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Kinetic study on CO_2 gasification of brown coal and biomass chars: reaction order

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HIGHLIGHTS

- Higher CO_2 partial pressure leads to higher gasification reaction rate.
- Reaction orders for coal and biomass chars pyrolyzed at high temperature are high.
- At low gasification temperature, reaction order for biomass is higher than coal.
- At high gasification temperature, reaction orders for biomass and coal are similar.
- Reasons for above behaviors are related to catalytic effect and pore distribution.

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ABSTRACT

The clean utilization of low-quality coal and biomass has been focused by researchers. Many researchers investigated the kinetics of coal and biomass gasification. Most of them focused on activation energy E and frequency factor A, and assumed the reaction order n as 1 without further study on it. In the present study, the gasification behavior of German Rhenish brown coal and wheat straw chars under different CO_2 partial pressure was studied in a small fixed bed reactor and the reaction order was determined. In addition, the effects of different feeds (biomass and coal), pyrolysis temperatures of chars and gasification temperatures on reaction order were investigated. The results showed that the reaction orders in this study ranged from 0.3 to 0.7. For all cases, higher CO_2 partial pressure leaded to higher reaction rate. For both Rhenish brown coal and wheat straw chars, the reaction orders increased with higher pyrolysis temperature. For wheat straw chars, the gasification temperature just had little effect on reaction order. However, for brown coal chars, reaction order increased at high gasification temperature. The possible mechanism was also provided as the effects of catalytic compounds and pore distribution, which were rarely found in literature.

1. Introduction

The continuing development of world economy needs more and more energy, which mainly comes from fossil fuels. Coal is worldwide one of the most important fossil fuels. However, abundant low-quality coal, especially brown coal, is difficult to use due to its high water content and low fixed carbon content. It is a significant issue to find an effective and clean way to utilize brown coal. In addition, extensive use of coal has caused some serious environmental problems, such as acid rain, water contamination and greenhouse effect restricting the development of the coal industry. Biomass is a kind of clean and renewable energy source and it is generally accepted as the energy, which would not accumulate the greenhouse effect in the atmosphere [1]. Despite biomass is the ancestor of coal, it has different chemical and physical properties. It contains low fixed carbon content, high moisture content. The low calorific value leads in a comparatively low energy density

Abbreviations: HKN, German brown coal; WS, wheat straw; B, pyrolysis temperature of 800 °C; E, pyrolysis temperature of 1000 °C; TGA, thermogravimetric analyzer; d, dry; SSA, specific surface area; R, reaction rate; P, partial pressure; n, reaction order; X, carbon conversion; k, reaction rate constant; $t_{0.5}$, time required to consumed 50% carbon content in char sample.

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and accordingly to a large volume, which is difficult to transport. Therefore an effective way to utilize this kind of renewable energy is necessary.

Gasification is such a useful technology with effective carbon utilization and also a reasonable way of reduction of atmospheric pollution. In addition, the kinetic study on char gasification is very important for a better understanding of the process and to design coal gasifiers. The gasification of char with CO_2 is a fundamental method to study the char reactivity. The kinetics of gasification reaction for different kinds of chars with CO_2 had been widely investigated [2–17]. However, most authors focused on activation energy E and frequency factor A, and assumed the reaction order n as 1. Only a few researchers determined the reaction orders of gasification process [2–4,12,13]. Ahn et al. [2] studied gasification kinetics of a sub-bituminous coal-char with CO_2 at elevated pressure and found: the apparent reaction order was 0.4 with a CO_2 partial pressures of 0.1–0.5 MPa at a temperature of 1300 °C and a total system pressure of 1.0 MPa. Kajitani et al. [12] investigated the CO_2 gasification rate analysis of four different coal chars in entrained flow coal gasifier and found the reaction orders varied from 0.43 to 0.56, showing coal types exhibited a large difference in the char gasification rate with CO_2, but did not give any explanation. Ollero et al. [13] studied on the CO_2 gasification kinetics of olive residue and found the reaction order was about 0.43 when CO_2 partial pressures varied from 0.02 to 0.05 MPa. Micco et al. [4] made study on kinetics of the gasification of Rio Turbio coal under different pyrolysis temperatures and found a reaction order was about 0.5 for char prepared at 850 °C, but no influence was found for char pyrolyzed at 950 °C.

When reviewing the results of the present literature, it can be found that most researchers [2,13] just calculated the value of reaction order as a normal kinetic parameter, without any interpretation for the value and consideration of any influence factor. Micco et al. [4] and Kajitani et al. [12] have already found reaction orders exhibited different values for different types of coal chars, but they did not give any explanation for the experimental behavior. Therefore, system study on the reaction order during gasification process should be carried out to fully understand the reaction mechanism. In the present work, the gasification behavior of Rhenish brown coal and wheat straw chars gasified at 800 and 1000 °C under ambient pressure with CO_2 concentrations ranging from 60 to 100 vol.% (rest N_2) was investigated, with the focus on the determination of the reaction order. The effects of process conditions such as pyrolysis temperature, gasification temperature and the influence of carbon conversion and char characteristics on reaction order have been studied in detail, which was rarely found in literature.

2. Materials and methods

2.1. Materials

Char samples, used in this study, were obtained from pyrolysis of a Rhenish brown coal (HKN) and wheat straw (WS). The raw samples were dried, milled and sieved to get a grain fraction of less than 2 mm, which is much bigger than particles usually used in TGA (<0.015 mm) [7]. This is more practicable for industrial production, since biomass is difficult to be grind into fine particles, which would come along with much higher energy consumption. The raw samples were pyrolyzed in a high temperature muffle furnace under ambient pressure in a nitrogen atmosphere with a final temperature of 800 °C (B) and 1000 °C (E) respectively, at a heating rate of 10 K/min. The samples were kept at final temperature for 30 min. Hence, there are four samples used in this study, WS-B (wheat straw char pyrolyzed at 800 °C), WS-E (wheat straw char pyrolyzed at 1000 °C), HKN-B (brown coal char pyrolyzed at 800 °C) and HKN-E (brown coal char pyrolyzed at 1000 °C). The characteristics of the char samples are illustrated in Table 1.

The proximate analysis is showing a decreasing volatile matter of brown coal and wheat straw chars with increasing pyrolysis temperature. The ash contents is around 24 wt.% (db) for wheat straw chars, which is much higher, than those of brown coal chars (about 9 wt.% db). The ultimate analysis indicates significant dropping hydrogen and oxygen contents with increasing temperature, while other contents stay comparatively constant. The loss of hydrogen could lead to lower reaction rates, because part of the carbon active sites are associated with bonded hydrogen. Furthermore, the functional groups, especially those containing oxygen, would decrease dramatically due to a reducing oxygen percentage. Therefore chars, produced at high temperature, should show lower reactivity.

To study the catalytic effect of mineral matters contained in wheat straw and Rhenish brown coal chars, the index of basicity [18] is calculated by Eq. (2.1).

$$\text{Index of basicity} = w(A) * \frac{Fe_2O_3 + CaO + MgO + Na_2O + K_2O}{SiO_2 + Al_2O_3} \tag{2.1}$$

$w(A)$ is the ash content of the sample, others are the content of various ash compositions. Since ashing processing is under oxidizing atmosphere (air), FeO in ash would transform into Fe_2O_3, which is used in Eq. (2.1). The index of basicity for all char samples was calculated as shown in Table 1. It can be seen, that for chars produced at the same pyrolysis temperature, the index of basicity of brown coal char was much higher than that of wheat straw char. It can be presumed, that the mineral matters in brown coal chars had bet-

Table 1
Analysis of Rhenish brown coal and wheat straw chars (proximate analysis, ultimate analysis, BET surface and pore size distribution of HKN and WS).

Sample	Wheat straw (WS)		Rhenish brown coal (HKN)	
	WS-B	WS-E	HKN-B	HKN-E
Ultimate analysis (wt.%). d				
Carbon. C	74.55	75.84	85.80	87.84
Hydrogen. H	0.68	0.24	0.93	0.32
Nitrogen. N	0.87	0.88	0.97	0.61
Sulfur. S	0.42	0.43	0.54	0.69
Oxygen. O (diff[a])	0.81	0.31	2.72	1.38
Proximate analysis (wt.%). d				
Ash	23.65	24.36	9.04	9.16
Volatile	4.06	3.09	5.16	3.00
Fixed Carbon	72.30	72.55	85.80	87.84
Ash analysis[b] (wt.%). d				
Na_2O	0.05	0.06	0.78	0.72
MgO	0.49	0.48	1.11	1.11
K_2O	3.36	3.13	0.05	0.05
CaO	1.77	1.71	4.74	2.74
Fe_2O_3	0.12	0.19	1.00	0.90
Al_2O_3	0.14	0.16	0.28	0.27
SiO_2	15.40	15.60	0.28	0.19
Index of basicity[c]	0.09	0.09	1.24	1.10
BET surface and pore size distribution				
BET surface area (m^2/g)	2	4	170	230
Porosity (%)	54	53	46	48
Pore volume (mm^3/g)				
Total pore	573	561	437	429
Macro pore	358	286	250	179
Meso pore	0	0	15	15
Micro pore	216	274	171	234

[a] Calculated by difference.
[b] Only oxides in Index of basicity are shown here.
[c] Index of basicity $= w(A) * \frac{Fe_2O_3+CaO+MgO+Na_2O+K_2O}{SiO_2+Al_2O_3}$.