Kinetics of rice husk char gasification

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Abstract

The gasification of rice husk char in carbon dioxide and steam was investigated for determining the kinetic parameters. Experiments were conducted with rice husk char in its original grain form in a silica tube reactor with steam at temperatures of 750°C, 800°C, 850°C and 900°C and experiments were conducted with rice husk char powder in a thermogravimetric balance in a carbon dioxide medium at temperatures of 750°C, 800°C, 850°C and 900°C. The data was analysed based on the volume reaction and shrinking core models. The activation energies obtained for the rice husk grain sample were 200 kJ/mol and for the rice husk powder, about 180 kJ/mol respectively. The results obtained are in good agreement with literature values of different char gasification reactions.

Keywords: Rice husk; Char gasification

1. Introduction

Rice husk is one of the major agro-based residues produced in large quantities in developing countries. It is mainly used for thermal application in boilers, furnaces, gasifiers etc. The design of gasifiers depends on the kinetic parameters for the gasification of char in addition to the pyrolysis kinetic parameters. The literature on kinetic studies on gasification of chars produced from biomass materials is limited compared to those of coal and wood char. 

Dutta et al. [1] investigated coal char gasification in carbon dioxide and found that the reaction can be represented by the homogeneous model with reaction orders of unity for both gas and solids. Golovina [2] investigated the C–CO₂ reaction at high temperatures and pressures. He reported that the reaction is first order at one atmosphere pressure. Reyes and Jensen [3,4] applied percolation theory for char gas reactions under kinetic and diffusion controlled situations.
Kwon et al. [5] studied the kinetics of char carbon dioxide gasification taking into account the effects of particle size, gas concentration etc. and reported that the overall reaction is chemically controlled and can be represented by the shrinking core model. Osafune and Marsh [6] have reported that for gasification of char in carbon dioxide in the temperature range 1140–1560 K, the data could be represented by the shrinking core model. Kovacik et al. [7] studied char gasification by carbon dioxide in fixed bed reactor. The data was analysed based on the volume reaction model and shrinking core model for individual grains. The kinetics parameters obtained by both methods were in good agreement. Shufen and Ruizheng [8] studied lignite char gasification in CO$_2$, H$_2$ and H$_2$O mixtures under pressure. They found that the reaction by steam and carbon dioxide could be represented by the shrinking core model, while with hydrogen the reaction could be represented by the volume reaction model. The activation energies for the char gasification reactions reported by the above investigators lie in the range of 200–360 kJ/mol. Groeneveld and Van Swaaij [9] studied gasification of wood char in a mixture of CO$_2$ and H$_2$. They reported that the reaction order is 0.7 with respect to steam and carbon dioxide with an activation energy of 215 kJ/mol based on the local volume reaction model. De Groot and Shafizadeh [10] investigated the gasification of cotton wood and Douglas fir chars in CO$_2$ and H$_2$O. They have reported that the reaction is zeroth order with dependency on the initial mass of the sample and reaction order of 0.6 with respect to the carbon dioxide partial pressure. The activation energies obtained for cotton wood are 200 and 190 kJ/mol and for Douglas fir are 222 and 258 kJ/mol in carbon dioxide and steam respectively. Standish and Tanjung [11] reported that for gasification of wood char particles in CO$_2$, the reaction can be represented by the shrinking core model. They have reported a generalised correlation equation for gasification rates in which the reaction order with respect to the partial pressure of carbon dioxide is 0.71. The activation energy reported is 210 kJ/mol. Edrich et al. [12] studied the Ponderosa pine char in CO$_2$. They have reported an activation energy of 142 kJ/mol. Nandi and Onischak [13] studied gasification of maple and jackpine wood chars in mixtures of steam, hydrogen etc. and reported activation energies in the range of 165–185 kJ/mol based on the homogeneous model. Gaur et al. [14] investigated the kinetics of corn cob char gasification in CO$_2$. They reported that the reaction rates decreased from 650°C to 750°C and then increased until 1000°C. The data above 750°C was well represented by the shrinking core model, and the activation energy obtained was 168 kJ/mol. Dasappa et al. [15] developed a model for
wood char particles in carbon dioxide and nitrogen mixtures considering the reaction kinetics by a multi-step reaction scheme and heat and mass transfer steps in the solid. They verified their model predictions with the experimental data of Standish and Tanjung [11] and found that the model predicts their data satisfactorily.

In the present work gasification of rice husk char in grain form with steam and in powder form with CO$_2$ was studied for determining the kinetic parameters. The data was analysed by widely accepted models like the homogeneous and shrinking core models. These models are simple to use and can easily be coupled with other rate processes occurring in the reactors, like moving bed, fluidised bed reactors for modeling purposes.

2. Experimental

2.1. Sample preparation

Rice husk char is prepared by heating rice husk in a nitrogen atmosphere to about 600–700°C in a batch pyrolyser. The powdered sample is made by grinding and sieving the char grain. The average size of the powdered rice husk char is about 10 μm. Proximate analysis of the rice husk char was performed as per ASTM D 3174-73 standards and found to contain fixed carbon 49.72%, ash content 46.02% and volatile matter 4.15%.

2.2. Experimental set-up

A silica tube reactor is made of a 4 cm i.d. and 40 cm long silica tube and consists of a pre-heating zone and a reaction zone in the middle. The reactor is heated by Kanthol heating elements wound on the silica tube separately in the two zones. Provisions are made for the flow of gases and sample holding from the top and for thermocouple insertion and for exit of the gases at the bottom. A temperature controller is used for maintaining the desired temperature in the reaction zone. Rice husk char, about 500 mg, is taken in a small fine stainless steel wire mesh basket and
Fig. 2. Fractional weight loss vs $t$ for rice husk powder at different temperatures.

Fig. 3. $-\ln(1 - X)$ vs $t$ for rice husk grain at different temperatures.
suspended through a stainless steel rod and positioned at the middle of the reaction zone. The reactor is flushed initially with nitrogen and the reactor is heated to the desired reaction temperature in the nitrogen atmosphere. The heating is continued at the reaction temperature for about 15 min to attain steady state temperature conditions. The reaction temperature is measured by a thermocouple fixed near the sample. Then, the nitrogen gas is switched off, and steam is passed through the reactor, generated from a small steam generator. The sample is reacted for a fixed time and then quickly lifted to the top of the reactor inside the silica tube where the temperatures are very low, and immediately, the steam is switched off and nitrogen allowed to pass through the reactor for cooling the sample. When the sample is cooled, it is removed from the reactor and weighed for determining the extent of conversion. In a similar manner experiments are carried out at the same temperature with different samples for different reaction times to obtain conversion against time data at a particular temperature. The experiments are carried out in the same manner at other temperatures also.

Experiments with powdered sample weighing about 10 mg are carried out in a thermogravimetric analyser (SII-SSC 5100). Rice husk char powder sample is initially heated in nitrogen atmosphere at a known heating rate of 50°C/min until the desired reaction temperature is reached and then maintained at that temperature for another 5 min. Then CO₂ is introduced by replacing N₂ gas. The reaction in CO₂ atmosphere is carried out under constant temperature condition at
the desired temperature. The reactions at other temperatures are carried out in a similar manner. The weight loss against time data is obtained from the instrument.

3. Results and discussion

From the weight loss vs time data, the fractional conversions with respect to time are calculated, taking into consideration of the composition of the char as determined by the proximate analysis. The fractional conversion vs time data for the rice husk grain sample and the rice husk char powder samples are shown in Figs. 1 and 2.

The rate equations used for determining the kinetic parameters are as follows. Volume reaction model:

\[
\frac{dX}{dt} = k_v(1 - X)C_{A0}
\]

or

\[
-\ln(1 - X) = (k_vC_{A0})t
\]  

Dutta et al. [1] have used a similar rate equation for describing the char–CO\textsubscript{2} reaction. Shrinking core model:

\[
\rho(-\frac{dr_c}{dt}) = k_vC_{A0}
\]
\[ t = \left( \frac{\rho R_p}{k_t C_{A0}} \right) \left[ 1 - (1 - X)^{1/3} \right] \] (4)

Several investigators have reported first order with respect to the reactant gas concentration for the char gasification reaction.

The data according to the homogeneous model, Eq. (2) for rice husk grain and powder samples and according to the shrinking core model, Eq. (4) for the rice husk powder samples are shown in Figs. 3–5. It is found that the data is represented quite satisfactorily by the rate equations except for the rice husk powder results at 900°C temperature. It can be concluded that at the higher temperatures of 900°C, the reaction mechanism is not only chemically controlled but could also be influenced by diffusional resistance. Consequently, for determining the kinetics parameters the data of at the 900°C temperature is excluded for rice husk powder. The rate constants are determined from the slopes of the lines from Figs. 3–5, and the Arrhenius plots are shown in Figs. 6 and 7. The rate constants are given by

rice husk grain \( K_v = 2.41 \times 10^{11} e^{-209325/RT} (m^3/s kmol) \) (5)

rice husk powder \( K_v = 8.1 \times 10^6 e^{-197141/RT} (m^3/s kmol) \) (6)

rice husk powder \( K_v = 5.53 \times 10^6 e^{-62950/RT} (m/s) \) (7)

![Fig. 6. Arrhenius plot for rice husk grain and powder.](image)
4. Conclusions

From the results obtained, it is observed that the gasification reaction of rice husk char is chemically controlled up to a temperature of 850°C, and above this temperature, diffusional resistance in the solid influences the overall reaction. The activation energies obtained by the volume reaction model and the shrinking core models are in close agreement. The activation energies obtained are in good agreement with the range of activation energies reported by several investigators for biomass char gasification reactions.

References