

Effects of Additives on Gasification of Unused Cedar Wood by Pyrolysis

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Abstract—Generating thermal power using fossil fuels is harmful to the environment. Efforts to decrease carbon dioxide emissions are being made in many countries, and the Japanese government has declared that by 2050 greenhouse gas (including CO₂) emissions in Japan will be zero. Japan has great forest resources, more than 70% of the land being forested. However, the Japanese forestry industry has suffered difficulties in recent years because increasing amounts of timber are being imported and concrete is being used increasingly by the construction industry. In this study, hydrotalcite (Mg₆Al₂(OH)₁₆CO₃·MH₂O) was added to unused cedar wood during low temperature pyrolysis to increase the amounts of flammable gases such as CH₄, C₂H₄, C₂H₆, C₃H₆, and C₃H₈ generated. Cedar wood from trees that had been felled but unused was placed in a metal reaction vessel with a predetermined amount of hydrotalcite and heated to 450 °C in a nitrogen atmosphere to achieve pyrolysis. The combustible gas components and condensed wood vinegar solution produced during pyrolysis were analyzed. The gases generated during cedar pyrolysis included CH₄, C₂H₄, C₂H₆, C₃H₆, C₃H₈, and CO₂. The amount of combustible gas produced increased as the amount of hydrotalcite added increased.

Index Terms—Biomass, hydrotalcite, pyrolysis.

I. INTRODUCTION

Increasing demand for fossil fuels has led to a global energy crisis [1]. At the 21st Conference of the Parties to the United Nations Framework Convention on Climate Change (also called COP21) held in Paris, France, in November 2015, the parties agreed to work toward limiting global temperature rise to a maximum of 2 °C. At COP21, the Japanese government set a goal of greenhouse gas emissions in Japan being 26% lower in 2030 than 2013. Interest in effective uses of biomass resources is increasing around the world because these could prevent fossil fuel use and protect the environment. Forests cover 67% of land in Japan, and the forested area has not changed for 40 a.

Before the Great East Japan Earthquake in 2011, there were 54 nuclear power plants in Japan. At that time, thermal plants, nuclear plants, hydroelectric plants, and renewable generation systems produced 63.1%, 31.3%, 5.1%, and 0.5%, respectively, of the electricity used in Japan. However, the nuclear power plants in Japan were gradually shut down after the Great East Japan Earthquake. As a result, electricity was produced by thermal power plants to replace the shortfall in electricity. Producing electricity from forest biomass would allow Japan to become less dependent on fossil fuels [2].

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The main types of biomass that are used to produce energy are wood, wood processing waste, agricultural waste, material derived from municipal waste, and sewage sludge [3], [4]. Biomass is relatively easy to obtain and can be used as a renewable alternative to fossil fuels for producing energy [5] to decrease emissions of CO₂, the main greenhouse gas [6]. Utilizing biomass to produce energy involves pyrolysis. Pyrolysis has also been performed to effectively recycle chemical products. Pyrolysis and chemical recycling have been investigated in many published studies [7]–[9], but pyrolysis is a very complex process that is affected by many parameters such as the pyrolysis temperature, additives, and systems used in the pyrolysis plant [10]. The main components of biomass are hemicellulose, cellulose, and lignin, which generally contribute 20%–40%, 40%–60%, and 10%–25%, respectively, of the total mass [11], [12]. It has previously been found that lignin gradually degrades over a wide temperature range of 280–600 °C but hemicellulose and cellulose degrade relatively quickly at lower temperatures of 200–350 °C [13]. Cracking liquid hydrocarbons creates gases and cracking gaseous hydrocarbons creates H₂ [14]–[18]. Heating organic materials in the absence of oxygen transforms the materials into char and gaseous and liquid compounds, and the products and yields depend on the temperature and heating rate [18]–[22]. The char and liquid compound yields decrease and the amount of gas produced increases when the pyrolysis temperature is increased, and pyrolysis at a low temperature gives a low yield of gas [23], [14]. The objective of the biomass gasification process is to maximize the amounts of gaseous compounds produced.

We have previously found that the gasification yield during the pyrolysis of natural organic materials can be maximized by adding a molecular sieve, a type of zeolite [24], [25]. Zeolite-based catalysts have been used when dehydrating and calcining oil at atmospheric pressure [26], [27]. Molecular sieves have been found to act as environmentally friendly catalysts [28]. It has been found that catalysis using zeolites allows efficient biomass pyrolysis at much lower costs than performing high-pressure hydrogenation [29].

We previously found that the presence of hydrotalcite during the pyrolysis of brominated plastics increased the oil yield and decreased the brominated compound content of the oil produced [30]. Hydrotalcite is a layered double hydroxide composed of metal complex hydroxides consisting of Mg²⁺ and Al³⁺ host layers and anionic species in the interlayer guest layers (Fig. 1). Interest in using hydrotalcite as a catalyst, to remove gas, and as an ion exchange material has been increasing in recent years. Using hydrotalcite as a catalyst has been found to increase the biodiesel yield from 62% to 77%. It has recently been found that the catalytic

properties of hydrotalcite can be improved by using particular Mg^{2+} and Al^{3+} molar ratios [31]-[33]. In this study, we investigated the effect of the presence of hydrotalcite during the pyrolysis of wood at 450 °C on the amount of gas produced and the combustible gas contents.



Fig. 1. Schematic diagram of hydrotalcite (courtesy of Kyowa Chemical Industry Co.).

II. EXPERIMENTAL

A. Materials

The samples were prepared from chipped Japanese cedar (SAMBU SUGI, Chiba, Japan). Synthetic hydrotalcite (KW-1000), which was used as an additive, was obtained from Kyowa Chemical Industry Co. The composition of the hydrotalcite is shown in Table I.

TABLE I: COMPOSITION OF THE HYDROTALCITE

Al ₂ O ₃ (wt%)	MgO(wt%)	Mg/Al ₂ O ₃	Na(wt%)
19.3	35.1	4.60	0.02

(Mg/Al₂=4.5)

A predetermined amount of hydrotalcite was mixed with 20 g of cedar wood to prepare each cedar wood/hydrotalcite sample. A predetermined amount of sodium hydroxide (Wako Co.) or methanol-washed sea sand (425–850 μm diameter; Wako Co.) was mixed with cedar wood to prepare mixtures for use in experiments for comparison with the experiments using cedar wood and hydrotalcite mixtures. The compositions of the mixtures that were used are shown in Table II.

TABLE II: COMPOSITIONS OF THE MIXTURES USED IN THE EXPERIMENTS (HT = HYDROTALCITE)

	Condition of sample	Rate of addition
I	Cedar	–
II	Cedar + HT	20:1
III	Cedar + HT	8:1
IV	Cedar + HT	4:1
V	Cedar + NaOH	8:1
VI	Cedar + NaOH	4:1
VII	Cedar + Sea Sand	4:1

The experimental setup is shown in Fig. 2. A sample mixture was placed in the metal reactor, then nitrogen was

passed through the reactor at a flow rate of 50 mL/min for 60 min to remove oxygen. The nitrogen flow was then stopped and pyrolysis was performed. The temperature of the part of the metal reactor containing the sample was determined using a thermocouple. The temperature was increased at 5 °C/min to 450 °C, then the sample was allowed to cool naturally. The gases generated during pyrolysis were cooled in a cooling tube and the condensate (“wood vinegar” solution) was collected. Non-condensable gases were bubbled through an alkaline aqueous solution and collected in a gas pack. This gas was called “decomposition product gas”.

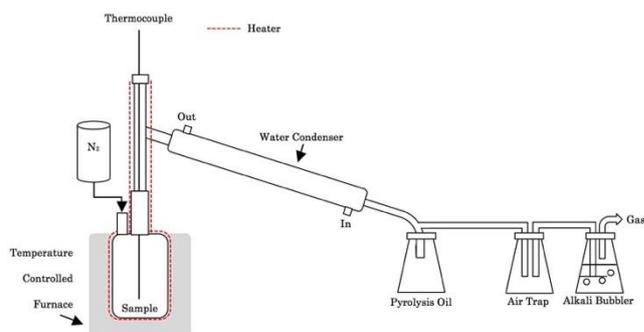


Fig. 2. Apparatus used in the experiments.

B. Analysis

The nitrogen, carbon, and hydrogen contents of the cedar wood were determined using a SUMIGRAPH NCH-22A total nitrogen, total carbon, and total hydrogen measurement system (Sumika Chemical Analysis Service, Tokyo, Japan). The sample combustion temperature was 800 °C. The nitrogen, carbon, and hydrogen contents of the cedar wood are shown in Table III [26].

TABLE III: NITROGEN, CARBON, AND HYDROGEN CONTENTS OF THE CEDAR WOOD

Element	Content (wt.%)
Nitrogen	1.5
Carbon	62.7
Hydrogen	8.9

Sample mass 19.75 mg

The wood vinegar solution produced during pyrolysis was diluted by a factor of 100 with hexane (special grade reagent; Wako Pure Chemical Industries, Osaka, Japan) and qualitatively analyzed using a QP2020NX gas chromatograph mass spectrometer (Shimadzu, Kyoto, Japan). The main compounds in the wood vinegar solution were identified using gas chromatography mass spectrometry spectral libraries. The carrier gas was pure helium. Separation was achieved using an Rtx-1 column (0.25 mm i.d., 0.25 μm film thickness). The oven temperature program started at 40 °C, which was held for 30 min, and then increased at 5 °C/min to 230 °C.

After pyrolysis, the hydrotalcite was structurally analyzed by X-ray diffractometry using a MiniFlex system (Rigaku, Tokyo, Japan). The gases produced were qualitatively and quantitatively analyzed using a GC-2014FID gas chromatograph (Shimadzu).

III. RESULTS AND DISCUSSION

A. Wood Vinegar

The wood vinegar solution was qualitatively analyzed by gas chromatography mass spectrometry. The main components were methanol and 4-nonenic acid, but toluene, cresol, and naphthalene were also present [26].

B. Residue

The degree to which pyrolysis affected the hydrotalcite structure was assessed by analyzing the hydrotalcite residue structure by X-ray diffractometry before and after pyrolysis. The X-ray diffractometry patterns are shown in Fig. 3.

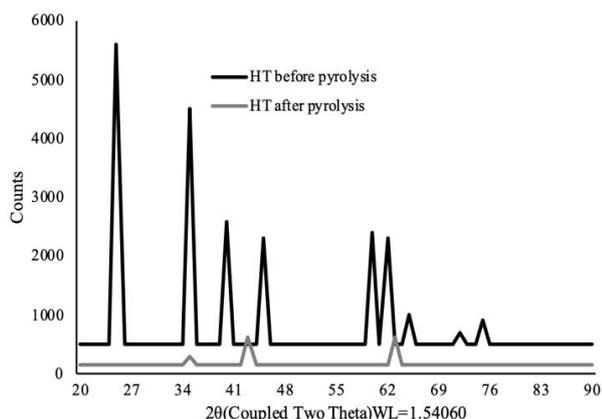


Fig. 3. X-ray diffractometry patterns for the hydrotalcite (HT) before and after pyrolysis.

We were concerned that the properties of hydrotalcite may change because of structural changes at around 450 °C. However, no marked structural changes were found to occur during pyrolysis, and we concluded that the interlayer water was removed but the properties of hydrotalcite did not change.

C. Gas Production

The gases that were generated were qualitatively and quantitatively analyzed by gas chromatography. The amounts of the combustible gases CH₄, C₂H₄, C₂H₆, C₃H₆, and C₃H₈ produced in the different tests were determined. The amounts of CH₄ produced are shown in Fig. 4, the amounts of C₂H₄, and C₂H₆ produced are shown in Fig. 5, and the amounts of C₃H₆ and C₃H₈ produced are shown in Fig. 6. The amounts of CO and CO₂ produced are shown in Fig. 7.

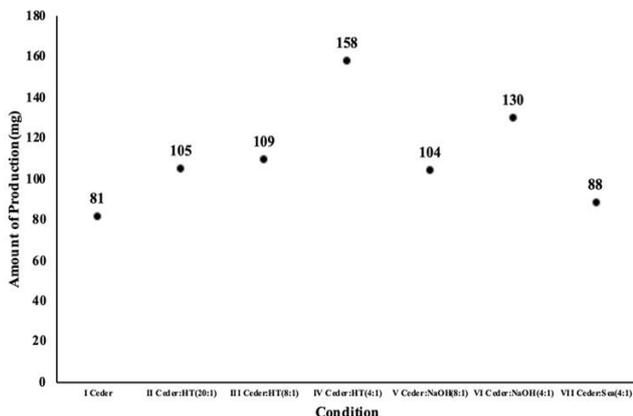


Fig. 4. Amounts of CH₄ produced.

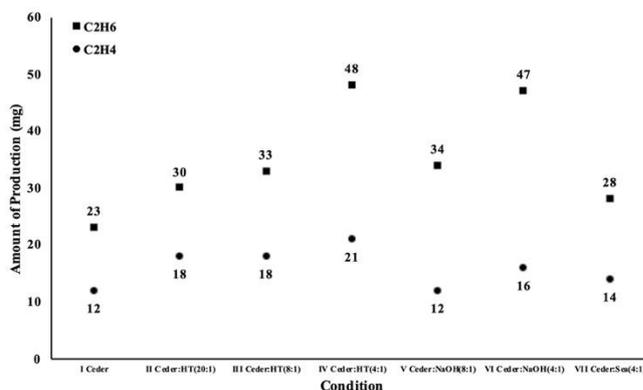


Fig. 5. Amounts of C₂H₆ and C₂H₄ produced.

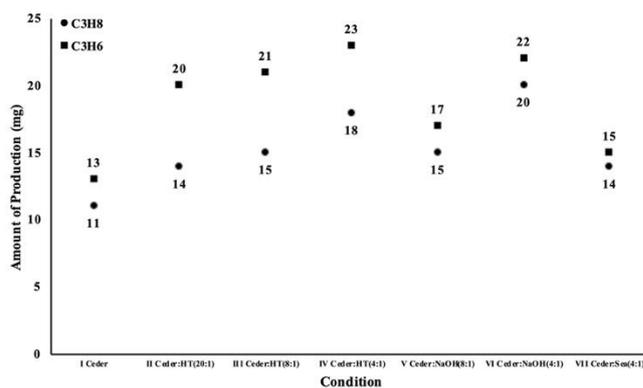


Fig. 6. Amounts of C₃H₈ and C₃H₆ produced.

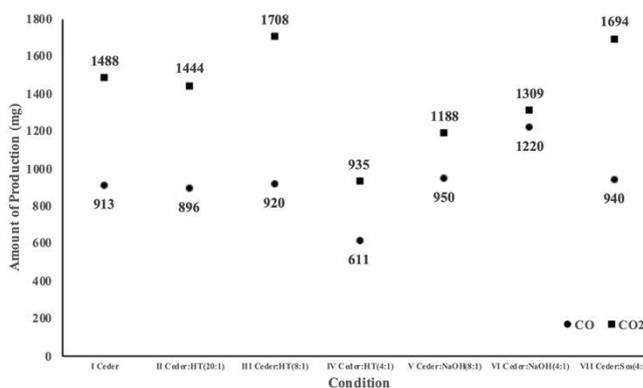


Fig. 7. Amounts of CO and CO₂ produced.

The amounts of combustible gases produced during the pyrolysis of mixtures of cedar wood and hydrotalcite were determined. Larger amounts of all of the combustible gases were produced in the test using Condition IV (a cedar wood: hydrotalcite ratio of 4:1) than in the tests using the other conditions. We concluded that this was caused by the catalytic effect of the hydrotalcite.

CO₂ was produced, but in terms of carbon emissions, the CO₂ produced by pyrolyzing cedar wood can be discounted. Hydrotalcite contains carbonate ions, which could be emitted during pyrolysis. However, the hydrotalcite we used was produced using seawater. Assuming that CO₂ from the atmosphere that had entered the seawater was emitted, we also assumed that CO₂ produced from the hydrotalcite could be discounted.

IV. CONCLUSION

Synthetic hydrotalcite was added to cedar wood and the

mixture was pyrolyzed at 450 °C to attempt to increase the amount of combustible gases produced from the cedar wood. The cedar wood to hydrotalcite ratio was found to affect the amount of combustible gases produced.

We concluded that catalysis by the hydrotalcite increased the amount of combustible gases produced. The synthetic hydrotalcite is a complex magnesium and aluminum hydroxide that may act as a catalyst. The main component of wood is cellulose, which is not hydrolyzed and is chemically stable. However, the synthetic hydrotalcite used in the study is basic and contains interlayer water. We concluded that decomposition of wood caused by heat in the metal reactor was accelerated because of the basicity of the hydrotalcite. The results for the pyrolysis of a mixture of cedar wood and sodium hydroxide, a strong base, indicated that the basicity of hydrotalcite explained some of the catalytic activity of the hydrotalcite.

The results for pyrolysis of mixtures of cedar wood and hydrotalcite indicated that the optimum cedar wood: hydrotalcite ratio was between 4 and 8.

About 1 mL of wood vinegar solution was produced during each pyrolysis experiment. Wood vinegar is acidic. We concluded that the combustible gas yield was affected by acid–base (neutralization) reactions between hydrotalcite and wood vinegar. We concluded that adding hydrotalcite decreased the amount of wood vinegar produced and therefore increased the amount of combustible gas produced.

The X-ray diffractometry results for the hydrotalcite indicated that the characteristic layered structure of hydrotalcite was retained even after pyrolysis at 450 °C. This suggested that the function of hydrotalcite was not lost at high temperatures.

The results indicate that adding hydrotalcite to cedar wood to give a cedar wood: hydrotalcite ratio of between 4 and 8 by mass can increase the amount of combustible gas produced during pyrolysis.

CONFLICT OF INTEREST

All authors declare that: i) no support, financial or otherwise, has been received from any organization that may have an interest in the submitted work and ii) there are no other relationships or activities that could appear to have influenced the submitted work.

AUTHOR CONTRIBUTIONS

R. Hanazawa, K. Nakamura, H. Kawaraya and R. Shimizu performed the experimental work and data analysis. The wording of the final paper was agreed upon by all authors.

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