



Research article

K₂CO₃-catalyzed steam gasification of ash-free coal char in a pressurized and vertically blown reactor. Influence of pressure on gasification rate and gas composition



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ABSTRACT

The K₂CO₃-catalyzed steam gasification of ash-free coal char was conducted in a pressurized and vertically blown reactor which was also characterized as a differential reactor. At a typical condition (total pressure, 0.5 MPa; steam partial pressure, 0.15 MPa; temperature, 750 °C; catalyst loading, 10%; superficial gas velocity, 55 cm s⁻¹), the gasification proceeded so fast that it was completed within 5 min. The dependence of either instantaneous gasification rate or average gasification rate on pressure was found to follow the Langmuir-Hinshelwood rate equation and the *n*th order rate equation, but the parameters for either rate equation varied with the carbon conversion. For a given coal char with a fixed catalyst loading, an overall kinetic model with the constancy of parameters is proposed to predict the gasification rate as a function of steam partial pressure, temperature and carbon conversion. While the elevation of steam partial pressure promoted the methanation mainly via the gas-char reaction, the yield of CH₄ was negligible. The gas composition was not in the equilibrium of water gas shift reaction.

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1. Introduction

Char gasification, a rate-controlling step in coal gasification, involves a complex heterogeneous reaction. There are many intrinsic and operation variables affecting the char gasification. The intrinsic variables link with the properties of char mainly including its carbonaceous structure, micro-porosity, and inorganics [1–3]. For a given char, the intrinsic rate of char gasification is dependent on some operation variables such as temperature, pressure, and gasifying atmosphere (partial pressures of reactant and product gases). Pressure is a crucial parameter for coal gasification because elevated pressure can appreciably augment the throughput of a gasifier not only by the gas concentrated effect but also by the accelerated gasification rate. Therefore, most commercial gasifiers are of pressurized type. The effect of pressure on the non-catalytic gasification has been studied extensively [4–11]. The Langmuir-Hinshelwood (L-H) rate equation and the *n*th order equation are widely accepted to describe the relationship between gasification rate and pressure for the steam gasification of coal char [4,7,9]. However, there remain two important problems. One problem arises from the inhomogeneous reactivity of coal char. The gasification rate changes with the burn-off or carbon conversion. The rate-pressure relationship is usually given at a fixed carbon conversion, for example, at a carbon conversion

of 0% [6,11], 10% [5,7], 20% [12], or 50% [9,13,14]. Such a relationship cannot represent the pressure effect over the entire range of carbon conversion. Aranda et al. reported that the reaction order and other kinetic parameters for the CO₂ or steam char gasification were variable with the carbon conversion [10]. Another problem is the diffusion effect on the kinetic parameters. The diffusion limitation can be difficult to thoroughly eliminate in a thermogravimetric analyzer (TGA) because of the limited gas flow velocity through the char or coal sample, although this device is widely used for determining the intrinsic kinetics of char gasification [7,10,15,16]. In most cases, the kinetic parameters obtained by TGA may not be truly intrinsic.

Catalytic coal gasification is distinguished from non-catalytic gasification by adding a catalyst to a reaction system to lower the gasification temperature and promote the gasification rate. The K₂CO₃-catalyzed coal gasification has been the subject of numerous studies over a long period of time [11,13–23]. Potassium carbonate is a superior catalyst, which can prominently promote the rate of char gasification at lower temperature. However, potassium carbonate is easily susceptible to deactivation when acidic minerals are present in coal [24,25]. Wang et al. reported that the use of an ash-removed coal (HyperCoal) may provide a way to avoid the catalytic deactivation [26]. Several studies were made with respect to the K₂CO₃-catalyzed gasification of ash-free coal [15,22]. However, there are only sporadic works pertaining to the pressurized K₂CO₃-catalyzed gasification. In the classical Exxon process, the mixture of steam with recycled gases (H₂ and CO) was used as a gasifying

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medium, and the gasification was operated at a total pressure of 3.5 MPa [18]. It was reported that this process produced a methane-rich gas. Tone et al. investigated the effect of steam partial pressure on the gasification rate of the K_2CO_3 -catalyzed coal char under a fixed total pressure of 1.5 MPa [27]. The first-order gasification rate ($r = \frac{dx}{dt}$, where x is carbon conversion, t is time) was found to peak at the carbon conversion of 0.3–0.4 irrespective of gasification temperature (700–800 °C), catalyst loading (6.3–10.9 g K/100 g °C) and steam partial pressure. The random pore model (RPM) could well describe the r - x profiles. From the gasification of coal char with 4.0 MPa steam and 10 wt% K_2CO_3 in a TGA, Mühlen and Sulimma observed that the one third-order gasification rate ($r = \frac{dx}{dt}(1-x)^{-2/3}$) was quasi-independent of carbon conversion in the range of 0.2–0.7 [28]. Bruno et al. compared the atmospheric steam K_2CO_3 -catalyzed gasification of coal char to the pressurized gasification performed in a fixed bed reactor [29]. Unexpectedly, a high pressure slowed down the gasification. An explanation for this result was the pressure-aggravated catalyst deactivation caused by the presence of mineral matter in coal char. Sharma et al. examined the effect of steam partial pressure on the steam gasification of ash-free char. They ascertained that the instantaneous gasification rate at the carbon conversion of 0.5 obeyed a power law with the steam partial pressure [22]. But their experiment was limited to a total pressure of 0.1 MPa.

From the K_2CO_3 -catalyzed steam gasification of coal char under atmospheric pressure in a horizontal boat reactor (HBR) [30–32], we found that for an ash-free coal char, the r - x profile typically displayed an arch-like shape with a maximal gasification rate at a higher carbon conversion of 0.5–0.6, consistent with the result obtained on a TGA [11,17,27,28] or a drop-down reactor [14] by other researchers. These kinetic characteristics cannot be tracked by the customary kinetic models including volumetric model (VM), shrinking core modeling (SCM) and random pore model (RPM) [33–35]. Nevertheless, it was reported that SCM and RPM were adaptable to describing the r - x profile obtained from the pressurized K_2CO_3 -catalyzed gasification [23,27]. A question is whether this contradictory result is attributed to the influence of pressure. Moreover, the kinetics of the K_2CO_3 -catalyzed char gasification determined by TGA and HBR in most studies may not be realistically intrinsic due to the diffusion limitation. It is needed to inspect the intrinsic kinetics by using a different reactor which can exclude the diffusion effect as far as possible. Recently, Kopyscinski et al. used a drop down reactor to investigate the K_2CO_3 -catalyzed gasification of ash-free coal using a binary gasifying agent (4:1 H_2O/H_2) under a total pressure of 2.5 MPa [14]. The reacting gas was allowed to pass through the coal particles in this type of reactor to eliminate the external and inter-particle diffusion. They observed that the catalytic char gasification was finished within 20 min at 725 °C.

On the other hand, the catalytic char gasification is perceived as an effective way to selectively manufacture hydrogen [21,30] or methane [18,36,37]. The gas composition is governed by various reactions such as the steam-char reaction and water gas shift reaction (WGSR), which can vary complicately with the gasification conditions such as the gasifying agent, temperature and pressure. In this respect, it remains debated whether the final gas composition is in the equilibrium of gas phase WGSR for the catalytic steam gasification [14,19,22]. In a previous study, we observed that the WGSR could be ignored in the catalytic steam gasification of ash-free coal char under atmospheric pressure at a low temperature below 750 °C, and the resultant gas composition was remote from the equilibrium of water gas shift reaction (WGSR) [33]. It has yet to be studied how the elevated pressure affects the gas composition for the catalytic char gasification.

In the present work, we undertake to investigate the K_2CO_3 -catalyzed steam gasification of ash-free coal char in a pressurized and vertically blown reactor. Our main objective is to address the influences of steam pressure on the gasification rate and gas composition. We also try to obtain the intrinsic kinetics of the catalytic char gasification by using this reactor. The detailed description and modeling of the diffusional effect exerted with a lower flow velocity will be presented in a following study.

2. Experimental

2.1. Samples

The coal sample of a Chinese YX lignite and the char preparation method used in this study were the same as used elsewhere [33]. The coal sample was sieved to the particle size of 0.074–0.15 mm. To avoid the effect of mineral matter on the catalytic deactivation, the coal demineralization was performed prior to charring. The coal sample was demineralized by the sequential HCl and HF leaching, and finally washed with distilled water to neutrality. The ash content decreased from 25.1% in the raw coal to 0.35% in the demineralized coal (all dry basis). The charring method was similar to the standard method for determining the volatile matter in coal (ASTM D3175-07), and only the temperature was altered. Briefly, a sample of demineralized coal was accurately weighed, and filled in a capped ceramic crucible, and then heated in an electric oven at 750 °C for a holding time of 30 min. The char sample was recovered and sieved to the particle size smaller than 0.15 mm. The mean particle sizes of char samples were determined by a laser diffraction particle analyzer (Beckman Coulter LS230). The mean particle size of the char sample was 0.032 mm. The char sample was determined by the proximate analysis, containing 5.2% volatile matter, 1.0% ash and 93.8% fixed carbon (all dry basis), and by the ultimate analysis, containing 94.5% carbon, 0.95% hydrogen, 2.7% nitrogen and 0.10% sulfur (all dry basis).

2.2. Gasification method

Char gasification was carried out in a pressurized reactor. The schematic diagram of reactor system is illustrated in Fig. 1. The pressure was controlled by a counterbalance valve and measured by two pressure gauges installed before and after the reactor. The flow rate of water was controlled by a micro-displacement pump, and steam was generated in an evaporator (400 °C). The tubular reactor (800 mm height, 17 mm inner diameter) was vertically installed. Ceramic pellets were packed in the lower part of reactor. Prior to gasification, the char sample was physically mixed with a predetermined proportion of a potassium carbonate reagent (analytic purity) in an agate mortar. A 0.2 g sample of the dried mixture was encased in a cylindrical wire mesh holder, which was placed on the ceramic filler bed where the temperature was assured to be flat. Prior to heating, the reactor system was tested

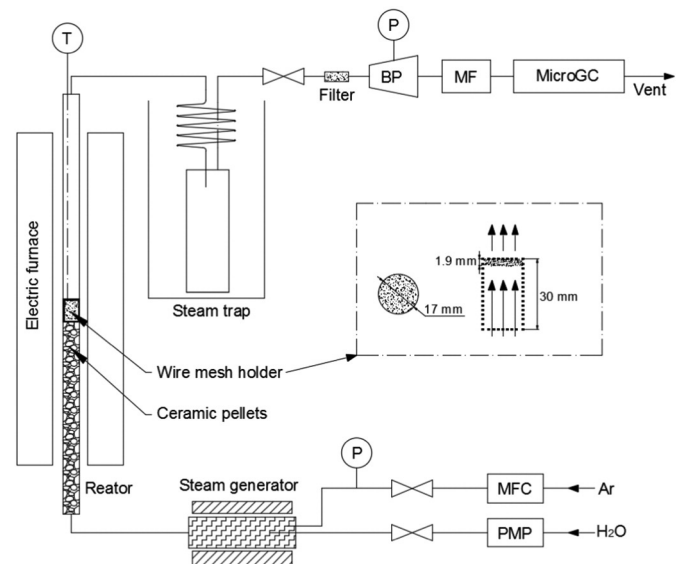


Fig. 1. Schematic diagram of pressurized reactor and apparatus system used for steam gasification. MFC, mass flow controller; PMP, piston micro-pump; P, pressure transducer; T, thermocouple; BP, back pressure valve; MF, mass flow meter.

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