

The Effect of Molecular Sieves on the Thermolysis of Cedar in a Tubular Furnace Reactor

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

Abstract—Japanese cedar was pyrolyzed using a tubular furnace reactor with added molecular sieves in an attempt to increase the quantity of methane produced. A predetermined mixture of molecular sieves and cedar were heated in the tubular furnace reactor up to 700 °C under a nitrogen atmosphere. The flammable gas and the residual substance provided by the thermolysis were examined. The yield of the CH₄, which is a combustible gas generated from thermolysis, was increased by adding 5A molecular sieves. In addition, the tubular furnace was found to cause complete thermolysis.

Index Terms—Thermal decomposition, tubular reactor, biomass, molecular sieves.

I. INTRODUCTION

Increasing demand for fossil fuel has led to a global energy crisis. Reserves of fossil fuels are limited and developments to improve the efficient production of renewable fuels are important [1]. Fossil fuels have played an important role in supplying fuel for transportation and have contributed to greenhouse gas (GHG) discharge that causes considerable environmental problems [2]. The 196 countries that participated in the United Nations Climate Change Conference of 2015 agreed to restrain the rise of the average global temperature to less than 2 °C by decreasing GHG discharge. The Japanese government set a target of decreasing GHG discharge by 26% of the 2013 level by 2030.

Japan had 54 nuclear power plants as of February, 2011 that contributed 31.3% of the national power supply, with fossil fuels generating 63.1%, waterpower 5.1%, and other renewable energy sources contributing 0.5%. However, the majority of these nuclear power plants have been shut down and remain offline following the Great East Japan Earthquake, and there is considerable need to discover an alternative energy to replace the lost energy production. Biomass has attracted increasing global interest over the past 20 years as a potential alternative to fossil fuels that can provide useful products by thermochemical conversion of renewable resources through thermolysis or gasification [3]–[5]. One of the best solutions to lower GHG emission is to use materials that are comprised of carbon as substitutes for fossil fuels, such as wood and wood processing waste, energy crops, agriculture and organic wastes, materials derived from wastes, and sewage sludge [6]–[10]. In addition, using biomass for energy supply is an attractive substitute for fossil fuels

because it does not contribute a carbon footprint and the energy generated is carbon neutral [6].

Japan has forests that account for approximately 67% of the country's land area, which could be an abundant source of biomass for thermochemical conversion to fuels. This biomass mainly consists of extracts (tannins, fatty acids, and resins), inorganic salts, and three main polymers (cellulose [9]–[13], hemicellulose [14]–[16], and lignin [17]–[19]). These three components are broken down by thermolysis at different temperatures and speeds. Cellulose, hemicellulose, and lignin decompose slowly over a wide temperature range of 280 to 600 °C. Degradation of these polymers occurs relatively fast at low temperatures between 200 and 350 °C when pyrolyzed in the absence of oxygen to form char, liquid and gas components [2], [20], [21]. Product distribution and yield are affected by temperature and the speed of pyrolysis [22], [23]. High temperature thermolysis decreases the proportion of char and increases the yield of the liquid and gas generated [10], [24], [25]. On the other hand, gas production and the yield of the char decrease with low temperature thermolysis, and the liquid component increases. Gasification of the biomass maximizes gaseous products under conditions that minimize char and ash [26]–[28]. Dehydration and de-carboxylation can be promoted by the use of pro-zeolite catalysts at atmospheric pressure [29], [30]. Molecular sieves are reported as effective cracking catalysts along with other zeolites [31]. These zeolites are an attractive low-cost substitute for traditional catalysts used in high pressure hydrogenation biomass thermolysis [29], [32], [33].

We have previously reported that the use of molecular sieves, which are a zeolite catalyst, for the pyrolytic decomposition of cedar increased the quantity of the flammable gas at the low temperature 450 °C [34]. In this study, the potential to increase thermolytic production of methane from cedar using catalytic molecular sieves in a tubular furnace reactor was investigated.

II. PROCEDURE

A. Materials

Japanese cedar wood chips were sourced from Sanbu, Chiba, Japan (SAMBU SUGI) and dried before use. Molecular sieves 3A 1/16 (diameter 1.4–2.0 mm), 5A 1/16 (diameter 1.4–2.0 mm), and 13X 1/16 (diameter 1.4–2.0 mm) were purchased from Wako Pure Chemical Industries. A predetermined quantity of molecular sieves was added to a 20-g sample of cedar and mixed for each experimental condition (Table I). Cedar alone was used as a control (condition I) and sea sand was used as an additive to establish

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if the influence of dispersive granules on the yields and distribution of products (condition VIII).

TABLE I: EXPERIMENTAL CONDITIONS

Condition of sample	
I	Cedar 20g
II	Cedar 20g + Molecular sieves 3A 20g
III	Cedar 20g + Molecular sieves 5A 20g
IV	Cedar 20g + Molecular sieves 13X 20g
V	Cedar 20g + Molecular sieves 3A 10g
VI	Cedar 20g + Molecular sieves 5A 10g
VII	Cedar 20g + Molecular sieves 13X 10g
VIII	Cedar 20g + Sea sand 20g

B. Verification of the Reactor

Previous pyrolysis experiments in a glass reactor at the low temperature range of 400 to 600 °C resulted in incomplete degradation, with a central part of the sample that was stable to thermolysis. Therefore, we switched from a glass reactor to a tubular furnace reactor, which heats the whole sample uniformly. When thermolysis was performed at a setting of 700 °C, the median temperature was 600 to 800 °C, and thermolysis occurred with a stable state throughout the temperature range.

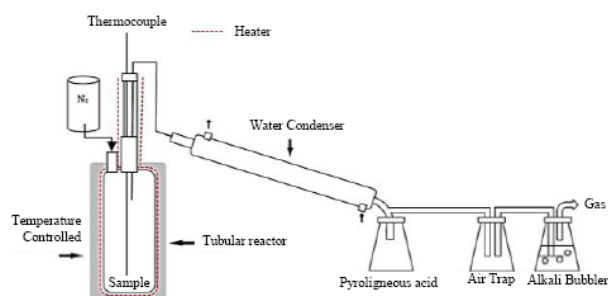


Fig. 1. Experimental apparatus.

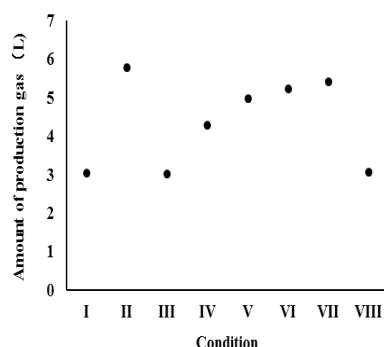


Fig. 2. Total volume of gas generated.

C. Experimental Apparatus Procedures

The experimental device used in this study is depicted in Fig. 1. A mixed sample of approximately 20 g of cedar and molecular sieves was placed in the tubular furnace reactor. Nitrogen gas was passed over the sample for 60 min at a flow of 50 mL/min to remove oxygen from the reactor before heating. The temperature rise was held below 10 °C/min and increased to 700 °C then heating was ceased and the reactor allowed to cool to room temperature. The non-condensable gas generated during thermolysis was collected in a gas pack after passing through an alkaline water solution (0.1 mol/L sodium hydroxide water solution). All the gas collected in the gas pack was assumed to be generated by the pyrolysis and the

gas and residual substance in a tubular furnace reactor were analyzed for each sample.

D. Analysis

The resolution gas generated was qualitatively and quantitatively analyzed using a SHIMADU GC2014FID. The cedar was observed before and after thermolysis by energy dispersive spectroscopy (EDS, BRUKER D2FAHSE) attached to an electron microscope (Hitachi high technology TM3030) using BURUKER QUANTAX energy dispersion type X-rays analysis. A cedar sample was combusted at a temperature of 800 °C and total nitrogen, carbon, and hydrogen measured using a SUMIGRAPH NCH-22A. The cedar was 1.5% nitrogen, 62.7% carbon, and 8.9% hydrogen by weight [34].

III. RESULTS AND DISCUSSION

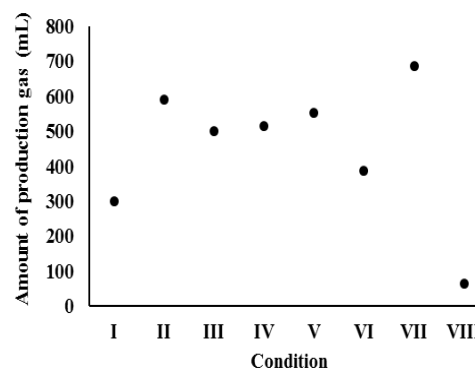
A. Gas Generation

The quantity of gas generated by thermolysis for each condition is shown in Fig. 2. The quantity of gas generated did not increase when unreactive granules were added to the cedar (condition I vs. condition VIII).

The amount of methane produced is shown in Fig. 3. Methane production increased with the addition of molecular sieves (conditions II–VII), and we infer that the molecular sieves have a catalytic effect. The yield of methane generated as a proportion of the total gas produced is shown in Fig. 4. The total gas produced is similar for conditions I and III (Fig. 2), but the methane yield of condition III is approximately 1.7 times that of condition I, demonstrating the improved efficiency of the gasification to useful products with molecular sieves.

The amount of carbon dioxide produced for each mixture is shown in Fig. 5. Production of carbon dioxide was lowest with conditions III and VI for the samples with molecular sieves, suggesting 5A molecular sieves are better at promoting thermolysis to form methane.

The yield of carbon dioxide as a proportion of the total gas produced is shown in Fig. 6. Unlike for thermolysis undertaken in a glass reactor, no pyrolytic acid was collected from the pyrolysis reactions in the tubular furnace reactor, suggesting that a temperature of 700 °C caused complete gasification.

Fig. 3. Volume of CH₄ in gas generated.

B. Residue

The EDS images of cedar with an equal amount of 5A molecular sieves before (condition 0) and after pyrolysis (condition III) are shown in Fig. 7(a) and (b), respectively.

In addition, Fig. 8 shows the proportion of carbon surface area for all conditions.

The carbon surface area increased after thermolysis for all conditions compared with condition 0. This shows that thermolysis had occurred for all the samples heated to 700 °C with or without the addition of molecular sieves.

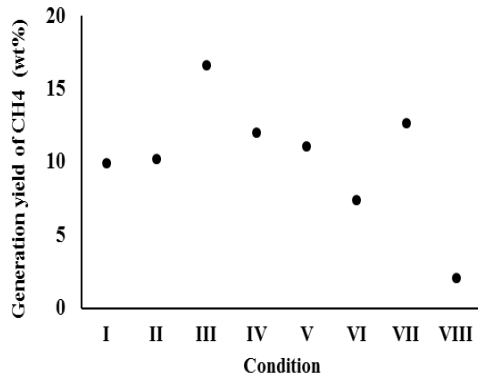


Fig. 4. Yield of CH₄.

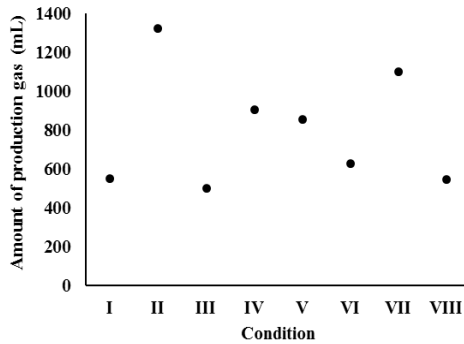


Fig. 5. Volume of CO₂ in gas generated.

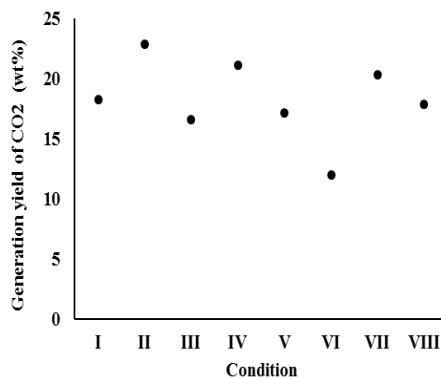
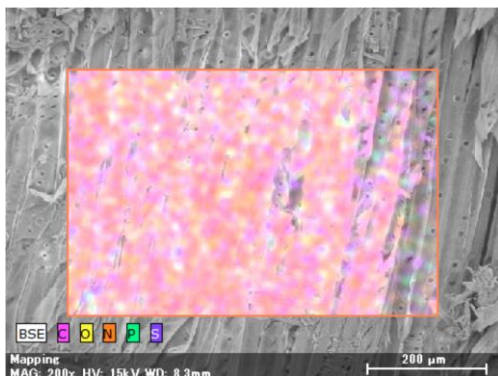
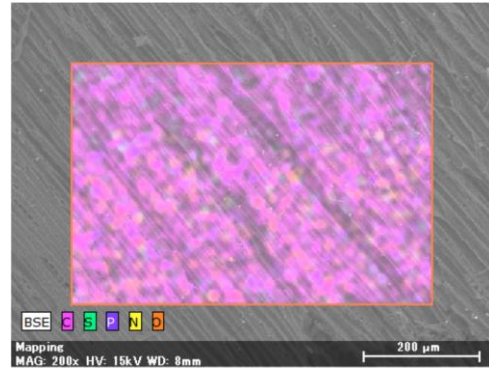


Fig. 6. Yield of CO₂.



(a)



(b)

Fig. 7. Energy dispersive spectroscopy images of cedar (a) before and (b) after pyrolysis.

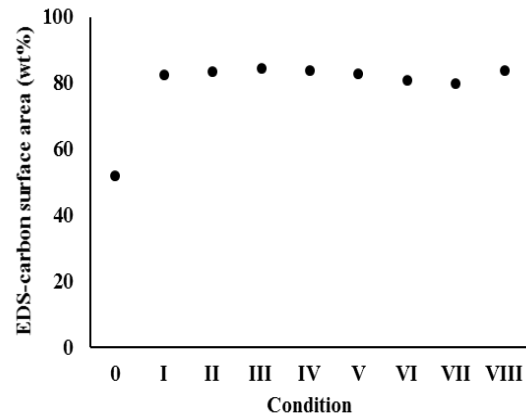


Fig. 8. EDS-carbon surface area.

IV. CONCLUSION

In this study, molecular sieves were added to samples of cedar and pyrolyzed using a tubular furnace reactor.

The cedar was degraded to gas and residue and these were examined.

Using molecular sieves minimized carbon dioxide emission compared with thermolysis of cedar only and the yield of methane reached a maximum of 16.6%.

From the EDS images, an increase in carbon surface area can be observed after thermolysis in all conditions. Therefore, it is presumed that pyrolysis is performed completely at 700 °C.

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