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# Conversion of Rice Straw into Methane Gas using Zeolites

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**Abstract:** In Japan, there is a large amount of biomass waste from agriculture to be used as resources. In this study, we examined the conversion of rice straw into methane gas by thermal decomposition using zeolite catalysts. Four types of zeolites, NaA, NaX, NaY and HY, with different properties, crystal structure, exchangeable cation and Si/Al ratio were used as catalysts. The mixture of rice straw and zeolite was added into the reactor, and the reactor was heated 400 $^{o}$C for 1 h in nitrogen atmosphere. The amount and composition of the gas generated during the heating, and the weight of residue were examined. The results show the conversion of rice straw into methane gas can be improved using zeolites, and faujasite zeolites having Na cation, NaX and NaY, could convert rice straw into the largest amount of methane gas in this experiment. With increasing the heating temperature, production of methane gas promotes due to the promotion of decomposition reaction. The valuable gas including methane can be obtained from rice straw by heating at higher than 600 $^{o}$C for 30 min with NaY addition of same weight to rice straw.

**Key words:** *Rice straw, Methane gas, Zeolites, pyrolysis*

## INTRODUCTION

As we face the problems of global warming and climate change, substantial research and development has focused on the use of biomass as an alternative to fossil fuels. The widespread availability of biomass has been widely recognized, as has its potential to supply much larger amounts of useful energy with fewer environmental impacts than fossil fuels [1].
Biomass is one of the promising forms of clean and green fuel that can meet day to day energy requirements, and its use predates the use of fossil fuels such as petroleum, natural gas and coal. Biomass makes a significant contribution (about 14 %) to global renewable energy utilization, while in rural areas of developing countries this contribution is up to 90 %. Since around 90 % the world production is expected to reside in developing countries by 2050, biomass is likely to remain a major source of energy for those large populations [2-4].
In our country for the recycling society formation, reuse of the biomass waste is an important problem. Energy supply in Japan is supported by the import of fossil fuel such as coal, oil and natural gas. Furthermore, after East Japan great earthquake disaster of 2011, the dependence of thermal power generation increases. In waste biomass utilization, “a biomass utilization promotion fundamental law” put into operation in June, 2009. Availability of non-edible biomass products, such as rice husk, rice straw and so on, for heat utilization is one of the method for use of biomass.
The biomass has low energy density to get energy efficiently, and many conversion technology of biomass into high-value products were studied. Biomass can be converted into higher-value products via either biological or thermochemical processes [5-7]. Biological conversion of low-value lignocelluloseic biomass still faces challenges related to low economy and efficiency [5]. Combustion, pyrolysis and gasification are three main thermochemical conversion methods. Biomass is traditionally combusted to supply heat and power in the process industry. The net efficiency for electricity generation from biomass combustion is usually very low, ranging from 20 % to 40 % [6]. Biomass co-fired in existing combustors is usually limited to 5 -10 % of the total feedstock due to concerns about plugging existing coal feed systems [7]. The processes of pyrolysis and gasification are thermochemical conversion technologies to convert

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biomass feedstock into higher heating value fuel [8, 9], and improve for effective production [10, 11].

One improvement method to promote the production of high value fuel includes the pyrolysis technique using the zeolite catalyst. Zeolites represent a well-known family of crystalline nano-porous materials with very relevant applications in many fields, especially as catalysts, adsorbents and in the formulation of detergents. Zeolites exhibit a combination of properties very well suited for catalyzing reactions of organic compounds, such as crystalline framework, hydrothermal stability, high surface area, uniform microporosity, hydrophobicity, shape selectivity, acid-base properties, and high resistance against deactivation by carbon deposition [12, 13]. These reasons, among some others, have prompted zeolites to be applied at a commercial scale in a number of relevant sectors. This is the case of the oil refining and petrochemical industries, fine chemistry and pollutants abatement, in which the use of zeolites has allowed developing a high number of commercial applications [14]. Likewise, one emerging field, which has arisen huge interest in recent years, is the use of zeolites as catalysts in biomass valorization processes to produce biofuels and/or bio-based chemicals that could lead to the replacement of fossil sources by renewable ones.

In Japan, rice is a staple food. Rice is the second world's largest cereal crop after wheat, and is a widely grown crop in Asia, but rice straw is produced as a by-product of rice production. Every kilogram of grain harvesting is accomplished by the production of rice straw to a tone of 1.0 – 1.5 kg [10]. In most parts of rice fields, open-field burning of rice straw is commonly practiced in the region when there is limited time to prepare a field for the next crop. However, open-field burning of crop residues is an uncontrolled combustion process during which air pollutants are emitted into atmosphere. These air pollutants have significant toxicological properties and are potential carcinogens [11]. Although wildfires are prohibited in cultivation fields of most countries, farmers usually keep on burning their crop by-products. Biomass burning is an important source of aerosol particles which may affect local and regional air quality, and also contribute to global climate changes.

In this study, the conversion of rice straw into methane gas using the zeolite catalysts for utilization of the waste as heat sources. Methane is a chemical compound with the chemical formula $CH_4$ (one atom of carbon and four atoms of hydrogen), and is the main constituent of natural gas. We attempted to convert agricultural biomass waste, rice straw, into the valuable fuel gas including mainly methane using typical synthetic zeolites, and the behaviors of gas generation during pyrolysis using zeolites were estimated.

## EXPERIMENT

### Rice straw and zeolites

Raw rice straw, which was collected from a cultivated area in Akita prefecture, Japan, first cut into 1 cm length, was then washed with distilled water, and dried and stored for use. Properties of rice straw sample are shown in Table 1, which was analyzed using JIS M 8812 and JIS M 8819.

Table 1 Properties of rice straw in this experiment.

| | Moisture | Ash | Volatile matter + fixed carbon | | | |
|---|---|---|---|---|---|---|
| | | | C | H | N | S |
| Content (%) | 7.3 | 11.6 | 39.2 | 6.3 | 0.6 | 0.8 |

Typical four types of synthetic zeolites, HY-type zeolite (HY) (HSZ-320HOA, Tosoh), NaY-type zeolite (NaY) (HSZ-320NAA, Tosoh), NaX-type zeolite (NaX) (Molecular Sieves 13X, Wako) and NaA-type zeolite (NaA) (Molecular Sieves 4A, Wako), were used in this study. These zeolite samples have different properties, such as crystal structures, exchangeable cations and Si/Al molar ratios in chemical composition, as shown in Table 2.

Table 2 Properties of zeolites used in this experiment.

| | HY | NaY | NaX | NaA |
|---|---|---|---|---|
| Crystal structure | Faujasite | | | Lynde Type A |
| Exchangeable cation | $H^+$ | $Na^+$ | | |
| Si/Al raito | 5.5 | | 1.23 | 1 |
| Average particle diameter (μm) | 6 | | 10 | 4 |
| Crystal size (μm) | 0.3 | | 0.5 | 0.2 |
| Specific surface area ($m^2/g$) | 550 | 700 | 525 | 650 |

### Pyrolysis

The experimental apparatus used in this study is shown in Figure 1. A mixture of rice straw (1.0 g) and zeolites (0 - 2.0 g) was added into a reactor. The reactor was purged with nitrogen gas at a flow rate of 100 mL/min for 30 min to remove oxygen. After nitrogen substitution, the flow of nitrogen gas at a flow rate 50 mL/min and the pyrolysis experiment was performed. Temperature of sample was measured as the setting temperature, and the temperature was increased to the setting temperature (300 - 700 $^oC$) at a heating rate of 6 $^oC$/min using an electric heater. After heating at setting temperature for 0 – 120 min, the reactor was cooled to room temperature, and the residue remained in the reactor after pyrolysis was collected to measure the weight of the residue and to be observed. The gases produced during heating were condensed through a water condenser and the condensable gases were recovered as oil. Non-condensable gases, which pass through the condenser, were collected in a gas pack via bubbling of alkaline aqueous solution. The total amount of the generated gas collected in the gas pack was measured by gas meter. The chemical compositions of collected gas were analyzed by gas chromatography (GC) (Shimadzu, GC-2014). The crystal structure of residue was identified with X-ray diffraction (Rigaku, MiniFlex600).

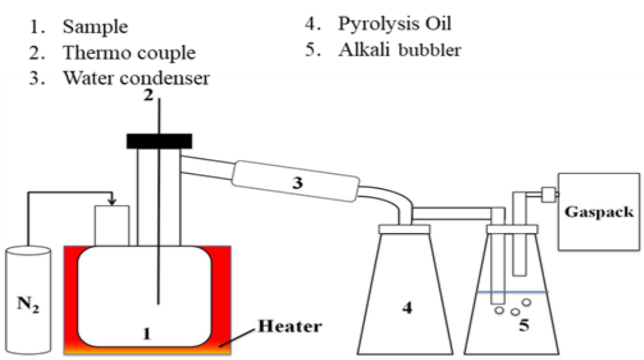



Figure 1 Experimental apparatus used in this experiment

## RESULT AND DISCUSSION

Table 3 shows the amount of the gas generated from rice straw during the experiment. The addition of zeolite is 1 g, setting temperature is 400 $^{o}$C, and heating time is 1 h. The generated amount of gas from rice straw increases with zeolite addition, and the highest amount of gas was generated using NaY. It is noted that no pyrolysis oil was generated during the experiment.

Table 3 Amount of gas generated during the experiment.

| | Amount of gas (L) |
|---|---|
| Rice straw | 5.2 |
| Rice straw + HY | 7.4 |
| Rice straw + NaY | 10.9 |
| Rice straw + NaX | 8.2 |
| Rice straw + NaA | 7.5 |

Figures 3 shows the amounts of various gases generated from rice straw. It is noted that the methane concentration in the generated gas is available for fuel (inflammability limit: 5 - 15 %). For crystal structure, faujasite-type zeolites, HY, NaY and NaX, produce higher amount of methane than Linde type A zeolite, NaA. For cation, NaX and NaY can produce higher amount of methane than HY. For Si/Al ratio, NaX and NaY produce almost same amount of methane gas. It is noted that amount of hydrogen was decreased by zeolite addition.

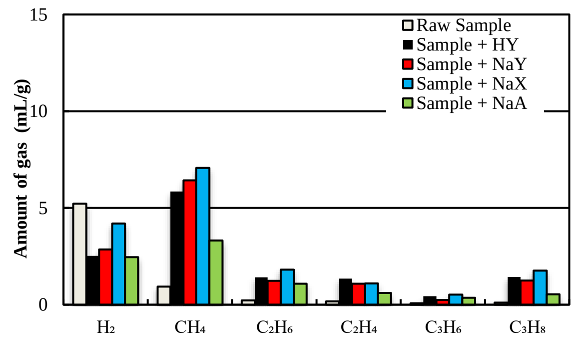



Figure 3 Amounts of various gases generated from rice straw

Figure 4 shows the weight of residue from rice straw after the experiment. The weight of the residue is correlated with amount of the generated gas. A small amount of residue remained in the reactor when a large amount of gas generated.

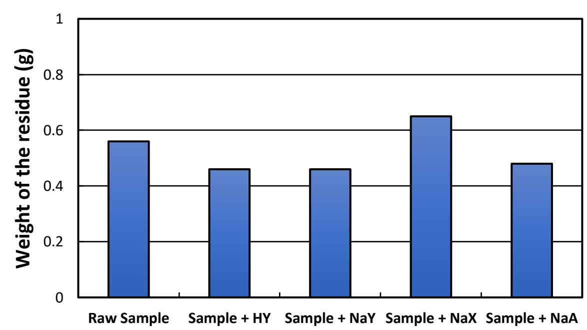



Figure 4 Weight of the residue after pyrolysis

From these results, faujasite-type zeolite including $Na^{+}$ is better materials for the conversion of rice straw into methane gas.

The behavior of the generated gas from rice straw using NaY zeolite was investigated.

Table 4 shows the amount of the gas generated from rice straw with various addition of NaY zeolite. Setting temperature is 400 $^{o}$C, and heating time is 1 h. The generated amounts of gas from rice straw increase with the zeolite addition, and are almost same amount regardless of amount of zeolite addition. It is also noted that no pyrolysis oil was generated during the experiment.

Table 4 Amount of gas generated during the experiment.

| | Amount of gas (L) |
|---|---|
| Rice straw | 5.2 |
| Rice straw + 0.5 g NaY | 9.0 |
| Rice straw + 1.0 g NaY | 10.9 |
| Rice straw + 2.0 g NaY | 11.0 |

Figure 5 shows the amounts of the gas generated from rice straw with various addition of NaY zeolite. With addition of 1.0 g of NaY, higher amount of methane gas was produced than the others, while the amount of hydrogen decrease with increasing NaY addition and those of other gases are almost same regardless of NaY addition.

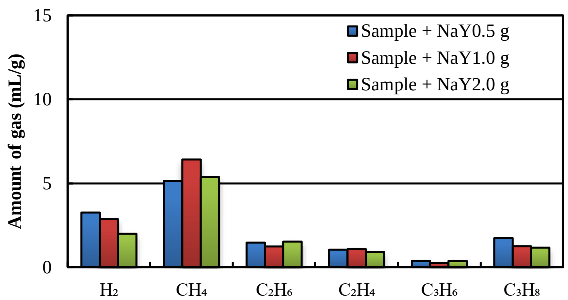



Figure 5 Amounts of various gases generated from rice straw with various addition of NaY.

Figure 6 shows the weight of residue from rice straw with various addition of NaY zeolite. The weights of the residue are almost constant, which are correlated with amounts of generated gas.

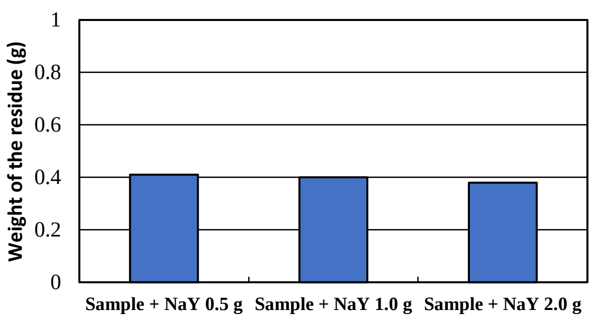



Figure 6 Weight of the residue after pyrolysis with various addition of NaY.

From these results, the mixture of 1 g of rice straw and 1 g of NaY is better condition for the conversion of rice straw into methane gas.

Figure 7 shows the amount of gas generated from rice straw with NaY addition during the heating at various temperatures. The mixture of 1 g of rice straw and 1 g of NaY is used for this experiment. Regardless of temperatures, the amount of generated gas increases rapidly within 30 min, and then be almost constant. With increasing the temperature to 500 °C, the amount of generated gas increases.

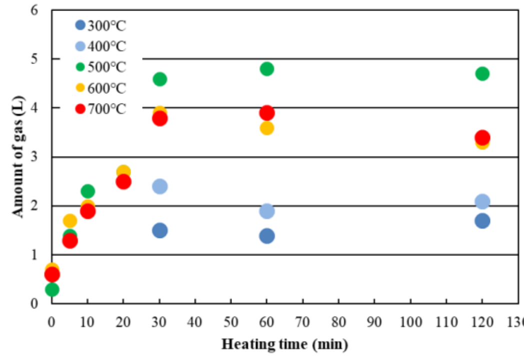



Figure 7 The amount of gas generated from rice straw with NaY addition during the heating at various temperatures.

Figure 8 shows the amount of various gases generated from rice straw with NaY addition during the heating at various temperatures. With increasing temperature, the amounts of all gases increases, while those of all gases gradually increase with increasing heating time.

Figure 9 shows the compositions of main gas species, $CH_4$, $H_2$, CO and $CO_2$, in the generated gases from rice straw with NaY addition during the heating at (a) 500 °C, (b) 600 °C and (c) 700 °C. With increasing the heating time, compositions of CO and $CO_2$ decrease and those of $H_2$ and $CH_4$ increase. With increasing the heating time to 120 min, composition of methane gradually increases at 500 °C, while those of methane almost constant at 600 °C and 700 °C. In addition, composition of $H_2$ is higher with increasing heating temperature. Therefore, the efficient conversion of rice straw into variable gas including methane can be done at more than 600 °C for 30 min with addition of NaY zeolite.

Figure 10 shows the reduction of the weight of residue after heating with NaY addition at various temperatures. With increasing the heating time, the weight of residue gradually decreases. The behaviors of decrease for the weight of residue are almost same at 500 °C, 600 °C and 700 °C. The weights of the residue gradually decrease within 30 min, and then become almost constant. The residual percent of the residue to rice straw after 30 min is approximately 10 % above 500 °C.

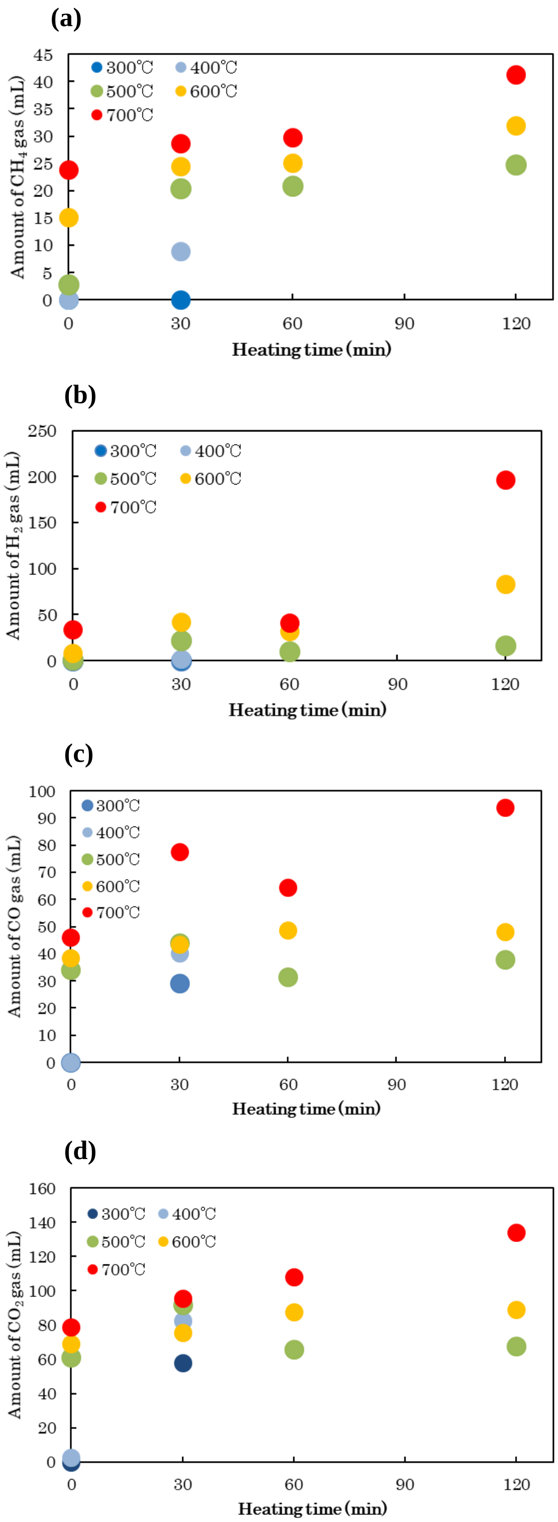



Figure 8 The amounts of various gases, (a) $CH_4$, (b) $H_2$, (c) CO and (d) $CO_2$, generated from rice straw with NaY addition during the heating at various temperatures.

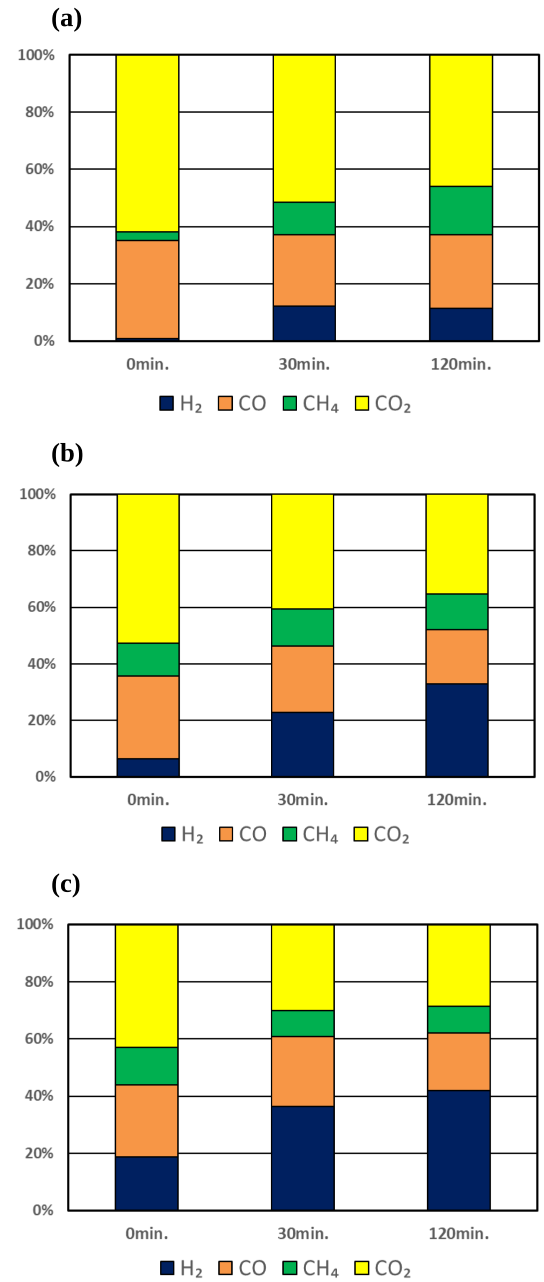



Figure 9 Compositions of main gas species, $CH_4$, $H_2$, CO and $CO_2$, in generated gases from rice straw with NaY addition during the heating at (a) 500 ºC, (b) 600 ºC and (c) 700 ºC.

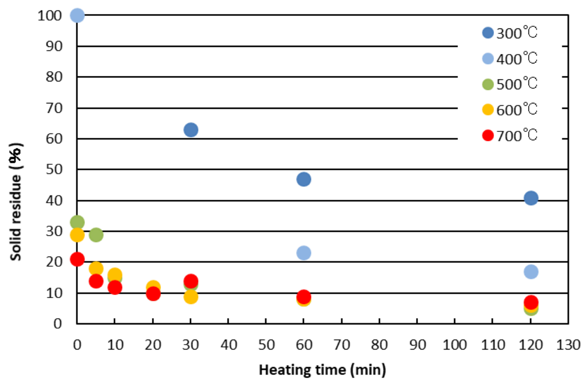



Figure 10 Reduction of the weight of residue after heating with NaY addition at various temperatures.

The experimental kinetic data were fitted using a pseudo-first-order kinetic model and a pseudo-second-order kinetic model, shown in liner equation (1) and (2), respectively;

$$\ln(w/w_0) = -k_1 \cdot t \qquad (1)$$

$$1/w - 1/w_0 = k_2 \cdot t \qquad (2)$$

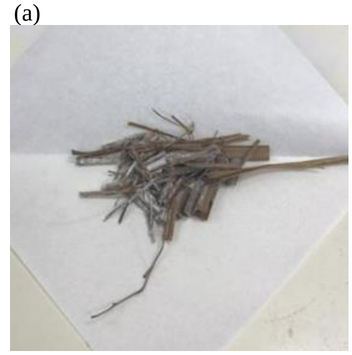
where $t$ is the measuring time (min), $w_0$ and $w$ are the residual weights at heating time = 0 and measuring time, respectively, and $k_1$ and $k_2$ are the reaction rate constant of a pseudo-first-order kinetic model and a pseudo-second-order kinetic model, respectively. The results of parameters are shown in Table 5. The reaction behavior is found to fit second-order-kinetics model better than first-order-kinetic model. With increasing heating temperature, $w_0$ decreases, which means that a large part of the reaction occurs during the time for rising temperature to setting temperature.

Table 5 Parameters for kinetics models

| | First-order-kinetics | | | Second-order-kinetics | | |
|---|---|---|---|---|---|---|
| | $k_1$ | $w_0$ | $R^2$ | $k_2$ | $w_0$ | $R^2$ |
| 300 | 0.0061 | 0.79 | 0.880 | 0.0107 | 0.79 | 0.925 |
| 400 | 0.0081 | 0.29 | 0.993 | 0.0528 | 0.36 | 0.999 |
| 500 | 0.0138 | 0.22 | 0.752 | 0.1334 | 0.29 | 0.930 |
| 600 | 0.0109 | 0.18 | 0.732 | 0.1018 | 0.18 | 0.893 |
| 700 | 0.0069 | 0.15 | 0.683 | 0.0661 | 0.15 | 0.807 |

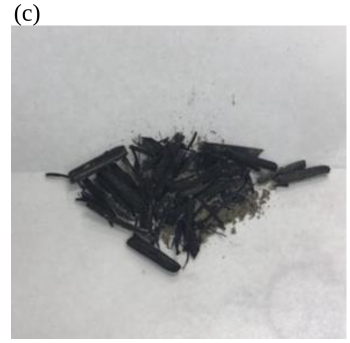
Figure 12 shows the photos of the residue after pyrolysis at (a) 300 °C, (b) 400 °C, (c) 500 °C, (d) 600 °C, and (e) 700 °C for 30 min. Carbonization of rice straw can be observed at 400 – 700 °C, while that cannot be observed at 300 °C.

(a)



(b)

(c)



(d)

(e)

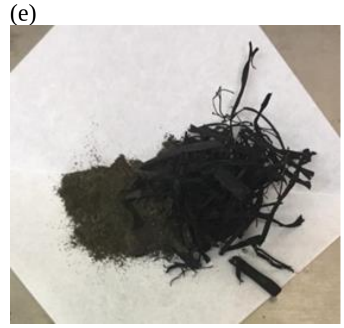


Figure 12 Photos of the residue after pyrolysis at (a) 300 °C, (b) 400 °C, (c) 500 °C, (d) 600 °C, and (e) 700 °C for 30 min.

Figure 13 shows XRD pattern of the mixture of rice straw and NaY before and after pyrolysis. There was no change of the zeolite crystal structure by the pyrolysis. In other words, the zeolite can keep the structure to be used as catalyst after pyrolysis.

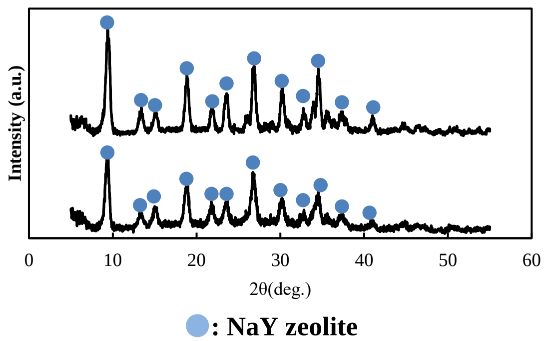



Figure 13 XRD patterns of the the mixture of rice straw and NaY before and after pyrolysis.

## CONCLUSION

In this study, conversion of agricultural biomass waste, rice straw, into methane gas using the zeolite catalyst for utilization of the waste. Faujasite type zeolite having Na (NaX and NaY) produced the highest amount of methane to be used as fuel. The sample with NaY zeolite (sample : zeolite = 1 : 1) can generate high amount of methane, and the gas including high content of methane can be obtained at higher than 600 ºC for 30 min. The weight of the residue is approximately 10 % of raw rice straw, and zeolite added into the reactor can keep the structure to be used as catalyst. NaY zeolite is effective additive for the production of high value gas including methane via pyrolysis of the biomass wastes.

## ACKNOWLEDGMENTS

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