

The Effect of Molecular Sieve Addition on the Thermal Decomposition of Japanese Cedar

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Abstract—The catalysis of Japanese cedar pyrolysis by 13X or 4Å molecular sieves at low temperatures has been investigated. Japanese cedar was placed in a glass reactor and heated to 450 °C under a nitrogen atmosphere to promote thermal decomposition. The flammable gas component, condensed wood vinegar, soluble gas component, and residue were examined. The gases detected included CH₄, C₃H₆, C₃H₈, and CO₂. The amount of combustible gases generated increased when thermal decomposition was undertaken with the addition of 13X molecular sieves. Moreover, tar was not generated when 13X molecular sieves were added.

Index Terms—molecular sieves, thermal decomposition, biomass

I. INTRODUCTION

Increasing demand for fossil fuels has led to a global energy crisis. The contribution of emissions from the combustion of fossil fuels on greenhouse gases (GHG) has also led to major environmental problems [1]. All but one of the 196 parties present at the 2015 United Nations Climate Change Conference agreed to an effort to suppress global temperature rise to less than 2 °C (compared with pre-industrial levels) by reducing GHG emissions. The Japanese government has set a target of reducing GHG emissions by 26% compared with 2013 levels by 2030.

Japan had 54 nuclear power plants prior to the Great East Japan Earthquake in 2011. Nuclear power provided 31.3% of the nation's electricity with the remainder supplied by thermal generation from fossil fuels (63.1%), hydroelectric (5.1%), and other renewable energy sources (0.5%). All but one of Japan's nuclear power plants have been shut down since the Great East Japan Earthquake. Biomass is a potential energy source to help replace the lost generation and decrease dependence on fossil fuels [2].

Biomass is a widely available source of renewable energy [3]. Biomasses used for energy generation include

wood and wood processing waste, energy crops, agricultural and organic waste, materials derived from municipal waste, and sewage sludge [4], [5]. Biomass is an attractive alternative to fossil fuels for energy supply because it is carbon neutral and does not contribute to the carbon footprint of energy generation [6].

Forests represent 67% of Japanese land area, with approximately two-thirds of them owned by the Japanese Ministry of Land. The area of forests in Japan has remained constant for the past 40 years. Forests present a potential source of biomass that can undergo thermochemical conversion to useful fuels.

Biomass primarily consists of extracts (tannins, fatty acids, and resins), inorganic salts, and three main polymers (cellulose [7]-[9], hemicelluloses [10]-[12], and lignin [13]-[15]). Lignin gradually degrades over a wide temperature range between 280-600 °C [8], whereas cellulose and hemicellulose degrade relatively rapidly at lower temperatures (200-350 °C) [1]. Organic material in biomass undergoes pyrolysis when heated in the absence of oxygen to form char, gases and liquids [16]. Changes to temperature affect the rate of pyrolysis [17], product distribution and yield [18], [19]. High-temperature pyrolysis decreases the yield of char and liquid compounds and increases the amount of gases produced [20]-[22]. Conversely, low temperatures decrease the yield of gases. Cracking the hydrocarbon fluids promotes the formation of gases and cracking of gaseous hydrocarbons leads to the formation of H₂ [21], [23]-[26].

Gasification of biomass maximizes gaseous products and minimizes the char and ash [27], [28]. Zeolite-based catalysts promote dehydration, decarboxylation, and can be used at atmospheric pressure [29], [30]. Molecular sieves, among other zeolites, are reported as effective cracking catalysts [31]. Zeolites are an attractive low-cost alternative to high-pressure hydrogenation for the catalysts of biomass pyrolysis [32], [33].

In this study, we investigate the effect of 13X molecular sieves (MS-13X) and 4Å molecular sieves (MS-4Å) on the gas generated during thermal decomposition of Japanese cedar at 450 °C.

II. EXPERIMENTAL

A. Materials

Samples of Japanese cedar wood chips “Sambu sugi” were sourced from Sanbu (Chiba, Japan) and MS-13X and MS-4Å were purchased from Wako Pure Chemical Industries, Japan. Five mixtures of cedar with or without molecular sieves were investigated, as shown in Table I.

TABLE I. EXPERIMENTAL CONDITIONS

Condition of sample	
I	Cedar 20 g
II	Cedar 20 g + Molecular sieves4Å 20 g
III	Cedar 20 g + Molecular sieves4Å 10 g
IV	Cedar 20 g + Molecular sieves13X 20 g
V	Cedar 20 g + Molecular sieves13X 10 g

B. Pyrolysis Temperature

Three pyrolysis temperatures were screened; 400, 500 and 600 °C. The residue, amount of gases produced, formation of tar (detected by coloration of the alkaline solution) and the resolution state were observed.

C. Experimental Apparatus and Procedures

The experimental apparatus used for pyrolysis is shown in Fig. 1. Cedar with or without MS-13X or MS-4Å was placed in a glass reactor and purged with nitrogen at a flow rate of 50mL/min for 60min. The reactor temperature was then raised to 450 °C at a rate of 5 °C/min. Heating was ceased once the temperature reached 450 °C and the reactor was allowed to cool to ambient temperature. Gases generated during the thermal decomposition were passed through a cooling tube to collect the wood vinegar. Non-condensable gases were collected in a gas pack after passing through an alkaline aqueous solution (0.1M sodium hydroxide).

The gas, wood vinegar, alkaline solution and residue in the glass reactor were analyzed to determine the chemical composition of the pyrolysis products.

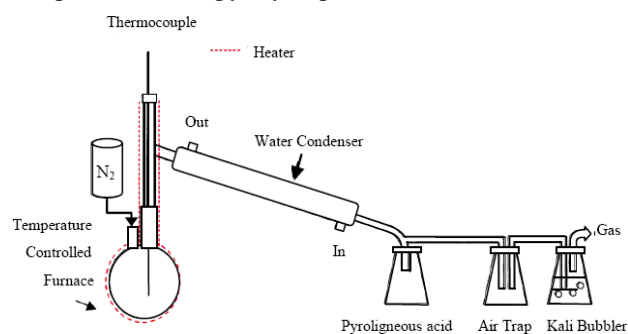


Figure 1. Experimental apparatus

D. Analysis

The elemental composition, total nitrogen, carbon and hydrogen, of the gases was measured using a NCH-22A Sumigraph (Sumika Chemical Analysis Service, Japan). The sample combustion temperature was set at 800 °C. Identification and quantification of the gases generated

were undertaken with a Shimadzu GC-2014-FID (Shimadzu Scientific Instruments, Japan) using helium as the carrier gas and a column.

Wood vinegar samples were diluted 100-fold with acetone (Wako Pure Chemical Industries) and analyzed by gas chromatography mass spectrometry on a Shimadzu GCMS-QP2010 ultra (Shimadzu Scientific Instruments) with helium as a carrier gas and a Rtx-1 column (inner diameter 0.25mm×0.25µm film thickness). The oven temperature was held at 40 °C for 30min then raised to 230 °C at a rate of 5 °C/min.

The alkaline solutions were diluted 100-fold with ultrapure water and subjected to qualitative analysis by HPLC ion chromatography on a Shimadzu IC system (Shimadzu Scientific Instruments) using a Shim-pack column (150mm×4.6mm) with a CDD-10Asp detector.

The surfaces of the molecular sieves were observed before and after use as an additive in pyrolysis using a Bruker Quantax scanning electron microscope with energy-dispersive spectrometry (Bruker D2 Phaser; Bruker, Billerica, MA, USA).

III. RESULTS AND DISCUSSION

A. Optimization of Pyrolysis Temperature

Pyrolysis at 400 °C resulted in incomplete decomposition of the wood chips. Complete decomposition of the samples occurred at both 500 and 600 °C. This contrasted with the amount of gas produced. At 400 °C, more than 1L of gas was produced but at 500 or 600 °C, the amount was less than or equal to 1L.

Tar formation occurs when thermal decomposition is carried out at a suitable temperature, but not at lower temperatures. The alkaline solution of the 400 °C treatment was colorless, whereas the solutions from the 500 and 600 °C treatments had notable coloration, indicating the presence of tar. We chose a pyrolysis temperature of 450 °C to maximize gas generation and ensure complete decomposition of the samples.

The results of pyrolysis at various temperatures are shown in Table II.

TABLE II. TEMPERATURE CONDITIONS

Pyrolysis temperature	400 °C	500 °C	600 °C
Residual substance	Non-resolution	Resolution	Resolution
Quantity of generation gas	More than 1L	1L or less	1L or less
Alkaline solution	Colorlessness	Tar generating	Tar generating
Resolution state	Resolution	Resolution	Lacking in the resolution

B. Gas Generation

The elemental composition of the gases collected from the pyrolysis of cedar are shown in Table III.

TABLE III. ELEMENTAL ANALYSIS OF PYROLYSIS GASES

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

Sample mass 19.75mg

The amount of methane gas generated by thermal decomposition under various conditions is illustrated in Fig. 2.) The amount of methane gas generated increased approximately 2.3 fold when an equal mass of MS-13X was added (condition IV) compared with cedar alone (condition I). Propylene production was also maximized with condition IV, with an approximately 4.8 fold increase compared with cedar alone (Fig. 3). Likewise, propane generation also increased with the addition of an equal mass of MS-13X (Fig. 4).

We infer that the addition of an equal mass of MS-13X promotes catalytic decomposition based on the amount of carbon dioxide present in the gases collected (Fig. 5).

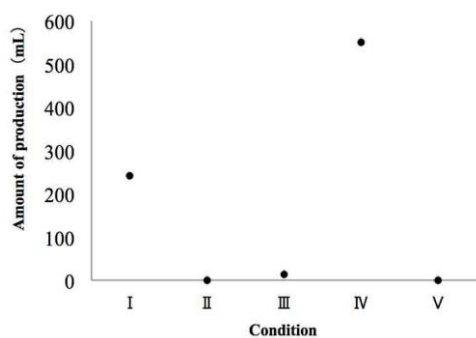


Figure 2. Content of CH₄ in generation gas

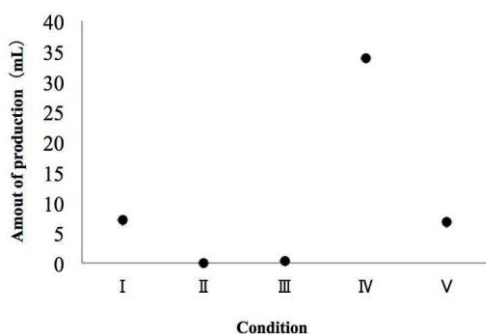


Figure 3. Content of C₃H₆ in generation gas

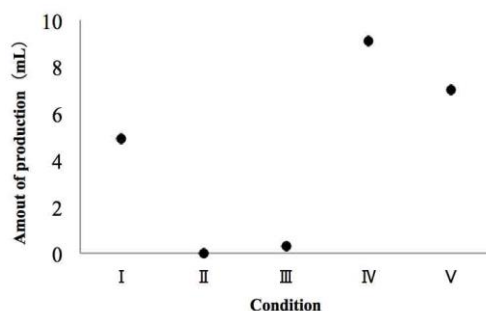


Figure 4. Content of C₃H₈ in generation gas

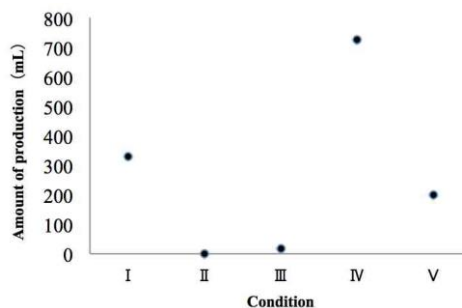


Figure 5. Content of CO₂ in generation gas

C. Wood Vinegar Analysis

Cresol and naphthalene are potentially useful components of wood vinegar because they exhibit antimicrobial activity. Under all the conditions tested, 4-hydroxy-4-methyl-2-pentanone, 3-methoxyphenol, cresol, 4-ethyl-2-methoxyphenol and naphthalene were obtained in the wood vinegar (Table IV).

TABLE IV. ANALYSIS RESULTS OF GC/MS

Detected ingredient	Condition				
	I	II	III	IV	V
Toluene	○	○	○	○	○
4-Hydroxy-4-methyl-2-pentanone	○	○	○	○	○
3-Methoxyphenol	○	○	○	○	○
Cresol	○	○	○	○	○
4-Ethyl-2-methoxyphenol	○	○	○	○	○
Naphthalene	○	○	○	○	○

○: detected

D. Soluble Gas

The soluble gases detected in the alkaline solutions are shown in Table V. Fluoride, chloride, nitrite, bromide, nitrate, and phosphoric acid ions were detected when pyrolysis was undertaken without additives (condition I). The addition of MS-4Å or MS-13X prevented the transfer of all ionic gases, except under condition II where trace levels of chloride and nitrite were detected. We attribute this finding to the ability of the molecular sieves to adsorb anions.

TABLE V. ANALYSIS OF THE IC

Detection ion	Condition				
	I	II	III	IV	V
F	○	nd	nd	nd	nd
Cl	○	○	nd	nd	nd
NO ₂	○	○	nd	nd	nd
Br	○	nd	nd	nd	nd
NO ₃	○	nd	nd	nd	nd
PO ₄	○	nd	nd	nd	nd

○: detected, nd: not detected

E. Residue

The surface structure of the molecular sieves before (Fig. 6(a)) and after use in thermal decomposition (Fig. 6(b)) was observed by EDS. The surfaces before and after pyrolysis were comparable with the exception of the nitrogen and carbon present, which exhibited a 2% and 8% increase, respectively, and a decrease in oxygen content of 8%, after pyrolysis.

When MS-13X was added, the alkaline solution remained colorless. This is presumably caused by the carbon-containing decomposition products being adsorbed by the molecular sieves.

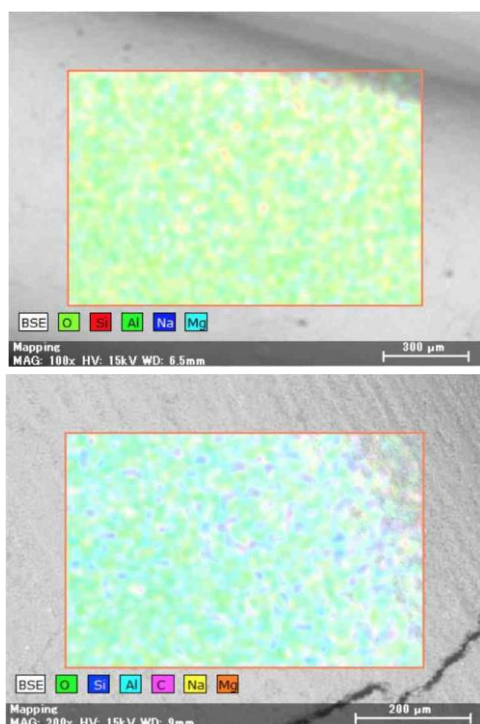


Figure 6. (a) EDS image of additives before pyrolysis (b) EDS image of additives after pyrolysis

IV. CONCLUSION

The addition of an equivalent amount of MS-13X increased the amount of flammable gas generated by the thermal decomposition of cedar. A high proportion of the biomass was converted to gaseous products, as demonstrated by the increased amount of total gases and carbon dioxide in the product gas. The formation of tar was prevented with the use of MS-13X by adsorption of non-volatile carbon onto the catalyst.

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