Fuel 207 (2017) 198–203

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Full length article

Competition between H_2O and CO_2 for active sites during co-gasification of bituminous coal and pineapple sawdust in an atmosphere containing H_2O, CO_2, H_2, and CO

Massoud Massoudi Farid [a], Jungho Hwang [b,*]

[a] CIC Virtuhcon, Institute of Energy Process Engineering and Chemical Engineering, TU Bergakademie Freiberg, 09599 Freiberg, Germany
[b] Department of Mechanical Engineering, Yonsei University, Seoul 03722, Republic of Korea

HIGHLIGHTS

- Coal–biomass blended char was gasified in a mixture of CO_2, H_2O, H_2, and CO.
- Char–H_2O and char–CO_2 reactions occurred on separate active sites.
- H_2 and CO had no effect on participation of active sites in the gasification.

ARTICLE INFO

Article history:
Received 2 March 2017
Received in revised form 30 May 2017
Accepted 19 June 2017

Keywords:
Vapor and carbon dioxide competition
Co-gasification
Coal
Biomass
Langmuir–Hinshelwood
Active sites

ABSTRACT

The competition between the H_2O and CO_2 for the active sites during gasification remains a controversial issue in the literature. In this study, the competition between the H_2O and CO_2 for the active sites during gasification of coal, biomass, and a mixture of coal and biomass using the Langmuir–Hinshelwood (L–H) kinetic parameters obtained in our previous two papers (Massoudi Farid et al., 2016, 2017) was investigated. It was found that the char–H_2O and char–CO_2 reactions occurred on separate active sites for all samples. For a constant CO_2 concentration, increasing the H_2O concentration caused an increase in the kinetic coefficient. The extent to which the kinetic coefficient increased became less pronounced as the amount of biomass in the co-gasified mixture increased. For a constant H_2O concentration, increasing the CO_2 concentration also increased the kinetic coefficient; however, the extent to which the kinetic coefficient increased was greater when the amount of biomass was higher. Additional experiments were conducted to study the effect of the co-existence of H_2 and CO on the competition between the char–H_2O and char–CO_2 reactions for the active sites. It was found that the char–H_2O and char–CO_2 reactions also occurred on separate active sites, even in the presence of both H_2 and CO.

1. Introduction

Coal is one of the main sources of global fuel, yet is also one of the most prominent sources of greenhouse gases, including CO_2. Co-gasification of coal with biomass is one method of reducing coal consumption and consequently gas emissions. The properties of coal significantly differ from those of biomass; therefore, it is important to develop in-depth understanding of the processes that occur in the co-gasification of these two fuels.

Char gasification of a mixture of coal and biomass with H_2O and CO_2 was investigated by Jeong et al. [1] and Jeong et al. [2], respectively, by expressing the kinetic coefficient as an Arrhenius equation. It was found that the gasification reactivity increased with increasing the amount of biomass, the random pore model (RPM) was the best in describing char gasification, and synergy effect with the addition of biomass was remarkable at all of the coal–biomass ratios. Massoudi Farid et al. [3] extended the works of Jeong et al. [1,2] by investigating the effects of H_2O and CO_2 partial pressures on the reaction kinetics. The reactivity of co-gasification of coal and biomass-blended char increased with partial pressure, and at the same partial pressure, reactivity of gasification with CO_2 was lower than that with H_2O for any sample except pure biomass sample. Moreover, Massoudi Farid et al. [4] studied the effect

---

Abbreviations: L–H, Langmuir–Hinshelwood; RPM, random pore model; XRF, X-ray fluorescence.

* Corresponding author.
E-mail address: hwangjh@yonsei.ac.kr (J. Hwang).

http://dx.doi.org/10.1016/j.fuel.2017.06.074
0016-2361/

of H_2 on the char-H_2O reaction kinetics of a coal-biomass mixture. Similarly, the effect of CO on the coal-biomass mixture char-CO_2 reaction was investigated by Massoudi Farid and coworkers [5]. It was concluded that the inhibition effect was stronger in the mixture sample than in the pure samples and for each sample, the inhibition effect was stronger for co-gasification at lower temperature.

In a real situation, however, H_2O and CO_2 can exist simultaneously. Therefore, the competition between these two species for occupation of the active sites in the gasification reactions of char with H_2O and CO_2 in a coal-biomass mixture should be investigated. Several studies have considered the co-existence of CO_2 and H_2O in coal char gasification or biomass char gasification [6–9]; however, there is no available literature on the gasification of char from a coal-biomass mixture in an atmosphere containing both CO_2 and H_2O.

The original Langmuir–Hinshelwood (L–H) equation can be used to explain char gasification in pure H_2O and CO_2 atmospheres. However, this equation cannot describe the competition between char–CO_2 and char–H_2O gasification, although these two gasification reactions occur at the same time in coal gasifiers [9]. Roberts and Harris [6], Mühlen et al. [10], and Zhang et al. [11] concluded that CO_2 gasification and H_2O gasification utilize the same active sites during coal gasification. On the other hand, Everson et al. [12] and Huang et al. [13] deduced that CO_2 gasification and H_2O gasification occur on separate active sites during coal gasification. Li et al. [14] reported that CO_2 gasification and H_2O gasification occur on separate active sites under atmospheric pressure, however, on common active sites under high pressures. Li et al. [14] also reported that neither of separate or shared active sites assumptions could express well the char gasification characteristics when the partial pressure of H_2O is particularly high. Umemoto et al. [9] stated that CO_2 gasification and H_2O gasification partially share the active sites during coal gasification and proposed a model based on their results. However, in their model, some of the parameters have to be determined by guessing.

Although the competition between the char–H_2O and char–CO_2 reactions in coal-char particles for the active sites remains a controversial issue, there are no studies on coal-biomass mixture char particles in the open literature. In this study, using the L–H kinetic parameters obtained in our previous two studies [4,5], the competition between the char–H_2O and char–CO_2 reactions is investigated for coal-biomass mixture char particles. Furthermore, in a real situation, H_2 and CO can both influence the char–H_2O and char–CO_2 reactions. In this study, the effect of the co-existence of H_2 and CO on the competition between the char–H_2O and char–CO_2 reactions is also investigated.

2. Experimental and modelling

2.1. Experiment conditions

Fig. 1 shows a schematic of the experimental setup. The setup includes a fixed-bed reactor with an alumina-tube with an inner diameter of 50 mm and a total length of 700 mm, an R-type thermocouple, a real-time gas analyzer (AO2020, ABB) equipped with non-dispersive infrared (NDIR) CO/CO_2 sensors, a steam generator with a peristaltic pump (Easy Load®, Masterflex), and N_2, CO_2, H_2, and CO capsules. Two grams of Shenhua coal (China), two grams of pine sawdust (Vietnam), and a two-gram mixture of coal and sawdust with a mass ratio of 1:1 were used as samples. The results of ultimate and proximate analyses of the original coal and biomass samples are presented in Table 1, and the results of the X-ray fluorescence (XRF) analyses are presented in Table 2.

Pyrolysis temperature should be high enough to be sure that all volatiles are evacuated from coal structure and pure char remains. According to the study of Chen et al. [15], yields of char, tar, and gas products from coal pyrolysis were changed when the pyrolysis temperature was lower than 900 °C. On the other hand, Yuan et al. [16] reported that biomass is much easier to crush to very small particles than coal during the pyrolysis process. Therefore, to prepare blended char with original morphology, the morphology of the biomass should not change during the pyrolysis process. In a study by Dall'Ora et al. [17], a pyrolysis temperature lower than 1100 °C and a heating rate of 10–20 $°C{\cdot}min^{-1}$ were recommended for preparation of pineapple char so that the char morphology might not change from its original state. Therefore, the temperature of the reactor was increased to 1000 °C, at a rate of 20 $°C{\cdot}min^{-1}$, after placing each sample at the center of the reactor. The reactor temperature was maintained at 1000 °C for 60 min to be sure that the pyrolysis was completed. N_2 gas (with purity of 99.999%) was flowed into the reactor at 3 $L\,min^{-1}$ during the pyrolysis.

The particle size of the original biomass samples (before pyrolysis) was 168 ± 77 μm (volume-equivalent diameter), whereas the particle size of the original coal samples was 65 ± 5 μm. However, after pyrolysis, the size of the biomass particles reduced to 104 ± 87 μm. Therefore, all the char particles (from coal and biomass) used in this study had sizes of less than 0.2 mm, as a result of which, it can be concluded that the carbon conversion was not affected by the particle size, as Zhang et al. [11]and Huang and coworkers [13] reported.

Based on our previous study [5], gasification of the all samples with CO_2 was under the chemical control regime when the temperature was lower than 900 °C. In the case of H_2O, gasification of coal and the coal-biomass mixture was under the chemical control regime when the temperature was lower than 900 °C; however, biomass gasification occurred under the chemical control regime when temperature was lower than 875 °C [4]. Therefore, all chars in this study were gasified under an atmosphere comprise of a mixture of CO_2, H_2O, CO, and H_2 with different concentrations at 875 °C; at which the N_2 gas flow was substituted by a mixture of N_2 and gasifying agents.

2.2. Kinetic modeling

The variation of the carbon conversion ratio with time can be expressed as:

$$\frac{dX}{dt} = k(T,\ P_i)f(X) \tag{1}$$

where X, $k(T, P_i)$, $f(X)$, T, and P_i are the carbon conversion ratio, the kinetic coefficient, the convergence dependency function of the reactivity, the temperature, and the partial pressure of gas species i (in this study, H_2O, CO_2, H_2, and CO), respectively.

Based on the L–H mechanism, $k(T, P_i)$ for the char-H_2O-H_2 reaction ($k_{H_2O-H_2}$) can be expressed as:

$$k_{H_2O-H_2} = \frac{K_1 P_{H_2O}}{1 + K_2 P_{H_2O} + K_3 P_{H_2}} \tag{2}$$

and for the char-CO_2-CO reaction (k_{CO_2-CO}) as:

$$k_{CO_2-CO} = \frac{K_4 P_{CO_2}}{1 + K_5 P_{CO_2} + K_6 P_{CO}} \tag{3}$$

where K_j (j=1–6) are kinetic parameters.

In the absence of H_2 and CO, the kinetic coefficient can be expressed as follows, provided that the char–H_2O and char–CO_2 gasifications occur at separate active sites: