Reaction kinetics of Powder River Basin coal gasification in carbon dioxide using a modified drop tube reactor

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HIGHLIGHTS

- The rate of Powder River Basin coal gasification was measured in carbon dioxide.
- A novel design of a modified drop tube reactor with rapid response analyzing system was developed.
- The reaction rate and carbon conversion was determined at 833–975 °C and 1–12 atm.
- The kinetics results can be described by the random pore model.
- Surface characteristics measurements (surface area measurements, scanning electron microscope images) were presented.

ARTICLE INFO

ABSTRACT

Carbon dioxide gasification and coal pyrolysis rates were measured in a modified drop tube fixed bed reactor, accompanied with a rapid response, real-time gas analysis system. Rapid heating and fast pyrolysis of the coal sample are intended to approximate the injection of ambient temperature coal into a fluidized bed gasifier. Experiments were done from 833 °C to 975 °C and from 1 atm to 12 atm in a 4:1 mixture of CO_2 and argon with coal particles ranging between 250 μm and 850 μm. Reaction rates and carbon conversions were calculated based on the CO signal from a quadrupole mass spectrometer. The random pore model closely fits the experimental results and fitting parameters are listed. Results from the effects of temperature and pressure, pyrolysis conditions, and characteristics of chars (surface area measurements, scanning electron microscope images) are presented.

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1. Introduction

1.1. Carbon dioxide gasification of char

Gasification is an incomplete combustion of a carbon-containing feedstock to produce syngas, including CO, H_2, CH_4, CO_2 and H_2O. Ideally, gasifiers convert the entire non-ash fraction of the feed into product gases, which preserve most of the heat of combustion value of the feedstock [1]. Reactions in gasifiers can be further divided into coal pyrolysis or devolatilization, char gasification, and gas phase reactions, among which char gasification with H_2O and CO_2 are the rate-determining steps [2]. A char gasification kinetics model can be used to improve the design of new gasifiers, and improve the conversion efficiency of existing gasifiers. The carbon dioxide gasification of char can be described as the following endothermic reaction:

$$C(s) + CO_2(g) \rightarrow 2CO(g) \quad \Delta H = 172.5 \text{ kJ/mol}(298 \text{ K}) \quad (1)$$
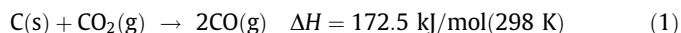
1.2. Laboratory techniques for measuring char gasification rates

Besides the influence of temperature and pressure on gasification rate, char reactivity is affected by the rank and types of coal, conditions of pyrolysis (temperature, pressure, heating rate), structural evolution [3], and ambient conditions in the gasifier. Several studies of gasification kinetics first prepared a char by pyrolyzing the feedstock, and then measured the char gasification rate [2–9]. This approach produces a consistent char for kinetic studies, but is not always representative of char formation in commercial gasifiers. In our research, we approximated the injection of ambient temperature coal particles into a hot, pressurized, fluidized bed gasifier. This approach combines pyrolysis and gasification in each experiment, with rapid heating and fast pyrolysis of the coal particles immediately followed by a char gasification.

Pressurized Thermogravimetric Analysis (TGA) has been widely used to measure gasification rates, especially at low temperatures

[2,3,6–9]. However, the sample in a TGA experiment is loaded into the reactor at ambient conditions and then is slowly heated to the measurement temperature [10]. The coal particle heating rate in a TGA experiment is much slower than the heating rate in a commercial fluidized bed or entrained flow gasifier. At low temperatures, gasification rates are controlled by char surface reaction rates, while, at higher temperatures, mass transfer rates can restrict the overall rate of gasification [1]. Zeng et al. [10] showed that mass transfer restrictions have a larger effect in TGA gasification experiments than in a laboratory fluidized bed gasifier experiments at the same conditions. Laboratory fixed-bed reactors [5,11] are also well developed, and this type of laboratory reactor allows gas to flow through the sample for good gas-carbon contact, avoiding diffusion restrictions. However, the issue of slow heating still exists in fixed bed reactors. Heating rates during the formation of char affects char gasification rates.

Rapid particle heating experimental techniques include the pressurized drop tube furnace (PDTF) and the pressurized entrained-flow reactor (PEFR). These techniques have been used to study coal gasification at high temperature (above 1000 °C) and high pressure in order to simulate the conditions in commercial entrained flow gasifiers [2,4,8,12,13]. These methods are rapid, single-point measurements, useful for reactions completed in a few seconds [11]. The overall gasification rates measured with these types of reactors include both surface reaction and mass transfer restrictions. Rates solely due to surface reactions cannot be readily measured with these techniques. Another laboratory reactor with rapid particle heating is the wire mesh reactor [14–16].

Means et al. [17] developed a modified drop tube reactor to investigate biomass-coal co-pyrolysis at conditions similar to those in a fluidized bed gasifier. The reactor body consists of a vertical, heated tube. Ambient temperature particles are dropped into the top of the tube, and a quartz frit in the center of the tube prevents the particles from falling further. This design has the high particle heating rate of a drop tube reactor, combined with the long residence time of a fixed bed reactor. Means et al. used a mass spectrometer to analyze effluent gas, but the response time of their analytical system was too slow to keep up with rapid pyrolysis reactions. Instead, they collected gas samples in bags that were later analyzed with a gas chromatograph. Sawettaporn et al. [18] conducted similar experiments, but these were limited to atmospheric pressure and there was no real-time gas analysis. Woodruff and Weimer [11] used real-time gas analysis, but their 30 s response time may be too slow to observe some phenomena.

Our reactor is very similar to the reactor used by Means et al. This provides rapid particle heating, as well as sufficient residence time to complete the gasification reactions at temperatures typical of fluidized bed gasifiers. We have greatly improved the mass spectrometer response time, which allows true real-time monitoring of reaction progress.

1.3. Reaction rate versus conversion models

In gasification, the size and morphology of char particles change as the char is consumed. Consequently, gasification rates are affected by the extent of reaction, X, where X equal to zero corresponds to no conversion and X equal to one corresponds to complete conversion of the non-ash fraction. The three most commonly used models used to describe gasification kinetics are: The volumetric model, which assumes that the reaction rate is proportional to the volume of the remaining char,

$$dX/dt = k(1 - X) \tag{2}$$

The shrinking core model, which assumes that the particles become smaller as the char gasifies, and that the gasification rate is proportion to the external particle surface area,

$$dX/dt = k_g(1 - X)^{2/3} \tag{3}$$

and the random pore model, which assumes that the gasification rate is determined by the rate of gasification of pore walls within the char particle.

$$dX/dt = k_p(1 - X)\sqrt{1 - \psi \ln(1 - X)} \tag{4}$$

where k_p is the reaction rate constant and ψ is a dimensionless structural parameter, given by:

$$\psi = \frac{4\pi L_0(1 - \varepsilon_0)}{S_0^2} \tag{5}$$

where L_0 and ε_0 are the initial pore length and porosity per unit volume and S_0 is the initial specific surface area. While ψ has physical meaning, it is typically used as a data fitting parameter.

The random pore model (RPM) was developed by Bhatia and Perlmutter [19]. Initially, pore diameters increase as the pore walls gasify, producing larger surface areas and faster gasification rates. Later, pores merge as pore walls disappear, leading to a loss of surface area. The random pore model is capable of describing systems with or without intermediate maximum in reaction rate versus conversion, and it is more flexible than other commonly used models [19,20]. For example, the RPM simplifies to the volumetric model when ψ is equal to 0, and it is nearly equivalent to the shrinking core model when $\psi = 1$.

2. Experimental methods

2.1. Sample preparation

The coal sample is from the Decker coal mine, which is in the north-west portion of the Powder River Basin in Montana, USA. The unground PRB coal was provided by Wyoming Analytical Laboratories, Laramie, WY and stored in a tightly sealed container to prevent loss of volatiles. Properties of the coal are shown in Table 1.

Samples were crushed using a glass mortar, and sieved to select particles sizes that range between 250 μm and 850 μm. Selected coal particles were dried at 80 °C for 2 days to remove free water. Dried particles were kept in a sealed glass bottle in a desiccator prior to gasification measurements. Fig. 1 shows the percentage of moisture (ASTM D3173-11) removed from the coal with time at 80 °C. The moisture level tends to stabilize after 24 h. A 48 h drying time was selected for subsequent tests, at which time most of the free water has been baked out while bound moisture is preserved.

Table 1
Proximate and ultimate analysis report of coal samples.

	As received wt%	Moisture free wt%	MAF basis wt%
Proximate analysis (Method: ASTM D5142)			
Moisture	24.29	N/A	N/A
Ash	3.62	4.78	N/A
Volatile Matter	29.42	38.86	40.81
Fixed Carbon	42.67	56.36	59.19
Total	100.00	100.00	100.00
Ultimate analysis (Method: ASTM D5142/5373)			
Moisture	24.29	N/A	N/A
Hydrogen	2.88	3.80	3.99
Carbon	56.48	74.59	78.33
Nitrogen	0.87	1.15	1.21
Sulfur	0.34	0.45	0.47
Oxygen	11.52	15.23	16.00
Ash	3.62	4.78	N/A
Total	100.00	100.00	100.00
Lower heating value, MJ/kg (Method: ASTM D5865)			
	22.03	29.09	30.55