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Reaction characteristics through catalytic steam gasification with ultra clean coal char and coal

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ABSTRACT

The direct production of methane through steam–coal gasification processing using a catalyst is one of the most attractive routes for the effective utilization of coal. In this study, a thermobalance was used to verify basic characteristics of carbon and steam reactivity using the ultra clean coal (UCC) char of Roto South with potassium carbonate at different conditions. The reactivity between carbon and steam was the highest at 800 °C, with catalyst (K_2CO_3) addition, 10 wt%, and the steam flow rate of 500 ml/min. At the optimized condition of thermobalance, syngas components of Roto South coal, which were produced in fixed-bed reactor, were observed through a Non-dispersive infrared sensor (NDIR) for 60 min. Methane concentration among the produced gases highly accounted for 36 vol% at 6 min. The volatile matter (VM) of coal was related to high methane production. From the X-ray diffraction (XRD) results, the crystallinity structure of K_2CO_3 was detected, as other potassium salts form, after 20 min.

1. Introduction

Natural gas, which accounted for 21% of the world's energy mix in 2010, is one of the cleanest and most efficient of all energy sources [1]. Recently, the increasing demand for natural gas and its high price has led to the production of synthetic natural gas utilizing a coal gasification process. Gasification technology not only satisfies future energy demand, but also provides environmental options. A major problem of commercial coal gasification in the production of fuel gas is the destruction of valuable volatile gas because of high operating temperatures. In particular, in a commercial SNG (synthetic natural gas) production plant, the process would mainly be divided by high-temperature gasifier and methanation processes, to produce high-concentration methane. However, the direct production of methane through gasification by using an alkali and alkaline-earth catalyst is one of the most attractive routes for the effective utilization of coal [2]. The characteristics of catalytic steam–coal and char gasification, there is (1) no oxygen injected in the gasifier, (2) all of the reactions are carried out at low temperature (600–800 °C), and (3) major heat input to the gasifier can be reduced (thermal neutral). First, reaction characteristics studies might be important for target gas production. The catalysis of coal gasification by an alkali and alkaline-earth salts, especially in potassium carbonate, has been studied widely. However, most of the fundamental studies have addressed the mechanism of CO formation, whereas the pathway of CH_4 formed during the catalyzed steam–char reaction has as yet received little attention [3]. The possible path pathways for methane production include direct reactions of carbon or carbon surface intermediates with H_2O or H_2. Possible pathways and overall reaction for methane production can be expressed as follows.

$$Gasification : 2C + 2H_2O \leftrightarrow 2H_2 + 2CO, \quad \Delta H^{\circ}_{1000} = +271.8\ kJ/mol$$

$$Water\ gas\ shift : CO + H_2O \leftrightarrow H_2 + CO_2, \quad \Delta H^{\circ}_{1000} = -34.8\ kJ/mol$$

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$$Methanation : CO + 3H_2 \leftrightarrow H_2O + CH_4, \quad \Delta H^{\circ}_{1000} = -225.4\ kJ/mol$$

$$Overall : 2C + 2H_2O \leftrightarrow CH_4 + CO_2, \quad \Delta H^{\circ}_{1000} = +11.6\ kJ/mol\text{-}CH_4$$

Several studies have indicated that alkali salts promote the reaction of hydrogen with coals and chars [4,5]. Direct hydrogenation of carbon is a capable pathway for methane production. Methane is also produced by reacting CO–H_2 mixtures with alkali salts, such as potassium carbonate [6,7]. Cabrera et al. [8] reported that the production of methane by direct reaction of H_2O with graphite was efficiently promoted by KOH at 252 °C. Understanding the condition of CH_4 formation is important, whether the molecule is considered to be a desirable or undesirable product between carbon and steam. However, there is no simple optimized condition to explain methane formation in a catalytic steam–coal environment. Therefore, it is important to verify the reactivity and kinetics of steam–carbon at various conditions for methane production.

In general, most of feedstock for studying in gasification is coal including mineral matter. The mineral matter influences on availability of plant operation. Many researchers have studied demineralization process using coal [9–11]. The demineralized fuel is called as ultra clean coal. The ultra clean coal, which has low oxygen/carbon ratio and high hydrogen/carbon ratio [12], is defined as a very low ash coal, which of ash amount is below 1 wt% [11] and consists of low molecular structure compared to no demineralized coal. In this study, ultra clean coal (UCC) char was used to define the optimum reaction condition for studying reactivity of carbon and steam through the thermobalance system, which is used to check the mass change of a sample in real-time. At high reactivity condition of carbon and steam, raw coal in a fixed-bed reactor can be adopted and analyzed for the reaction characterization of CH_4 formation through a Non-dispersive infrared sensor (NDIR).

2. Experimental section

2.1. Sample preparation

Two types of samples, UCC char and raw coal of Roto South, were used in the experiment. The UCC coal and raw coal were crushed in a fan type disk mill, and then separated to below 75 μm. In particular, the UCC char for the experiment was made with a muffle furnace. The muffle furnace temperature increased from ambient to 800 °C at 10 °C/min in a N_2 purge environment. After increasing the furnace temperature to 800 °C, the sample was maintained at 800 °C for 30 min.

UCC char and raw coal were dried in an electric oven at 60 °C for 24 h, before the experiments. The properties of the samples for the experiment are shown in Table 1. UCC char was used for kinetic study of the steam–carbon reaction. The raw coal was used to verify the gasification gas components at high reactivity condition of catalytic steam–UCC char gasification.

2.2. Experimental apparatus and procedure

2.2.1. Thermobalance

UCC char is better for reactivity and kinetic study between carbon and steam, because UCC char includes more carbon contents than raw coal. This means that UCC char has good reactivity, regardless of the reaction hindrance of any other factors. Thermobalance can be used to continuously verify carbon weight loss, using an electric balance. The thermobalance, which is shown in Fig. 1, is mainly made of a gas preheater, steam generator, main furnace, sample basket and electrical balance. The main reactor for the steam gasification consists of 12.2 cm i.d*80 cm height of stainless steel, and an electric furnace which can heat up to a maximum 1000 °C. Steam was generated through the electrical steam generator, which can transform water (up to 36 ml/min) as a steam. The flow rate of steam was controlled by a micro-pump. The inner temperature of the main reactor was controlled by general K-type thermocouples, located in the bottom, middle and top section of the reactor. The stainless-steel wire mesh sample basket was suspended from an electrical balance, and the mass change signal of balance was continuously recorded by a personal computer during the experiment. When the reactor of temperature, normally from 600 to 800 °C, was heated up to the desired reaction temperature with nitrogen purge, a sample basket-loaded UCC char sample of 1 g was injected through the hatch, and the location of the sample basket was controlled by operating a motor driven winch. Once the mass of the sample basket became constant, a mixture gas of both steam and nitrogen was introduced into the reactor to gasify the UCC char sample. The mass change of sample was recorded every 2 min, through a personal computer.

2.2.2. Fixed-bed reactor

According to the reaction temperature of UCC char–steam gasification using thermobalance, syngas composition of raw coal was produced from a fixed-bed reactor, and analyzed by using an NDIR. The fixed-bed reactor is shown in Fig. 2. The system composition is similar to

Table 1
Composition of Roto South coal and UCC char.

		Roto South	
		Raw coal (no de-ash treatment)	Ultra clean coal char
Proximate analysis (wt%, dry basis)	Fixed carbon	48.49	82.92
	Volatile matter	49.30	16.53
	Ash	2.21	0.55
Ultimate analysis (wt%, ash-free basis)	Carbon	64.70	88.14
	Hydrogen	4.74	3.52
	Nitrogen	2.32	1.20
	Oxygen	28.13	7.13
	Sulfur	0.11	N.D