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The Solar-Driven Coal/Fe₃O₄ Redox System

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Abstract: The solar-driven endothermic reaction of coal and magnetite was studied for mixing solar and fossil energies. The overall reaction can be represented by CHₓ + Fe₃O₄ = CO + 3FeO + 1/2xH₂ where x depends on the coal (x=0.2 in our study). Laboratory experimental studies with an equimolar mixture of anthracite coal and Fe₃O₄ powder using an infrared furnace showed rapid gas evolution above about 1200°C and 1 bar, producing FeO(s) and a gas mixture containing a CO/CO₂ molar ratio of 4.5. Solar-driven experiments were conducted using a high-flux solar furnace. Samples were directly exposed for short time intervals to a solar flux irradiation of 300 W/cm². The carbon content decreased rapidly after only 1 second exposure, suggesting efficient heat transfer and chemical conversion by direct absorption of concentrated solar energy at the reaction site. The proposed solar thermochemical process offers the possibility of performing simultaneously the gasification of coal and reduction of iron oxide, and for producing a fuel with an upgraded calorific value.

1. INTRODUCTION

The conversion of concentrated solar radiation to chemical energy enables solar energy storage and transportation. Examples of high-temperature reactions that are attractive candidates for solar thermochemical conversion processes are the reduction of metal oxides and the gasification of coal [1-3]. The combination of the these two reactions can be represented by Eq. (1), where x is the mole ratio of hydrogen content to carbon content in the coal. Reaction (1) is endothermic (∆H=193 kJ/mol, assuming graphite for coal) and involves the mixing of fossil energy (coal and solar energy process heat). The hydrolysis of FeO produces H₂ and Fe₃O₄ (Eq. (2)), the latter being recycled to the solar process.

\[ \text{CH}_x + \text{Fe}_3\text{O}_4 = \text{CO} + 3\text{FeO} + \frac{1}{2}x\text{H}_2 \quad (1) \]

\[ 3\text{FeO} + \text{H}_2\text{O} = \text{Fe}_3\text{O}_4 + \text{H}_2 \quad (2) \]

In a previous paper [4], we described kinetic studies that were conducted on reaction (1) both in an infrared furnace and in a high-flux solar furnace. This note summarizes the main results obtained.

2. EXPERIMENTAL

Coal (Idemitsu Coal Laboratory) and magnetite powder were thoroughly mixed (Coal/Fe₃O₄ = 1(C):1.1(O)). The reaction cell was placed in an infrared furnace and the sample feeder was fixed on top of the reaction cell. Ar or He gas was introduced through the sample feeder and the reaction cell. After the furnace temperature (F-Temp) had been adjusted to 900-1300°C, the sample was dropped into the reaction cell from the sample feeder. The temperature of the sample in the reaction cell (S-Temp) was measured with a thermocouple. The evolved gases were monitored by MS and the change in the flow rate was recorded. All the outlet gases were collected into a sampling bottle during the reaction and their composition was quantitatively measured by gas chromatography. The nature of the solid phase was determined by X-ray diffractometry with FeKα radiation.

The experimental set-up for the solar driven coal gasification consisted of a solar receiver-reactor that was positioned with its axis perpendicular to the axis of the primary solar concentrator. The mixed sample of coal and magnetite powder was pressed into 1 cm diameter pellets, and placed in a rotating sample holder. The window of the target was shut with a blind and the inside of the quartz cover was filled with Ar gas at 1 atm. The evolved CO gas was monitored at the carrier gas outlet. The solar radiation intensity was measured optically on a Lambertian target using a CCD camera. The irradiation time was changed by 0.1 sec intervals using an electromagnetic controller.

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3. RESULTS AND DISCUSSION

Figure 1 shows the evolution profiles of gaseous products monitored by MS for CO\textsubscript{28} and CO\textsubscript{2}(44) using the laboratory scale experimental setup at F-Temp of 1100°C (sample = 0.1g). The main products were CO, H\textsubscript{2} and CO\textsubscript{2}. The profiles indicate that the reaction was completed within 30 sec. When the sample was dropped into the reaction cell, the S-Temp decreased from 1300°C to 500°C, then increased to around 1200°C in 30 sec. The evolution of CO\textsubscript{2} in this reaction system may be due to the low temperature of the sample at the initial stage of reaction. This CO\textsubscript{2}-evolution reaction could be suppressed by increasing the S-Temp as rapidly as possible. However, in the present experimental system, the S-Temp could not be increased more rapidly because of the technical limitations of the electric furnace. It was observed that the low-temperature period at the initial stage of the reaction became longer and the peak intensity representing CO\textsubscript{2} evolved increased when the F-Temp was lowered. This result suggests that if we could supply heat energy at a faster rate, the CO/CO\textsubscript{2} ratio in the evolved gas could be increased. The CO/CO\textsubscript{2} ratio was 0.5 at an F-Temp of 900°C and 4.5 at 1200°C. X-ray diffraction patterns showed that the Fe\textsubscript{3}O\textsubscript{4} phase was almost completely changed to the wutite phase (FeO). The sum of the CO, CO\textsubscript{2} and H\textsubscript{2} contents in the gaseous products was approximately equal to the values calculated from the chemical composition of the coal sample, indicating that coal reacts with Fe\textsubscript{3}O\textsubscript{4} at a temperature around 1200°C according to Eq. (1).

![Figure 1: Gas evolution Profiles from Coal/magnetite mixture using an infrared furnace](image1)

![Figure 2: Coal consumption rate using a high-flux solar furnace](image2)

Results from the solar-furnace experiments (irradiation intensity = 303 W/cm\textsuperscript{2}) are given in Fig. 2 (sample = 0.2g). Changes in the carbon content in the sample and the ratio of peak intensities, I\textsubscript{311}(Fe\textsubscript{3}O\textsubscript{4}) to I\textsubscript{200}(FeO), in X-ray diffraction patterns are plotted against the irradiation time. The carbon content decreased rapidly between 0.8 sec and 1.0 sec and is accompanied by the rapid decrease in the peak intensity ratio, indicating that Fe\textsubscript{3}O\textsubscript{4} changed to FeO. Evolution of CO was observed after 1.0 sec irradiation. The S-Temp increased rapidly at temperatures above 1200°C with irradiation intervals between 0.8 and 1.0 sec, and the reaction proceeded according to Eq. (1). The efficiency of converting solar energy to chemical energy was evaluated to be 47%. When the solar flux intensity was 188 W/cm\textsuperscript{2}, the reaction did not proceed even after 1.0 sec irradiation. In the present solar experimental setup, pellets were used in order to determine the quantitative relationship between the irradiation intensity and the reaction rate. The induction time of 0 to 0.8 sec at an irradiation intensity of 303 W/cm\textsuperscript{2} is probably due to the heat loss to the surroundings, which can be decreased by improving the reaction system. The reaction rate is fairly high for a solid-solid reaction using the present reaction system, suggesting that the reaction proceeds via a solid-gas reaction step. The release rate of the lattice oxygen from Fe\textsubscript{3}O\textsubscript{4} is high and oxygen gas is continuously supplied for gasifying. The direct irradiation of the reactants provided an efficient means of heat transfer directly to the reaction site, where the energy is needed.

References