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Influence of Molecular Sieves Is Added in the Thermal Decomposition of Rice Husk

N. Morita, M. Nakayasu, Y. Kawabata, and H. Nakagome

***Abstract*—This research reports the energy release of rice chaff by pyrolysis. In Southeast Asia, rice is a staple food, and an abundance of chaff remains after rice cleaning the rice. Most chaff is spread on farmland or used as livestock feed. However, there is still a large amount of discarded chaff. In this study, This research was gasified chaff to evaluate its energy conversion using pyrolysis. This research investigated the effect of molecular sieves, which are a column filler, as an additive. The pyrolysis was performed under highly efficient conditions to measure any catalytic effects. Methane gas is a decomposition product and its release was the focus of this work as well as analyzing the amount of emitted carbon dioxide Adding molecular sieves 3A increases methane gas release and decreases carbon dioxide.**

***Index Terms*—Molecular sieve, pyrolysis, rice husk.**

I. INTRODUCTION

Interest is increasing for the utilization of biomass resources because fossil fuels are drying up and environmental protection is becoming more important worldwide [1].

Not only for the utilization of biomass resources, pyrolysis is important for effective chemical conversion in other fields such as recycling. There are abundant studies investigating pyrolysis and chemical recycling [2]-[13], but pyrolysis is a complicated process influenced by many factors [14]-[17]. The main component of lignocellulosic biomass is hemicellulose, cellulose, and lignin at contents around 20–40%, 40–60%, and 10–25%, respectively [18].

Lignin is gradually broken down in a wide temperature range of 280–600 ℃, and hemicellulose and cellulose can decompose quickly at low temperatures around 200–350 ℃ [19].

The char and liquid compound yield decrease when pyrolysis of biomass is performed at a high temperature, and the quantity of emitted gases increases, but the yield of the gas decreases at low pyrolysis temperatures. The cracking of liquid hydrocarbons promotes the formation of gases, and the cracking of a gaseous hydrocarbon promotes the formation of H_2 [20]-[26]. Plants containing mainly wood, wood processing waste, energy crops, and farm products, as well as parts of organic waste, city garbage, and sewage grime can be used for biomass in energy conversion [27], [28].

The biomass is available widely and carbon neutral, creating a fuel source with a lower carbon footprint than fossil fuels as an energy supply [29], [30].

The zeolite catalyst, molecular sieves, used under atmospheric pressure in dehydration has been reported as eco-friendly [31]. In addition, the zeolite catalyst has shown high performance in biomass pyrolysis, lowering the expense compared with alternatives such as high-pressure hydrogenation [32]. We have reported the increase of product oil by pyrolysis of plastics by adding molecular sieves [33]-[36].

In this study, aimed to analyze the change in the product gas quantities during pyrolysis at 700 ℃ when using molecular sieves as an additive and the change in the combustible gas amounts.

II. EXPERIMENTAL

A. Materials

The biomass sample was Japanese rice chaff Koshihikari from Yamanashi Prefecture, Japan. Molecular sieves 3A, 4A, 5A, and 13X as rods 1/16 inch in length were purchased from Wako Pure Chemical Industries Co., Ltd, Osaka, Japan.

Sea sand (methanol washing product, 425–850 µm, Wako Pure Chemical Industries Co., Ltd.) was used as a control additive. The experiment conditions are shown in Table I.

TABLE I: EXPERIMENT CONDITIONS OF RICE HUSK (RH) PYROLYSIS

	Experiment Condition
I	Rice Husks
II	RH + Molecular Sieves 3A（1:1）
III	RH + Molecular Sieves 5A（1:1）
IV	RH + Molecular Sieves 13X（1:1）
V	RH + Molecular Sieves 3A Powder（1:1）
VI	RH + Molecular Sieves 5A Powder（1:1）
VII	RH + Molecular Sieves 13X Powder（1:1）
VIII	RH + Sea Sand（1:1）

B. Pyrolysis

The experimental device is shown in Fig. 1. Twenty grams of chaff and any additive (20 g) were placed inside the glass reactor and flushed with nitrogen gas for 60 minutes at 50 mL/min to remove oxygen.

The flow of nitrogen gas was stopped for the pyrolysis tests. The sample part of the glass reactor was heated and monitored using a thermocouple from room temperature to 700 ℃ at

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10 ℃/min.

The gas generated during pyrolysis passed into a condenser and was collected in a container as pyrolysis acid. The non-condensable gas was collected using a gas pack by bubbling through an aqueous alkaline solution.

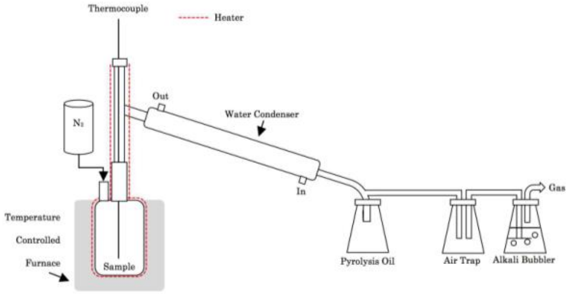


Fig. 1. Experimental apparatus.

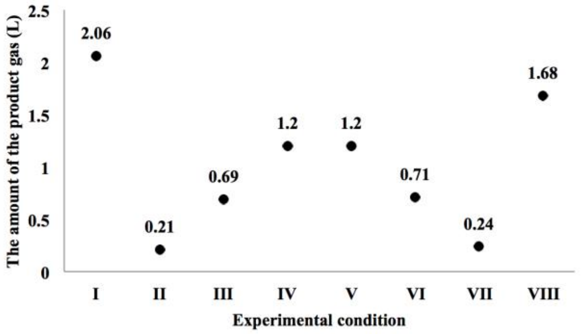


Fig. 2. Product gas release.

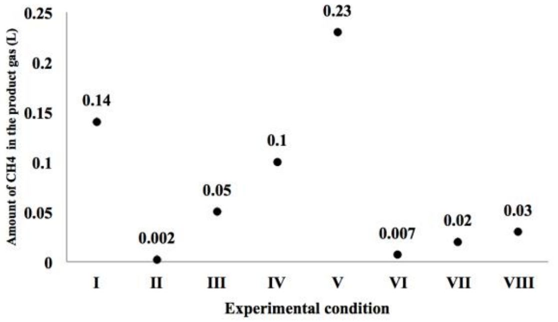


Fig. 3. Methane release.

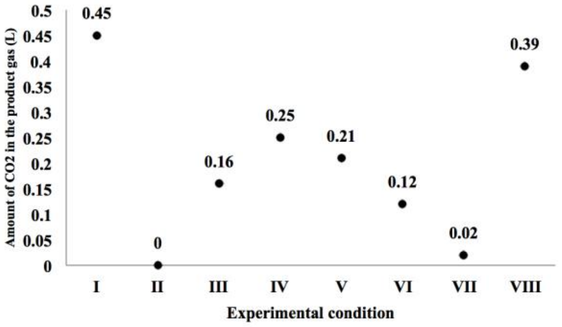


Fig. 4. Carbon dioxide release.

C. Analysis

Qualitative and quantitative analyses were performed using gas chromatography on a Shimadzu GC2014 (Kyoto, Japan) equipped with a flame ionization detector.

The residual substance was analyzed with a Hitachi TM3030 scanning electron microscope coupled with energy dispersion spectroscopy (EDS; Bruker QUANTAX, Billerica, MA, USA).

The surface of each sample was element distribution mapped using EDS to measure residual carbon.

III. RESULTS AND DISCUSSION

A. Decomposition Gas

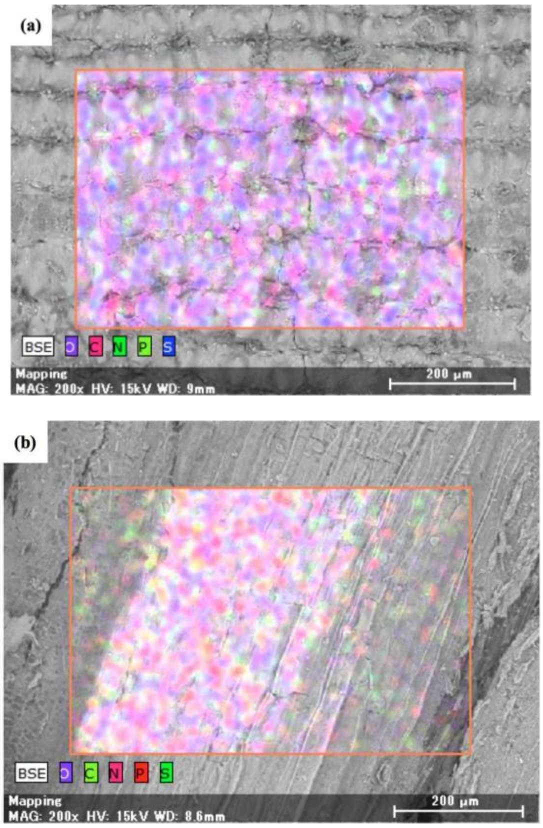
Fig. 2 shows the product gas amounts from the different pyrolysis conditions. In addition, methane quantities are shown in Fig. 3, and carbon dioxide in Fig. 4.

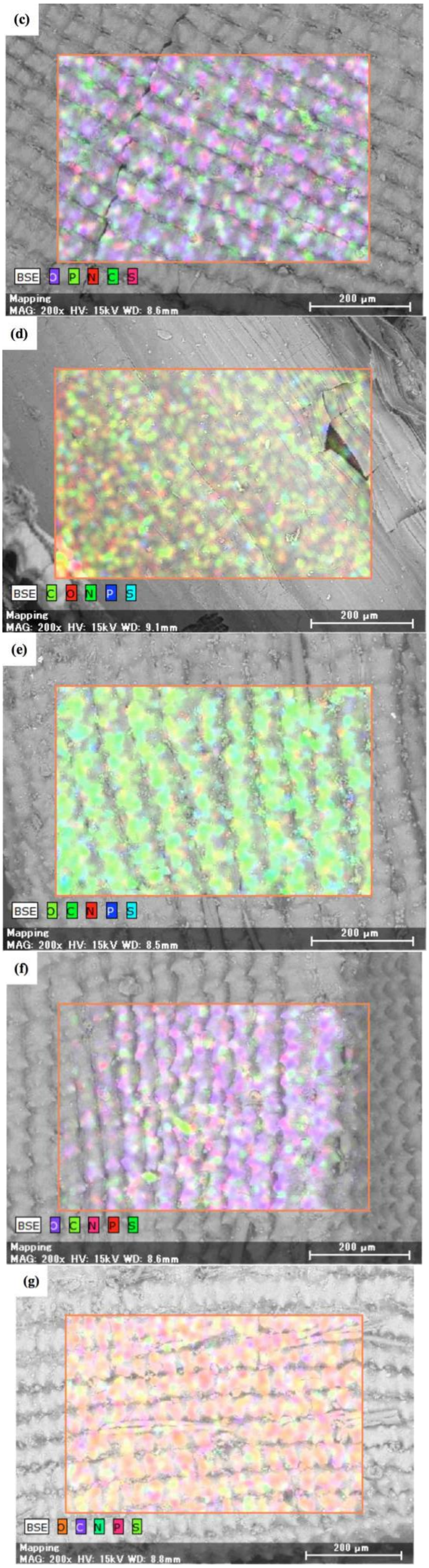
As shown in Fig. 2, condition I, which was a condition without additive, generated the highest amount of product gas. Condition V, with powder-form molecular sieves 3A at 1:1 ratio with rice husk showed the highest methane production, nearly double that of condition I (Fig. 3) and decreased carbon dioxide release to half that of condition 1 (Fig. 4).

B. Residue Analysis

In this study, EDS was used to observe residues on the sample surface and element distribution mapping to measure residual carbon was performed (Fig. 5). Residual carbon and residual oxygen in all conditions are shown in Fig. 6. Condition VI requires verification again, but since the remaining value shows a generally constant value, it can be said that it was properly pyrolysis under all conditions. The surface carbon content of rice hulls before thermal decomposition was 24.17%. The amount of surface carbon from state I without additives after pyrolysis decreased to 17.09%.

This decrease was due to the surface carbon becoming gas. Condition V using powdered molecular sieve 3A as an additive showed that methane gas production efficiency was high because residual carbon decreased to 18.11% and methane release was higher than condition I.





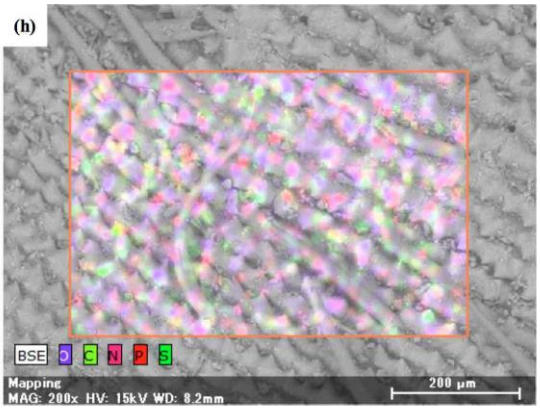


Fig. 5. Energy dispersive spectroscopy images of the (a) rice husks before pyrolysis and residues after pyrolysis for (b) condition I, (c) condition II, (d) condition III, (e) condition IV, (f) condition V, (g) condition VI and (h) condition VII.

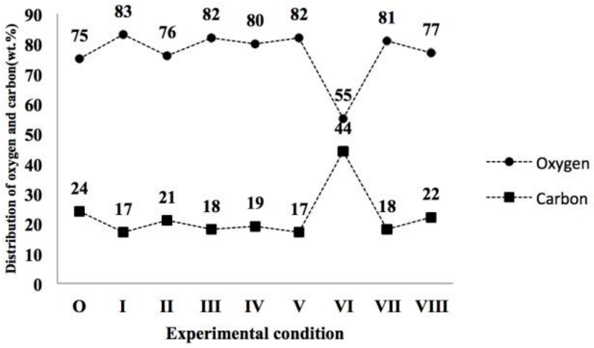


Fig. 6. Distribution of residual carbon and residual oxygen by EDS observation.

IV. CONCLUSION

This research increased methane gas release during pyrolysis of rice husk by adding molecular sieves as a catalyst. Comparing additive conditions for pyrolysis, methane gas release is increased over that without additives by processing molecular sieves 3A into a powder form and using a 1:1 ratio. Molecular sieves were added uniformly and the powder form of molecular sieves is important to achieve a catalytic effect for methane release. In addition, the quantity of carbon dioxide emission is reduced using molecular sieve additives because of adsorption, but this is not sufficient for carbon neutral biomass utilization.

In this study, it was suggested that addition of additives in the form of powdered molecular sieve 3A increases the content of methane while suppressing gas evolved, and can suppress the discharge of carbon dioxide.

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