301-305 (2000).