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CO_2 Gasification of Six Types of Chars from Indonesian Sugarcane Bagasse

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Abstract

The present authors investigated CO_2 gasification of chars from the pyrolysis of six different types of Indonesian sugarcane bagasse with a main purpose of quantitative understanding of the kinetics/mechanism of the gasification. The kinetic analysis revealed simultaneous progress of non-catalytic gasification and catalytic one under the catalysis of inherent alkali and alkaline earth metallic species, and much more importance of the latter. The newly proposed kinetic model quantitatively described the time-dependent changes in the mass-based char conversion over its range up to 99.99% or even higher by assuming distributed initial activity and deactivation kinetics of the inherent catalytic species. It was also demonstrated that the non-catalytic gasification occurred obeying first order kinetics with respect to the residual mass of char, and this demonstrated that physical properties of the char such as micro-porosity and specific surface area were not factors influencing the kinetics.

1. Introduction

Gasification with carbon dioxide as gasifying agent has been drawing attention in academic and industrial fields of thermochemical processing of biomass. It offers an advantage as it can help reducing carbon emission compared to the conventional technologies. [1] Adopting biomass for the CO_2 gasification process is more desirable than that of fossils. Biomass chars has higher reactivity than coal char, attributable to the possession of inherent catalytic elements including sodium (Na), potassium (K), and calcium (Ca). [2] It is therefore reasonable to apply the catalysis in the low temperature gasification with high cold gas efficiency. [3] This study was utilizing sugarcane bagasse (SCB) as the source of chars. Bagasse known as squeezed fibrous residue and has a relatively high content of the aforementioned catalytic species. [4]

Biomass gasification is a complex process involving water evaporation, pyrolysis that forms volatiles and char, combustion and/or gasification of the volatiles and char. [5] Since the char gasification process is the slowest step in the over-all process of biomass conversion, quantitative understanding and prediction of the characteristics of the char gasification, is essential for designing gasifier and optimization of operating conditions.

There have so far been a number of general or detailed kinetic models for steam and/or CO_2 gasification of chars, but it should be stated here that none of those models can either describe or predict the kinetics of char conversion over its entire range (i.e., 0 to 100% or near 100%). Several types of the existing models, such as shrinking core (SC) models, grain-core (GC) models and random-pore (RP) models, have frequently been employed for describing the kinetics. [6-8] The present authors' preliminary investigation, however, showed that all of those models were inappropriate due to inconsistency with the real mechanism of the gasification.

The present authors here propose a new kinetic model, the assumptions of which are in agreement or consistent with the mechanism of the char gasification. This study focused on characteristics of char gasification, results of kinetic analysis of the char gasification by the proposed model, and also discusses the catalysis of the inherent AAEM species in the gasification.

2. Experimental

2.1. SCB samples.

Six different types of SCBs were pulverized to sizes smaller than 150 mesh and dried in air at 100°C prior to use. The samples were then subjected to ultimate analyses. The individual type of SCBs and chars are hereafter distinguished by abbreviations.

Portion of SCBs samples were washed with 1N HCl aqueous solution at 60°C for 24 h for removal of major portions of catalytic AAEM species. In addition, for lightly removal of AAEM, SCBs were washed with warm deionized water instead of acid at 60°C for 24 h.

2.2. Char preparation

Every SCBs was pyrolyzed in atmospheric flow of high purity N_2 through a fixed bed reactor with a heating rate, peak temperature and holding time of 30 $°C.min^{-1}$, 600°C and 15 min, respectively. The acid-washed and hot-water- washed SCBs were pyrolyzed under the same conditions as above. The acid washed and hot water washed SCB X are referred to as AW-X (e.g., AW-MK) and HW-X (e.g., HW-MK), respectively. The contents of AAEM species in the char from original/pretreated were quantified by applying sequences of careful combustion (ashing), ash dissolution and then ion chromatography.

2.3. Gasification of chars

SCBs samples were subjected to the gasification. A thermogravimetric analyzer (TGA; Hitachi Hi-Tech Science Corp., model STA7200) was used. The char sample was heated in atmospheric N_2 flowing at 700 ml-stp/min up to 900°C, which was held for 10 min. The atmosphere was then switched to 50:50 (in vol) mixed gases of N_2 and CO_2 without changing the total flow rate.

3. Results and Discussion

The study successfully describe the mechanism non-catalytic gasification of six different types of SCB chars as seen in **Figure 1**. The model can also describe the catalytic gasification over the entire range of conversion (from X= 0 up to 0.9994).

The rate constant of non-catalytic gasification, k_{nc} and the zero-th order rate constant for the gasification that is catalyzed by n-th catalyst, k_{cn} were attained by the parallel kinetic model which is shown in the following equation;

$$\frac{dX}{dt} = k_{nc}\left(1-X\right) + \sum_{n} k_{cn} \tag{1}$$

k_{cn} is depend on the decreasing mass of the chars, m_{cn} and the intrinsic rate k'_{cn}. During the process of gasification, the catalytic species dispersed in the carbon matrix undergoes deactivation by their coalescence and growth. The deactivation of the catalyst is described as the function of catalyst concentration, C_{cn}, which increasing with the conversion (X). The rate of catalyst deactivation is given by

$$\frac{dm_{cn}}{dt} = -k_{loss\text{-}n} C_{cn} = -k_{loss\text{-}n} \frac{m_{cn}}{1-X} \tag{2}$$

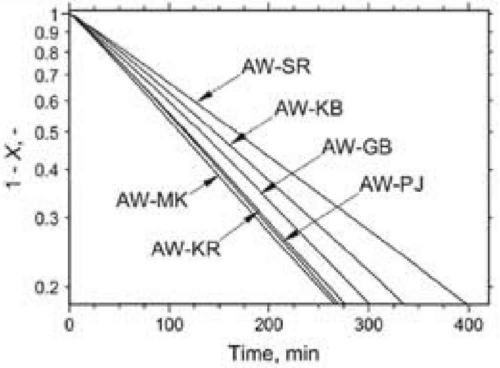

Figure 1. Time-dependent change in 1–X with time for gasification of chars from the acid-washed SCB.

The model assuming n number of catalyst with one catalyst precursor (C1prec) which is transformed into C1 exclusively. Therefore eq.2 is revised to

$$\frac{dm_{c1}}{dt} = k'_{c1prec} C_{c1prec} - k_{loss\text{-}1} C_{c1} \quad n=1 \tag{3}$$

$$\frac{dm_{cn}}{dt} = -k_{loss\text{-}n} C_{cn} \quad n \geq 2 \tag{4}$$

The initial rate of catalytic gasification (i.e., that at $t = 0$) is given by

$$\sum_{n=1} k_{cn,0} = \sum_{n=1} k'_{cn} m_{cn,0} = \text{ICA-1} \tag{5}$$

ICA-1 represents the initial catalytic activity. When the catalyst precursor, $C1_{prec}$, is present in the char, it is also reasonable to define the initial activity taking the concentration of $C1_{prec}$ as the potential catalyst into consideration.

$$k'_{c1} m_{c1prec,0} + \sum_{n=1} k_{cn,0} = \text{ICA-2} \tag{6}$$

The result of the kinetic analysis shows that k_{nc} was in a relatively narrow range of 4.2×10^{-3} – 6.5×10^{-3} min^{-1}. While in the catalytic gasification, the rate constant varied depending on the parent char.

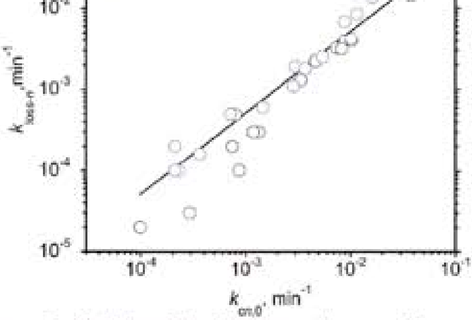

Figure 2. Relationship between $k_{cn,0}$ and $k_{loss\text{-}n}$. The rate constants for all of the six chars are summarized in the figure.

It was found that the inherent catalyst had widely distributed in the initial activity and

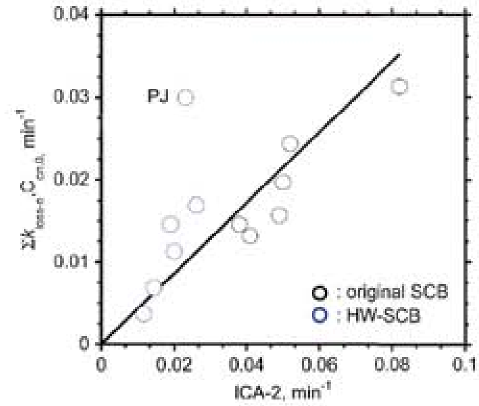

Figure 3. Relationship between ICA-2 and overall rate of catalyst deactivation at t = 0, $\Sigma k_{\text{loss-}n}C_{cn,0}$.

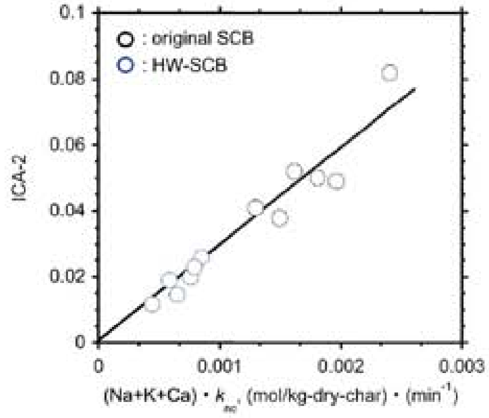

Figure 4. Relationship between ICA-2 and the product of total content of AAEM species (Na, K and Ca) in the char and k_{nc}.

tendency of deactivation. **Figure 2** plots $k_{\text{loss-}n}$ against $k_{cn,0}$ for all the six chars, showing its linear relationship with the initial activity. Thus, the more active underwent more rapid deactivation in the terms of rate constant. It is also proved in **Figure 3**, that the overall rate of catalyst deactivation is roughly proportional to ICA-2 that represents the initial and overall catalytic activity. **Figure 4** shows the relationship of ICA-2 with the initial and total concentration of Na, K, and Ca, which has been multiplied by k_{nc} as the non-catalytic reactivity of char, assuming that the rate of catalytic gasification is not only a factor of catalyst activity, but also the intrinsic reactivity of char. It is seen that ICA-2 increases in linear manner with the corrected catalyst concentration, though there is an exception. This trend suggests similar initial molar activities of Na, K, and Ca catalysts, but further examination of such similarity is required.

4. Conclusion

This study have successfully analyzed and modeled the kinetics of the CO_2 gasification of the twelve different types of chars from SCBs, drawing and confirming the non-catalytic and catalytic mechanisms of the gasification. The kinetic model describes the kinetics quantitatively over the entire range of the char conversion. The overall initial catalytic activity is roughly proportional to the total molar concentration of Na, K and Ca, and also is also a strong factor for the deactivation kinetics.

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