

Effect of the Addition of Hydrotalcite in the Pyrolysis of Unutilized Wood on Gas Production

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Abstract—Reduction of carbon dioxide emissions from the use of fossil fuels is taking place in many countries. In addition, thermal power generation is damaging the environment. Japan has declared that it will reduce its emissions of greenhouse gases, including CO₂, to zero by 2050. Japan is a forest-resource-rich country, and more than 70% of its land area is covered by forest. In recent years, however, Japan's forestry industry has decreased owing to the increase of imported timber and the increase in concrete construction. In this study, synthetic hydrotalcite (Mg_{1-x}Al_x(OH)₂(CO₃)_{x/2}·mH₂O) was added to unused cedar wood during pyrolysis and gasification at low temperature, and its effect on the production of combustible gases, CH₄, C₂H₄, C₂H₆, C₃H₆ and C₃H₈, was investigated. A mixture of cedar wood, which was undistributed after being cut in Japan, and a predetermined amount of synthetic hydrotalcite was placed in a metal reactor and subjected to pyrolysis under a nitrogen atmosphere at temperatures up to 500 °C. The mixture was then heated to a temperature of 500 °C. The components of the gas produced by pyrolysis were CH₄, C₂H₄, C₂H₆, C₃H₆, C₃H₈, and CO₂. The amount of synthetic hydrotalcite addition during pyrolysis affected the amounts of the combustible gases produced.

Keywords—biomass, pyrolysis, hydrotalcite, greenhouse gases, combustible gases, unused resources, forest resources

I. INTRODUCTION

Green House Gas (GHG) emissions from the combustion of fossil fuels pose a major environmental challenge to the global environment [1]. The increased demand for fossil fuels has led to a global energy crisis. At the 21st Conference of the Parties of the United Nations Framework Convention on Climate Change held in Paris, France, in November 2015, efforts to limit the global temperature increase to less than 2 °C (1.5 °F) were agreed upon by 196 countries and regions. At the 21st Conference of the Parties, the Japanese government set the goal of reducing GHG emissions by 26% from 2013 levels by 2030, and it declared that it will achieve zero GHG emissions by 2050. In recent years, there has been growing worldwide interest in the effective use of biomass resources in view of the depletion of fossil fuels and environmental protection. In Japan, 70% of the country's land area is forested. However, there has been no change in the forest area over the past 40 years. In other words, it is an underutilized resource. Japan's power source mix is estimated to be 31.3% nuclear, 63.1% thermal, 5.1% hydro, and 0.5% renewable energy. In Japan, 54 nuclear power plants were in operation until the Great East Japan Earthquake of 2011. However, after the Great East Japan Earthquake, nuclear power plants were shut down one after another. This shortage in power generation was covered by thermal power generation, which continues to this day.

Although thermal power generation in Japan emits less carbon dioxide, a GHG, than thermal power generation in other countries, biomass, which utilizes forest resources, is a precursor to reducing the dependence on fossil fuels [2].

II. LITERATURE REVIEW

Biomass resources are relatively easy to obtain, and they can be used as a renewable alternative to fossil fuels for energy supply [3] and to reduce CO₂ emissions, the main component of GHGs [4]. The biomass used for energy mainly includes wood and wood processing waste, agricultural waste, and plants derived from municipal waste and sewage sludge [5, 6]. Pyrolysis plays an important role in chemical conversion, such as in recycling of chemical products. Although there is a wealth of literature on pyrolysis basic surveys and chemical recycling [7–9], pyrolysis is a very complex process, and it is affected by many parameters, such as the pyrolysis temperature, additives, and the plant systems [10, 11]. Previously, we reported that gasification can be maximized by adding molecular sieves, a type of zeolite, to the pyrolysis of natural organic materials [12]. Zeolite-based catalysts have been used for dehydration and oil calcination under atmospheric pressure [13, 14], and molecular sieves have been reported to be an environmentally friendly catalyst [15]. Furthermore, it has been reported that the zeolite-catalyzed route of high-performance biomass pyrolysis of oil is preferred because it has much lower costs than alternative high-pressure hydrogenation [16].

The major components of biomass resources are hemicellulose, cellulose, and lignin, and they generally contain 20%–40% hemicellulose, 40%–60% cellulose, and 10%–25% lignin [17]. According to previous literature, lignin is gradually degraded over a wide temperature range from 280 to 600 °C, while hemicellulose and cellulose can be degraded relatively quickly at lower temperatures of 200 to 350 °C [18]. In addition, there is a tendency for the yield of char and liquid compounds to decrease and the yield of gases to increase when the pyrolysis of biomass is performed at higher temperature, while the yield of gases decreases when the pyrolysis is performed at lower temperature. It has been reported that heating of organic materials in the absence of oxygen transforms them into char, gas, and liquid compounds, and the products and yields depend on the temperature and rate [19–22]. The goal of biomass gasification is to maximize the amounts of the gaseous products.

We previously reported that the addition of synthetic hydrotalcite in the pyrolysis of brominated plastics increases the yield of the product oil and reduces the content of bromine

compounds in the product oil [23]. Hydrotalcite is classified as a layered double hydroxide. It is composed of complex metal hydroxides, consisting of a host layer of divalent Mg^{2+} and trivalent Al^{3+} with anion species in the guest layer between the host layers (Figs. 1 and 2).

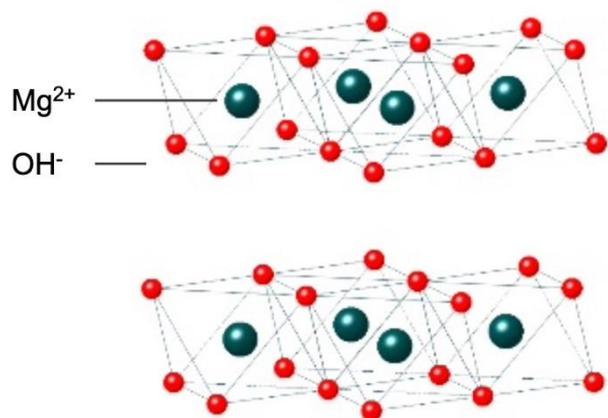


Fig. 1. Schematic diagram of magnesium hydroxide.

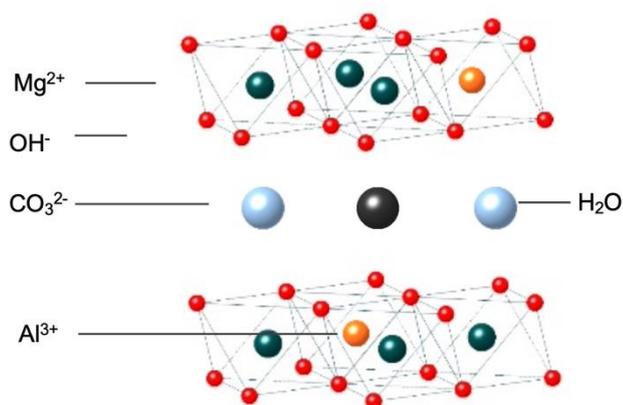


Fig. 2. Schematic diagram of hydrotalcite.

The hydrotalcite used in this study has the same basic structure as magnesium hydroxide $Mg(OH)_2$, but it is known to have a strong ability to react with acids and to exchange ions at pH of 3.5 to 5. It is mainly used in industrial applications as a heat stabilizer for polyvinyl chloride, a film insulator for agriculture, and an acid-receptive agent for rubber and plastics, and in pharmaceutical applications as an antacid agent for gastrointestinal drug ingredients.

In recent years, hydrotalcite has received increasing attention as a material for catalysts and gas removal, and as an ion exchanger, and it has been reported that the catalytic properties of hydrotalcite can be improved by setting the molar ratio of divalent Mg^{2+} to trivalent Al^{3+} in hydrotalcite as a parameter [24–26].

Previously, we reported that the addition of hydrotalcite as an additive in the pyrolysis of forest residues promotes pyrolysis and increases the yield of the produced oil [27]. In this study, we investigated the effect of synthetic hydrotalcite with different composition ratios as an additive on the combustible gas production during the pyrolysis of cedar wood, which is an unutilized resource.

III. MATERIALS AND METHODS

Chipped Japanese cedar (*Sambu Sugi*, Chiba, Japan) was

used as the sample. The additives, synthetic hydrotalcite (KW-1000 and KW-2000), were obtained from SETOLAS Holdings Inc. (Takamatsu City, Japan). The composition ratios of KW-1000 and KW-2000 are given in Table 1.

Table 1. Composition ratios of KW-1000 and KW-2000 (wt.%)

Substance	Al_2O_3	MgO
KW-1000	33.4%	61.0%
KW-2000	19.7%	34.9%

A predetermined amount of synthetic hydrotalcite was added to 20 g of each cedar sample to make a mixed sample. In addition, predetermined amounts of sodium hydroxide (Wako Co., Ltd.) and sea sand (methanol washed, 425–850 μm , Wako Co., Ltd.) were added to cedar samples for comparison. The experimental conditions are given in Table 2.

Table 2. Experimental conditions

Condition	Sample	Additive
I	Cedar	-
II	Cedar + HT (KW-1000)	10 g
III	Cedar + HT (KW-1000)	2 g
IV	Cedar + HT (KW-1000)	1 g
V	Cedar + HT (KW-2000)	10 g
VI	Cedar + HT (KW-2000)	2 g
VII	Cedar + HT (KW-2000)	1 g
VIII	Cedar + NaOH	10 g
IX	Cedar + Sea Sand	10 g

The experimental setup used in this study is shown in Fig. 3. The mixed sample was placed in a metal reactor, and nitrogen gas was flowed at a flow rate of 50 mL/min for 60 min to remove oxygen from the reactor.

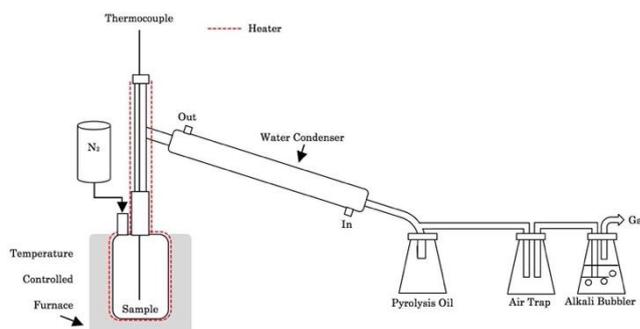


Fig. 3. Experimental apparatus.

After nitrogen replacement, the nitrogen gas flow was stopped and the pyrolysis experiments were performed. The temperature of the sample portion of the metal reactor was measured by thermocouples as the decomposition temperature, and the temperature was increased to 500 $^{\circ}C$ at a rate of 5 $^{\circ}C/min$.

After the temperature reached 500 $^{\circ}C$, the sample was allowed to cool naturally. The non-condensable gases generated during pyrolysis were collected in a gas pack through bubbling an alkaline solution (0.1 mol/L, NaOH), and they were qualitatively and quantitatively analyzed as the decomposition product gas.

Because the main use of the synthetic hydrotalcite used in this study is in pharmaceutical packaging, the structural changes of hydrotalcite for conditions II and V were investigated by X-Ray Diffraction (XRD) to determine the structural changes caused by heating.

The gases produced by the pyrolysis of cedar wood were qualitatively and quantitatively analyzed by a gas chromatograph (GC-2014FID, SHIMADZU). Because non-agglomerated gases may contain halogens, the alkaline solution (0.1 mol/L, NaOH) that passed through the system was diluted 50-fold and qualitatively analyzed by an ion chromatograph (IC-20, SHIMADZU).

IV. RESULT AND DISCUSSION

A. Analysis of the Produced Gas

The gases generated by the pyrolysis of cedar wood were qualitatively and quantitatively analyzed by gas chromatography, and the results are shown in Figs. 4–8.

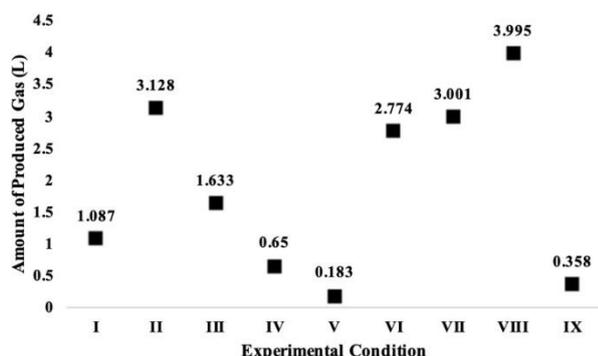


Fig. 4. Amounts of product gas produced under the different experimental conditions.

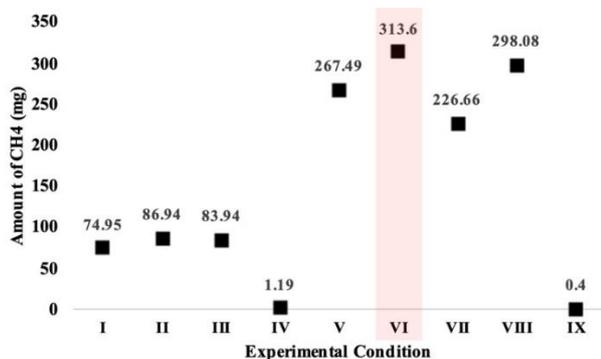


Fig. 5. Amounts of CH₄ produced under the different experimental conditions.

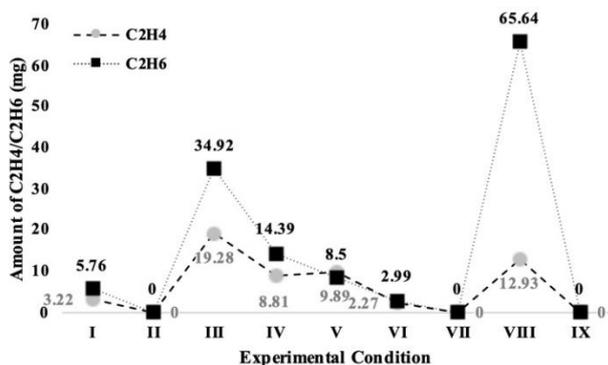


Fig. 6. Amounts of C₂H₄ and C₂H₆ produced under the different experimental conditions.

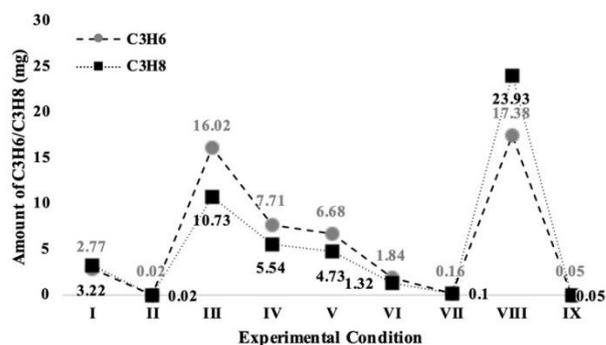


Fig. 7. Amounts of C₃H₆ and C₃H₈ produced under the different experimental conditions.

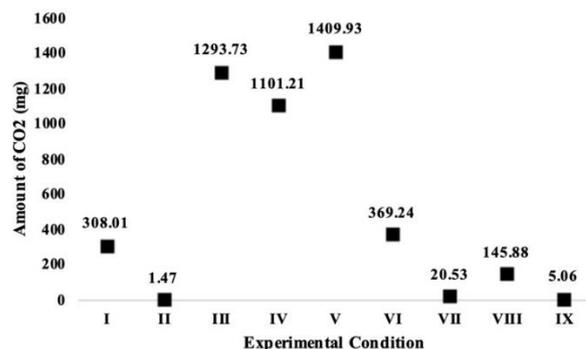


Fig. 8. Amounts of CO₂ produced under the different experimental conditions.

The results of qualitative and quantitative analysis of the product gases suggested that the addition of 2 g of KW-2000 increased the amount of CH₄ produced more than the addition of NaOH, which is generally used as an alkaline catalyst in pyrolysis. For the addition of 2 g of KW-2000, the amounts of C₂H₄, C₂H₆, C₃H₆, and C₃H₈ were lower than those under the other conditions. It can be inferred that the resolution of KW-2000 was superior to that of the other additives. However, the analytical results suggested that there is an optimal additive amount.

KW-1000 is a synthetic hydrotalcite with Mg/Al₂ = 4.5. KW-2000, which showed the strongest effect on the pyrolysis of cedar wood, was produced by calcination of KW-1000 to eliminate interlayer water, interlayer anions, and the hydroxy groups coordinated to Mg and Al. KW-2000 is more alkaline than KW-1000.

The amount of CO₂ produced increased with the addition of synthetic hydrotalcite, which was inferred to be hydrotalcite-derived carbonic acid.

B. Ion Chromatography Analysis of the Alkaline Aqueous Solutions

The results of qualitative analysis of the alkaline solutions (0.1 mol/L, NaOH, diluted 50-fold) obtained by ion chromatography are given in Table 3.

Table 3. Ion chromatography results of the alkaline solutions

	I	II	III	IV	V	VI	VII	VIII	IX
Cl	○	nd	nd	nd	nd	nd	nd	nd	nd
Br	nd	nd	nd	nd	nd	nd	nd	nd	nd

nd: not detected

C. Residue

The structural changes of KW-1000 and KW-2000 for

conditions II and V were verified by XRD, and the XRD patterns are shown in Figs. 9 and 10, respectively.

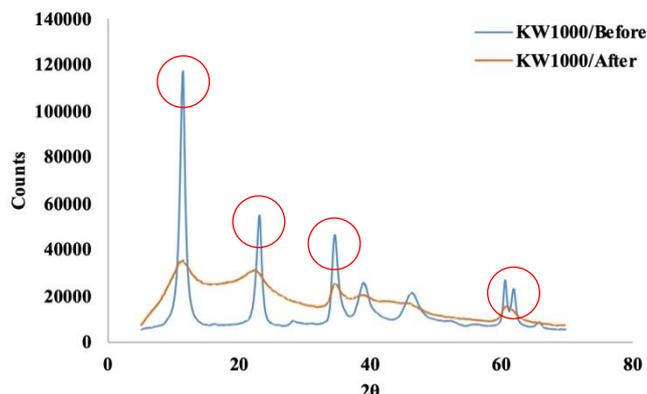


Fig. 9. XRD patterns of KW-1000 before and after pyrolysis.

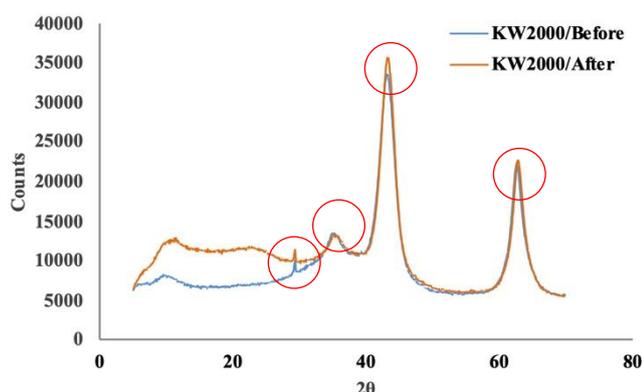


Fig. 10. XRD patterns of KW-2000 before and after pyrolysis.

Although the intensities of the diffraction peaks of KW-1000 were lower after pyrolysis, the peak values were confirmed, so it can be inferred that the layer structure of hydrotalcite was not destroyed (Fig. 9). KW-2000 was not affected as much as KW-1000 by pyrolysis (Figs. 9 and 10).

V. CONCLUSION

In this study, synthetic hydrotalcite was used as an additive in the pyrolysis of cedar wood, which is an unutilized resource, at 500 °C to achieve highly efficient gasification. The synthetic hydrotalcite used in this study is used in industrial applications as a heat stabilizer for polyvinyl chloride, a film insulator for agriculture, and an acid-receptive agent for rubber and plastics, and in pharmaceutical applications as an antacid agent for gastrointestinal drug raw materials. The results suggested that the addition of synthetic hydrotalcite as an additive in pyrolysis allows pyrolysis at relatively low temperatures and increases the amounts of combustible gases produced. In particular, KW-2000 had a strong effect on the pyrolysis of cedar wood, and the amount of combustible gases produced was higher than when NaOH, a representative alkali catalyst, was added.

The increase in combustible gas production with the addition of synthetic hydrotalcite is believed to be due to the catalytic effect of synthetic hydrotalcite, which is a composite hydroxide of magnesium and aluminum. The main component of wood is cellulose, which is chemically and physically stable. However, the synthetic hydrotalcite used in this study was alkaline, and it is presumed that the

decomposition of cellulose was accelerated in the metal reactor owing to the decomposition reaction caused by heat and the hydrolysis reaction caused by the alkalinity of the synthetic hydrotalcite. Although sodium hydroxide is a strong base, the results suggested that synthetic hydrotalcite (KW-2000) is superior to sodium hydroxide as an additive in terms of resolution.

The results suggested that the optimum addition rate of synthetic hydrotalcite is approximately 0.1 relative to the mass ratio of cedar.

XRD analysis of the synthetic hydrotalcite indicated that the layered structure, which is the characteristic structure of hydrotalcite, was retained after pyrolysis at 500 °C, suggesting that the functionality was not lost owing to the high temperature.

These results suggest that pyrolysis of cedar with synthetic hydrotalcite (KW-2000) at a ratio of approximately 0.1 by mass can increase the amounts of combustible gases produced.

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

M. Arai, A. Ri, Y. Kodama, and Y. Katako performed the experimental work and data analysis. The wording of the final paper was agreed upon by all authors.

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