A kinetic study of in situ CO$_2$ removal gasification of woody biomass for hydrogen production

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Abstract

Woody biomass was gasified in steam at high temperature ($\sim$923 K) and pressure ($\sim$6.5 MPa) in the presence of a CO$_2$ sorbent using a batch reactor with 50 cm^3 capacity; this process is termed "in situ CO$_2$ removal gasification." Gas, tar, and char were obtained as the products. The evolved CO$_2$ was completely absorbed in the sorbent, and no CO$_2$ was in gas phase. The product distribution at different reaction temperatures ranging from 473 to 923 K was examined to obtain fundamental information on the biomass degradation during the gasification. The reaction model proposed by Shafizadih and Chin was applied. The kinetic constants of the primary and secondary degradations were calculated from the product distribution.
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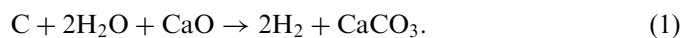
1. Introduction

There has been considerable focus on hydrogen as an energy carrier because only water is produced when it is used and an energy device with high efficiency, such as a fuel cell, can be developed. In Japan, hydrogen stations have been constructed in order to demonstrate its feasibility, and hydrogen fuel cell vehicles have been introduced. Many efforts are underway to establish the hydrogen society.

At present, hydrogen is produced by reforming of naphtha or natural gas or obtained as a byproduct from coke production. However, hydrogen production from renewable resources is expected to gain importance in the future. Only biomass is a renewable and organic resource, and it can be directly converted into hydrogen [1].

Steam gasification using a CO$_2$ sorbent, termed "in situ CO$_2$ removal gasification," is a hydrogen production method from biomass. In situ CO$_2$ removal gasification is carried out at high temperature (873–973 K) and pressure ($\sim$60 MPa), and clean gas, mainly hydrogen, can be produced from carbonaceous materials since CO$_2$ is absorbed in the CO$_2$ sorbent, CaO, during the gasification. Based on the principle proposed by Lin et al. [2–5], the theoretical overall reaction equation is as follows:

$$C + 2H_2O + CaO \rightarrow 2H_2 + CaCO_3. \tag{1}$$

The obtained CaCO$_3$ can be regenerated by calcination:

$$CaCO_3 \rightarrow CaO + CO_2. \tag{2}$$

Since the reaction heat absorbed during the calcination is generated during the carbonation, the gasification (1) is exothermic. Generally, in the case of the production of hydrogen via gasification, three processes are needed: steam gasification, water–gas shift reaction, and CO$_2$ removal process. In the in situ CO$_2$ removal gasification, these three reactions can occur in a single reactor, and therefore, high conversion efficiency is expected.

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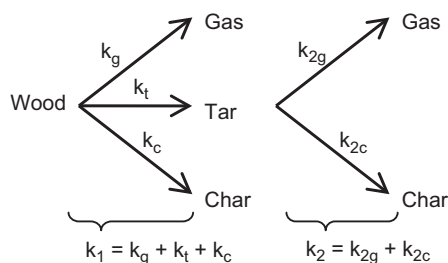E-mail address: minowa.tom@aist.go.jp (T. Minowa).

Fig. 1. Reaction model of wood pyrolysis proposed by Shafizadih and Chin.

Table 1
Properties of Japanese oak (*Quercus serrata*)

Proximate analysis (wt%)				Ultimate analysis (wt%), daf[a]		
VM[b]	Mois[c]	FC[d]	Ash	C	H	O[e]
82.4	5.2	11.8	0.6	47.6	6.1	46.3

[a]Dry ash free basis.
[b]Volatile matter.
[c]Moisture.
[d]Fixed carbon.
[e]By difference.

In order to develop the gasification process, the effects of the operating conditions on the gasification should be examined. In a previous study, we have clarified the effects of temperature, pressure, ratio of calcium to wood, etc., on the gasification yield and properties of the gas by using a batch reactor to obtain fundamental information [6,7]. In this paper, we focus on a kinetic parameter for the design of the apparatus or process. A gasification model for wood pyrolysis, shown in Fig. 1, has been proposed by Shafizadih and Chin [8]. In this model, wood is first degraded into gas, tar, and char by primary degradation. The tar is then decomposed into gas and char by secondary degradation. Many kinetic studies for various pyrolysis and gasification processes have been carried out using this model [9–18].

In a previous study, we gasified wood at different reaction temperatures up to 923 K and the effect of the temperature on the gasification was discussed [19]. In the present study, the result was reconsidered for a kinetic study and the kinetic constants of in situ CO_2 removal gasification were examined from the product distribution with the reaction model proposed by Shafizadih and Chin.

2. Experimental

2.1. Materials

Japanese oak (*Quercus serrata*, $150-250\,\mu m$) dried overnight in an oven was used as the woody biomass feedstock for the experiments. The proximate and ultimate analyses are shown in Table 1. Here, in the ultimate analysis, oxygen was determined by difference and includes trace elements that were relatively small such as nitrogen and sulfur. Commercial calcium hydroxide powder ($Ca(OH)_2$) (Wako Pure Chemical Industries, Ltd., Japan) was employed as a CO_2 sorbent without further preparation.

2.2. Reaction

The experiments were performed using an autoclave (inner volume ca. $50\,cm^3$). In order to adjust the molar ratio of C:Ca:H_2O to 1:2:6, 0.34 g of Japanese oak, 2.06 g of $Ca(OH)_2$, and 1.0 g of distilled water were placed in the autoclave. Nitrogen gas was used to set the initial pressure
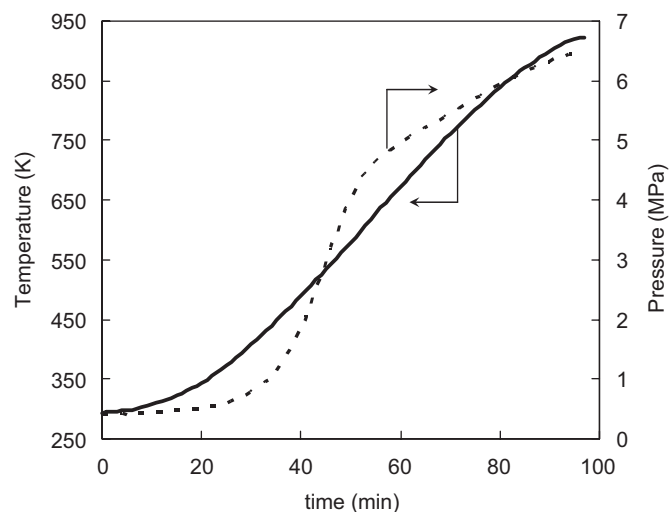

Fig. 2. Typical profiles of temperature and pressure in the autoclave vs. reaction time.

to 0.4 MPa. The autoclave was then heated to a desired temperature of 473–923 K in an electric furnace. The pressure in the autoclave increased autogenously with increasing temperature. When the desired temperature was attained, the electric furnace was immediately removed and the autoclave was cooled to the room temperature by means of an electric fan. Typical profiles of the temperature and pressure in the autoclave against the reaction time are shown in Fig. 2. Since the profiles were well reproduced, the reaction temperature can be considered to be a function of reaction time in this study.

2.3. Separation scheme and definition of products

Fig. 3 shows the separation scheme and definition of products after the temperature in the autoclave reached the room temperature. The product gas was expelled from the autoclave with N_2 and collected into a gas sampling bag. The gaseous composition was analyzed with a GC/TCD (GC323, GL Sciences Co.) and a GC/FID (GC353B, GL Sciences Co.). Then, the autoclave was opened and mixture (a) was removed by washing with water. The aqueous solution was separated by filtration. Inorganic and organic