



# In-situ reforming of the volatiles from fast pyrolysis of ligno-cellulosic biomass over zeolite catalysts for aromatic compound production



Kazuhiro Uemura<sup>a</sup>, Srinivas Appari<sup>b</sup>, Shinji Kudo<sup>b</sup>, Jun-ichiro Hayashi<sup>a,b,c</sup>, Hisahiro Einaga<sup>d</sup>, Koyo Norinaga<sup>a,b,\*</sup>

<sup>a</sup> Interdisciplinary Graduate School of Engineering Sciences, Kyushu University, Kasuga 816-8580, Japan

<sup>b</sup> Institute for Materials Chemistry and Engineering, Kyushu University, Kasuga 816-8580, Japan

<sup>c</sup> Research and Education Center of Carbon Resources, Kyushu University, Kasuga 816-8580, Japan

<sup>d</sup> Department of Energy and Material Sciences, Faculty of Engineering Sciences, Kyushu University, Kasuga 816-8580, Japan

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## ABSTRACT

Characteristics of in-situ catalytic reforming of the products derived from fast pyrolysis of biomass were studied with an originally designed analytical pyrolysis technique. The volatile products derived from ligno-cellulosic biomass as well as cellulose, xylan, and lignin were converted using a two-stage tubular reactor at 550 °C over various zeolite catalysts with different acidities and pore structures. HZSM-5 exhibited the best performance for converting the cedar derived volatiles to arenes, which mainly composed of benzene, toluene, and naphthalene with a selectivity of 26% on carbon basis. The HZSM-5 had a little effect in increasing the yields of the arenes for xylan and lignin, while it had a significant effect for cellulose, showing that more than 30% of carbon in cellulose was converted into arenes. A reaction pathway analysis for reforming of volatiles suggested that alkyne and diene such as acetylene, propyne, and cyclopentadiene are the important precursors of the major aromatic hydrocarbon products such as benzene, toluene, and naphthalene. The formations of those intermediates were also confirmed experimentally in an early stage of the in-situ reforming.

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## 1. Introduction

Ligno-cellulosic biomass such as agricultural residues, short rotation woody crops, herbaceous crops, forestry residues, and waste paper is considered to be a promising source for renewable liquid fuel [1–3]. The fast pyrolysis of biomass is one of the viable processes to convert it into liquid fuels, which are referred to as bio-oil. Bio-oil is considered to be a promising alternative fuel, produced by simple methods with high efficiency [4,5]. However, the quality of bio-oil is much lower than that of the conventional petroleum-based oil because of its thermal instability, acidic nature, and low calorific value [6]. The effective upgrading techniques are needed to meet the standards of the conventional fuel [7–9].

Catalytic reforming is one of the promising ways to upgrade crude bio-oil. There are few reports that investigate in-situ reforming of volatiles derived from the fast pyrolysis of biomass [10–12]. For example, Carlson et al. [11], investigated the conversion of biomass into aromatics by thermal decomposition in the presence of zeolite catalysts using pyroprobe analytical pyrolyzer. They reported that more than 30% aromatic compounds were obtained from cellulose

with zeolite catalyst (ZSM-5, SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 60) at the optimal reactor conditions. The high conversion efficiency from those carbohydrates which are free from aromatic structures to aromatics should be of great interest. However, the mechanistic interpretations for this process are limited since the complex processes such as primary pyrolysis and reforming of volatiles over catalysts as well as nascent char are simultaneously occurred in the pyroprobe reactor. The volatile–char interaction is known to have a positive effect on tar destruction [13,14].

The objective of this work is to study experimentally the in-situ reforming characteristics of the products from the fast pyrolysis of biomass over various zeolite catalysts under minimized volatile–char interactions by using a two-stage tubular reactor which is directly connected to a gas analysis system. The tubular reactor was divided into two zones by a filter, the first zone is used for fast pyrolysis of biomass, and the other zone is used for catalytic reforming. The reactor has a set-up to control the contact times of the nascent volatiles over the catalyst. Moreover, a reaction pathway included in the conversion into arenes is also proposed based on the detailed chemical kinetic model proposed previously [15].

## 2. Experimental

Biomass pyrolysis with in-situ catalytic reforming experiments was carried out in a U-shaped two-stage tubular reactor (TS-TR) at 550 °C.

\* Corresponding author at: Institute for Materials Chemistry and Engineering, Kyushu University, Kasuga 816-8580, Japan. Tel.: +81 92 583 7794; fax: +81 92 583 7793.

E-mail address: [norinaga@cm.kyuhsu-u.ac.jp](mailto:norinaga@cm.kyuhsu-u.ac.jp) (K. Norinaga).

All experiments for fast pyrolysis with reforming were carried out at 550 °C in the presence of inert gas helium or nitrogen. A schematic representation of the reactor is shown in Fig. 1. The TS-TR was made-up of quartz and divided into two zones by a quartz wool filter; the first zone is used for fast pyrolysis of the biomass and the second zone is used for catalytic reforming of volatiles derived from the biomass on zeolite catalysts. The second zone of the reactor is loaded with zeolite particles. Table 1 shows the characteristics of the five zeolites with different acidities and pore sizes. All catalysts are purchased from Zeolyst International and Tosoh. The inner diameters of the pyrolysis zone and the reforming zone were 6 and 4 mm, respectively.

Japanese cedar (C: 50.2; H: 6.3; O: 42.3 wt.%, dry basis), cellulose (Sigma Aldrich), lignin (Kishida Chemical Co., Japan), and xylan (Tokyo Chemical Industry, Japan) were used as samples in this study. Sawdust of cedar was used and the diameter was in the range of 0.50 to 1.18 mm. Xylan was used as a model compound for hemicellulose. Approximately 1.0 mg of the sample was wrapped with a sheet of stainless (SUS316) wire mesh with a mesh opening of 45 μm and dried in vacuum oven at room temperature overnight. The mass of the wrapped sample was measured immediately after drying to determine the exact dry mass of the sample, which was subsequently fixed at the upper part of the TS-TR. The reactor was heated to 550 °C by external furnace, after stabilizing the heated section of the TS-TR, the sample was dropped into the bottom of the first tube, where the biomass sample was fast-pyrolyzed. The volatiles and char were formed in the first zone of the reactor. The volatiles released were subsequently swept off into the catalyst bed for reforming. The residence time (0.02 to 0.16 s based on catalyst bed length) of the volatiles in the catalytic zone was controlled by the amount of loaded catalyst varying from 0.012 to 0.11 g in the second zone of the reactor.

The reformed products were introduced into gas chromatographs (Shimadzu GC 2014 or GC 2010) with helium or nitrogen used as carrier gas. The products were exhaustively analyzed by using three different columns and two different detectors (TCD and FID). More than 40 compounds were identified and quantified. Inorganic gasses such as H<sub>2</sub>, CO, CO<sub>2</sub>, and H<sub>2</sub>O were separated by Gaskuropack 54 column (GL Sciences Co. Ltd.) and detected with TCD. The packed column Gaskuropack 54, consists of polymer beads with highly cross-linked styrene–divinylbenzene copolymer, can able to separate these products. Light hydrocarbons such as alkanes, alkenes, and alkynes, and

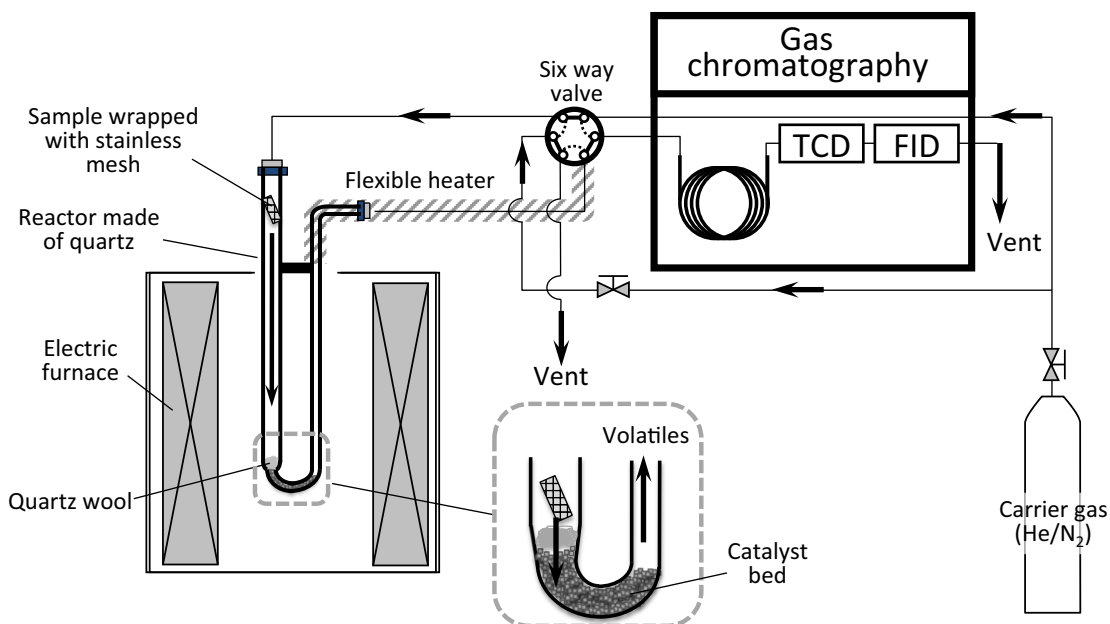
**Table 1**  
Characteristics of the zeolite catalysts.

Zeolite (frame structure)	SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> , mol/mol	Na <sub>2</sub> O, wt.%	Unit cell size, Å	Surface area, m <sup>2</sup> /g
HZSM-5	23	0.05	–	425
Mordenite	20	0.08	–	500
Y-type-1	5.1	2.8	24.5	730
Y-type-2	400	0.05	500	620
β-Type	500	0.1	3000	400

oxygenated compounds such as methanol, ethanol, acetaldehyde, furan, acetone, propanol, acetic acid, hydroxyl acetone, furfural, and furan were quantified by the same column with FID. Another packed column VZN-1 (GL Sciences Inc.) is used for separating alkene, alkyne, and diene with FID. Since the packed columns have some limitations in detecting high-molecular weight compounds, these compounds were quantified by GC equipped with a capillary column (CP PoraBOND, Agilent Technology, Co. Ltd.). High molecular weight compounds such as mono- and bicyclic aromatic compounds were detected by PoraBOND column. The quantifications of the products were conducted based on the external calibration method which uses response vs amount functions that are subsequently used to estimate amounts of analyte in a separately analyzed sample as long as the standard compounds for the target products were available. The effective carbon number concept [16] was also employed for estimation of the amounts of products of which standards were unavailable. The detailed procedure was published elsewhere [17]. The product yields were calculated based on the carbon content in the feedstock. The yields were calculated according to the equation

$$Y_i = \frac{A_i}{\left(\frac{A_{\text{CH}_4}}{N_{\text{CH}_4}}\right) * R} * M_i * x_i * \frac{1}{W_{c-\text{feed}}}$$

where,  $Y_i$  is the yield of the  $i$ th component (mol-C/mol-C in feed),  $A_i$  is the peak area in the chromatogram,  $R$  is the relative response,  $x_i$  is the ratio of carbon weight to the molecular weight of the  $i$ th component, and  $W_{c-\text{feed}}$  is the carbon weight in cedar, and  $N_{\text{CH}_4}$  are the moles of CH<sub>4</sub> in the standard gas.



**Fig. 1.** A schematic representation of the experimental set-up for studying the kinetics of in-situ reforming of volatiles derived from the fast pyrolysis of cedar.

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