

The Reactivity of Coal Char in Chemical Looping Gasification and Combustion

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INTRODUCTION

Chemical looping is one of the clean coal technologies to utilize coal. It is an oxygen transporting process using a solid oxygen-carrier to provide oxygen for the fuel conversion. Chemical looping combustion (CLC) with gaseous fuels has been intensively studied and developed in the past years and reviewed by Adanez *et al.* [1]. More recently, focus has been on solid fuels because of rich solid fuel resources [2-7]. Syngas-CLC and direct solid fuel CLC are two major types of coal CLC processes that have been proposed [1]. In syngas CLC, coal is first gasified to syngas (CO and H₂) then the syngas reacts with an oxygen carrier in a reduction reactor [3, 8]. In direct solid fuel CLC, coal is directly fed as a fuel to the CLC reactor. In-situ Gasification Chemical-Looping Combustion (iG-CLC) [9, 10] and Chemical-Looping with Oxygen Uncoupling (CLOU) [4] are two proposed processes in the direct solid fuel CLC.

In the iG-CLC process, coal is physically mixed with the oxygen-carrier in the fuel-reactor. Prior to reaction with the oxygen-carrier, coal is devolatilized and gasified in-situ by H₂O and/or CO₂, supplied as a fluidizing agent, to produce syngas. Eventually, the carrier reacts with the volatiles from coal pyrolysis and the syngas from char gasification. In this process, the char gasification rate is the limiting step because the gasification rate is slower than the syngas reaction with the carrier [2]. In the CLOU process, coal is burned with gaseous oxygen released by the oxygen-carrier in the fuel-reactor. Like conventional coal combustion, coal is devolatilized to generate volatiles and char then the volatiles and the char are combusted with gaseous oxygen. CO₂ or H₂O is used as carrier gas [4]. As a result, CLC studies of char gasification under H₂O or and CO₂ are needed.

Oxygen-carriers are the key to the chemical looping technology. For the combustion of gaseous fuels such as natural gas and syngas, synthetic oxygen-carriers are studied most often in the literature along with natural minerals. Active single metal oxides (CuO, Fe₂O₃, NiO, Mn₃O₄, etc.) or mixed metal oxides are supported on an inert support

(Al_2O_3 , SiO_2 , MgAl_2O_4 , TiO_2 , ZrO_2 , etc.) [1]. For the CLOU process, three identified metal oxide systems are $\text{CuO}/\text{Cu}_2\text{O}$, $\text{Mn}_2\text{O}_3/\text{Mn}_3\text{O}_4$, and $\text{Co}_3\text{O}_4/\text{CoO}$ [4]. The Cu based oxygen carrier (mainly CuO) is used in all proposed solid fuel chemical looping processes. The CLOU is proposed in higher temperature $900\text{--}950^\circ\text{C}$ [11] compared to the proposed syngas-CLC and iG-CLC processes at lower temperature ($\leq 850^\circ\text{C}$). Oxygen carriers with fuels at both temperatures need to be studied.

Principle coal gasification reactions are steam gasification, carbon dioxide gasification, hydrogasification, and partial oxidation. All reactions take places simultaneously. The gasification rates are functions of temperature, pressure, gas composition, and the nature of the coal. Figure 1 shows the equilibrium constants for these reactions as a function of temperature [12]. As expected, CO_2 and steam gasification reactions are thermodynamically favored at higher temperature. The rate of CO_2 gasification is slower than steam gasification.

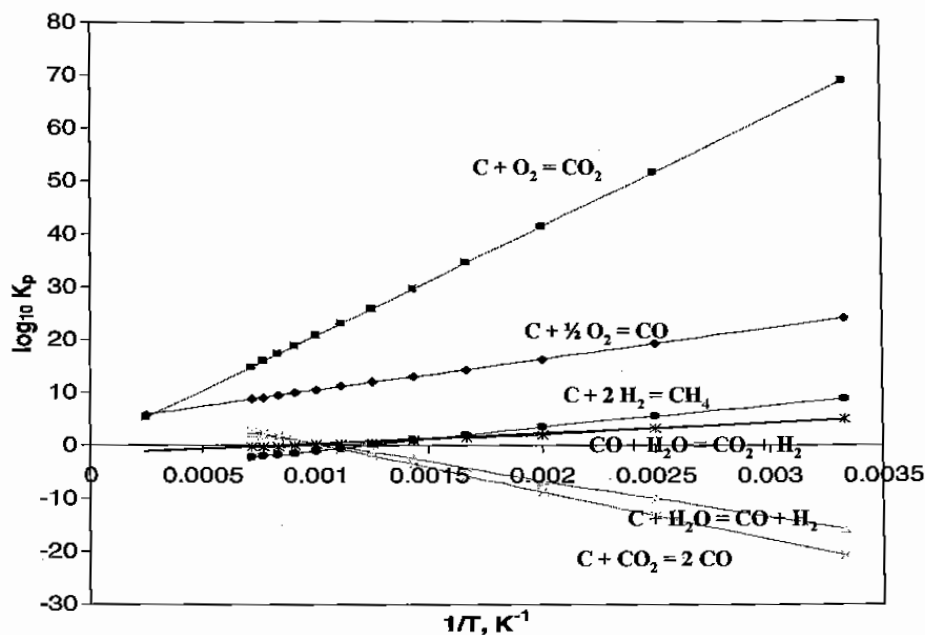


Figure 1. Equilibrium constant for the principle gasification reactions [12].

In this study Powder River Basin (PRB) sub-bituminous coal char and a Cu-based oxygen carrier were selected. The reactivity of coal char in chemical looping gasification and combustion were investigated with a low ratio of CuO and coal char so that both combustion and gasification reactions take place. The objective of this study is to investigate the reactivity of coal char under H_2O with oxygen-carriers at different reaction temperatures.

EXPERIMENTAL

Sample preparation

Experiment materials used in this study were coal char and oxygen carriers. The char samples were prepared by pyrolyzing Powder River Basin (PRB) sub-bituminous coal with particle size 106-180 μm . The pyrolysis was conducted at 1000°C in a fixed bed reactor. A pyrolysis temperature higher than the iG-CLC temperature was selected to avoid volatile generation during the char reaction. Reactions of solid char and solid oxygen carrier were studied. The oxygen carrier was cupric oxide (CuO) powder with 99.99% trace metals basis from Sigma-Aldrich. The mixture of char and CuO samples are weighted and physically mixed together before each test.

Experimental set-up and procedure

The experiments of char combustion and gasification with the oxygen carrier were carried out in a fixed bed reactor at atmospheric pressure. A schematic diagram of the experimental setup used in this study is shown in Figure 2. The reactor consisted of a tube furnace (ThermoScientific Lindberg/Blue M TF55030A-1) and a quartz tube. The test temperatures were 850°C and 950°C and were measured using a k-type thermocouple placed next to the sample. Process gases were argon (Ar) or H₂O-Ar mixture that is generated using a water vapor generator (L&C Science and Technology HG-100). The gas flow rate was controlled by mass flow controllers at 200 sccm. Approximately 10 mg of char and/or 82 mg of CuO were loaded into a CoorTek porcelain combustion boat in the middle of the tube prior to testing. Air in the system was purged out using Ar. The system was preheated to 400°C to shorten the time for heating up the system to the test temperature and because no reaction takes place at that temperature. Water vapor was added to the system as required. When the system was stable, the furnace was heated to the test temperature at a heating rate of ~65°C/min and held to finish the reaction. The beginning and end of the reactor was maintained at a temperature of 120°C by external heat tapes to prevent water condensation. The product gases were sampled approximately every second by a quadropole mass spectrometer (QMS) (Pfeiffer Ominstar GSD 301) until the reaction ceased. The QMS was calibrated to quantitatively measure the gas constituents of Ar, CO, CO₂, CH₄, H₂, and H₂O.

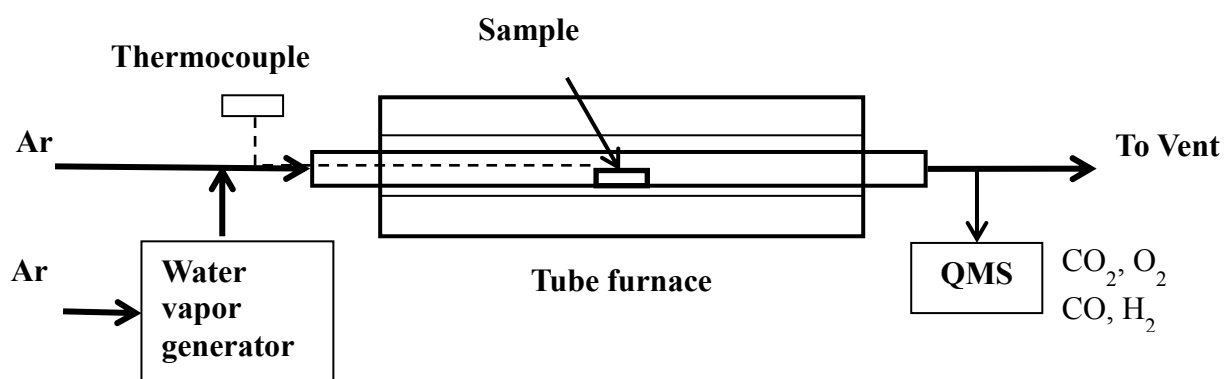


Figure 2. Schematic diagram of the experimental setup used in this study.

Data analysis

The oxygen carrier CuO releases O₂ and reduces to cuprous oxide (Cu₂O) upon heating. It reacts according to following equation:



The reactivity of the oxygen carrier is quantified in terms of oxygen uncoupling, X and oxygen uncoupling rate, dX/dt. X is calculated as:

$$X = \frac{w}{w_{red}} \quad (2)$$

Where w is the mass of accumulated oxygen generated over the reaction time t and w_{red} is the mass of the oxygen generated when the sample CuO is fully converted to Cu₂O according Equation 1.

The reactivity of coal char is quantified in term of gas yield or conversion efficiency, Y and carbon conversion rate, dY/dt. Y is defined as:

$$Y = \frac{w_c}{w_0} \quad (3)$$

Where w_c is the mass of accumulated carbon in carbon containing gases in the outlet stream over the reaction time t. In this study the carbon containing gases are mainly CO₂ and CO. For Y_{co}, w_c is the mass of carbon in CO only. The w₀ is the mass of the coal char sample, which is essentially carbon with mineral matter and some of the nitrogen and sulfur [13].

RESULTS AND DISCUSSION

Oxygen uncoupling (CuO to Cu₂O) at 850°C and 950°C in Ar and Ar+H₂O environments

Figure 3 shows curves of the oxygen uncoupling and oxygen uncoupling rates of CuO vs the reaction time in inert gases of Ar and Ar+H₂O. The measured sample temperatures vs time are also displayed in the figure. As CuO is heated from room temperature to 400°C in Ar or Ar+H₂O environments, there is no reaction. After increasing the temperatures above 600°C, oxygen is generated by CuO conversion to Cu₂O (Equation 1) (Figure 3 a). For both tests at the temperatures of 850°C and 950°C, CuO is fully converted to Cu₂O with the final oxygen uncoupling X=1 (Figure 3) and the final remaining sample colors are red indicating Cu₂O. The oxygen uncoupling rate curves have two peaks, a very small one and a big one (Figure 3 b)). For CuO at the test temperature of 850°C, the oxygen uncoupling rate curve has a broad peak with the oxygen uncoupling rate R_{max}=0.08 min⁻¹ at the final temperature 850°C. The curve for CuO at the test temperature of 950°C has a sharp peak with the maximum rate R_{max}=0.39 min⁻¹ at the temperature T_{max}=922°C. The CuO oxygen uncoupling rate at 950°C is almost five times faster than the rate at 850°C. Also, the oxygen concentrations are higher for the test at 950°C compared to one at 850°C.

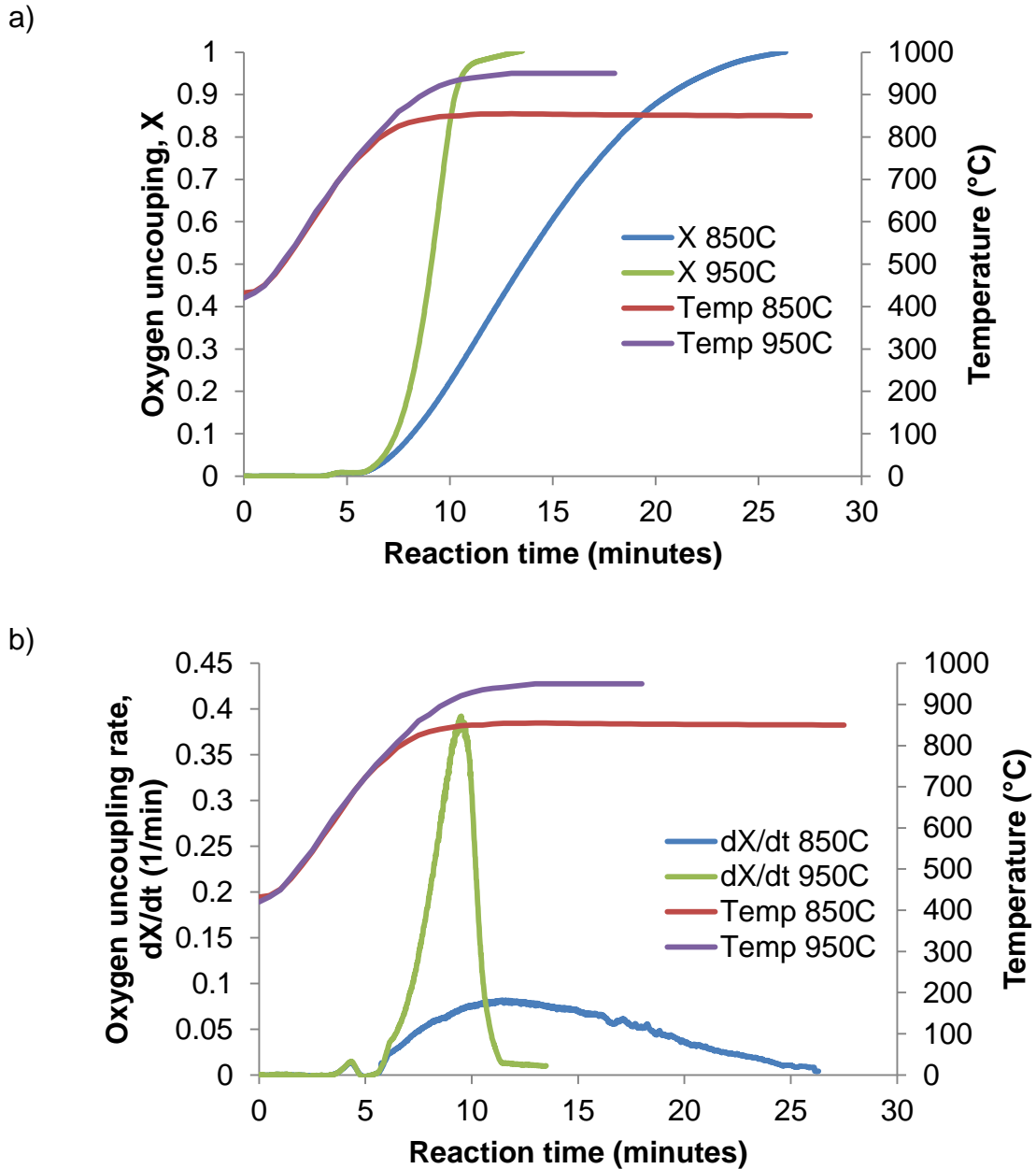


Figure 3. The curves of CuO oxygen uncoupling (X) (a) and oxygen uncoupling rates (dX/dt) (b) vs. time at 850°C and 950°C. The curves of measured sample temperature vs time during the CuO reduction reaction at beginning at 400°C.

The Char and CuO reaction in Ar environment

Figure 4 shows curves of carbon conversion rates (dY/dt) vs time of the CuO and coal char reactions at 850°C and 950°C in an inert gas of Ar. As the mixture of CuO and char is heated from room temperature to 400°C in Ar, there is no reaction. Increasing the temperatures above 600°C, carbon dioxide (CO₂) is mainly generated for both tests

at 850°C and 950°C. For the test at 950°C, carbon monoxide (CO) is also produced above 830°C with the final carbon conversion $Y_{co}=0.14$ (Figure 4). In this study the ratio of coal char and CuO is ~8, which is not enough CuO to convert all of the coal char. The final carbon conversions of char is $Y=0.29$ for the test at 850°C and $Y=0.56$ for the test at 950°C. If CuO is fully converted to Cu_2O , 82mg of CuO releases 8.2mg gas O_2 Cu_2O . If Cu_2O is further and 3mg of carbon in the 10mg of char used in this study is

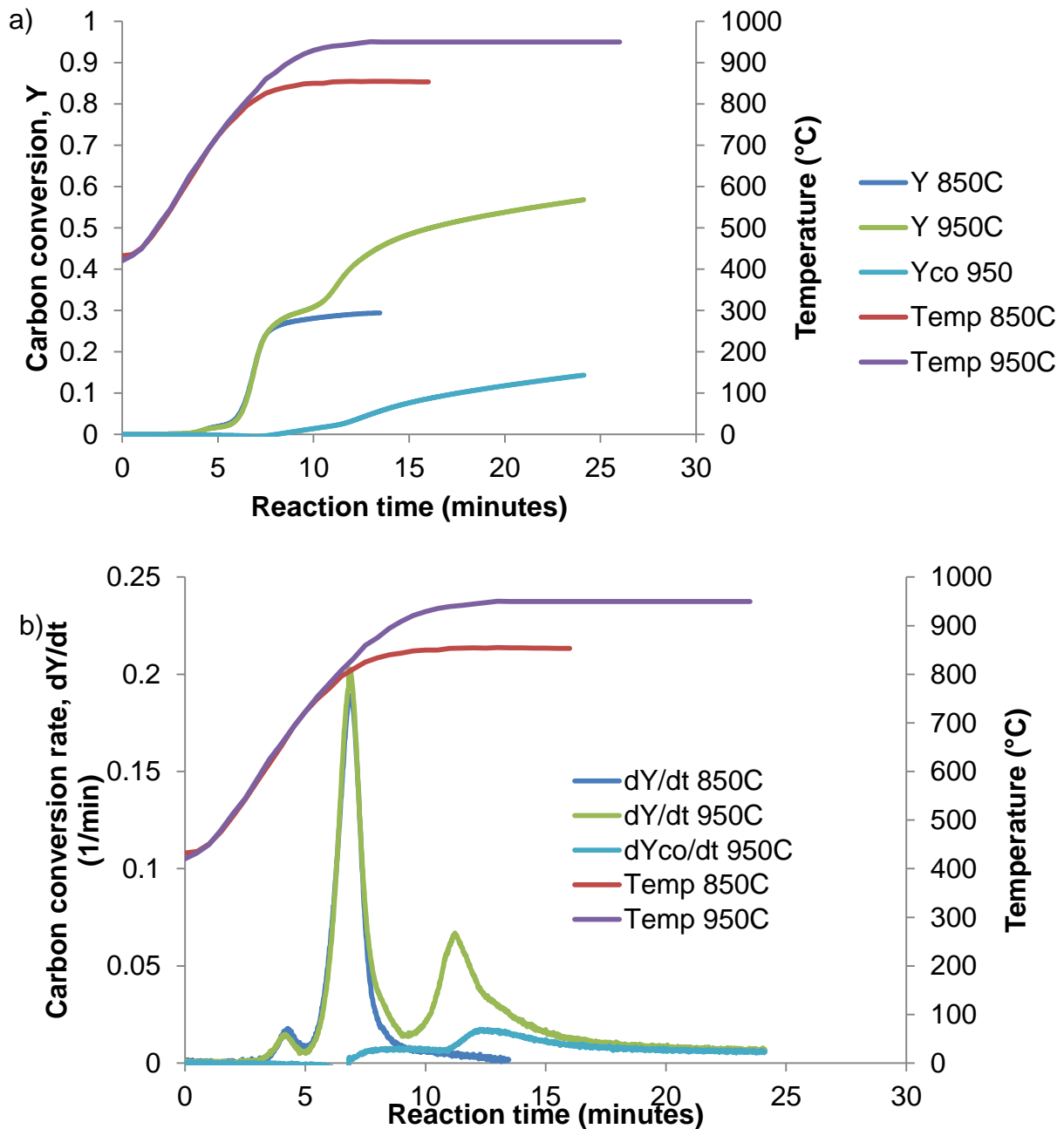


Figure 4. The curves of carbon conversion rates (dY/dt) vs time of the CuO and coal char reactions at 850°C and 950°C in Ar. The curves of the measured sample temperatures vs time during the reactions at beginning of 400°C.

combusted to CO_2 . In this case, the carbon conversion is 0.3, which matches the results of tests at 850°C . Additionally, the remaining sample is red indicating reduced by carbon to Cu and generated CO_2 , another 3mg of carbon is converted, so the carbon conversion is 0.6, which matches the result of test at 950°C and also the remaining sample is a reddish-orange color (Cu). The extra carbon in the system with CO_2 produces CO at high temperatures due to char gasification. On the other hand, CO also can react with $\text{CuO}/\text{Cu}_2\text{O}$ and reduce them to Cu. The carbon conversion rate curves for both of tests have a very small peak from CuO uncoupling O_2 to react with char (Figure 3 b and Figure 4 b). Following that, a sharp peak is observed with the maximum rate $R_{\text{max}}=0.19 \text{ min}^{-1}$ at the temperature $T_{\text{max}}=810^\circ\text{C}$ for the test at a temperature of 850°C . There is a similar peak with the maximum rate $R_{\text{max}}=0.20 \text{ min}^{-1}$ at the temperature $T_{\text{max}}=830^\circ\text{C}$ for the test at temperature 950°C . The test at 950°C has an extra peak with the maximum rate $R_{\text{max}}=0.067 \text{ min}^{-1}$ at the temperature $T_{\text{max}}=940^\circ\text{C}$.

Impact of water on the char and CuO reaction

The CuO and char reactions in $\text{Ar}+\text{H}_2\text{O}$ generate mainly CO_2 , H_2 and CO for both tests at 850°C and 950°C . CO and H_2 are generated starting at same time but the H_2 concentrations are much higher than CO (data not shown). The final carbon conversions in $\text{Ar}+\text{H}_2\text{O}$ are similar, $Y=0.86$ at 850°C and $Y=0.84$ at 950°C . Compared to the test in Ar, the final carbon conversion in $\text{Ar}+\text{H}_2\text{O}$ increased 197% for the test at 850°C and 47% for the test at 950°C . The high final carbon conversions of the reactions in $\text{Ar}+\text{H}_2\text{O}$ are due to the char gasification with water in Ar. The remaining sample is a reddish-orange color (Cu). Both CO and H_2 can react with $\text{CuO}/\text{Cu}_2\text{O}$ and reduce them

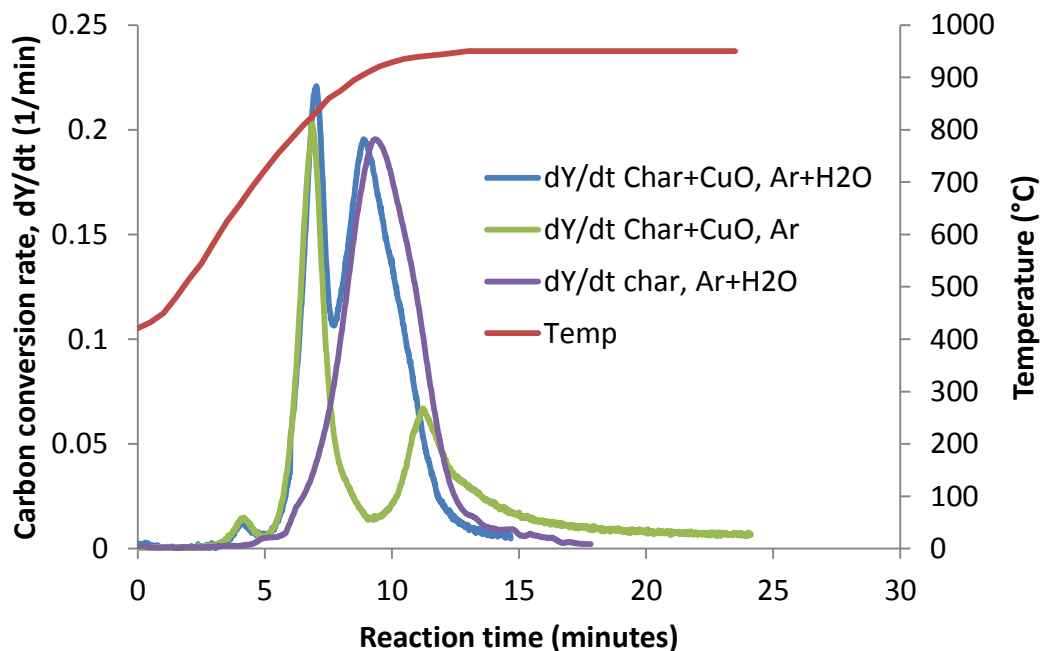


Figure 5. The curves of carbon conversion rates (dY/dt) vs time of the CuO and coal char reactions in $\text{Ar}+\text{H}_2\text{O}$ and Ar, also the coal char gasification at 950°C . The curve of the measured sample temperatures vs time during the reactions at beginning of 400°C .

to Cu. Figure 5 shows curves of carbon conversion rates (dY/dt) vs time of the CuO and coal char reaction at 950°C in Ar+H₂O and also in Ar. The first two peaks are the same for reactions in both environments. For the reaction in Ar+H₂O the third peak has the maximum rate $R_{max}=0.20 \text{ min}^{-1}$ at the temperature $T_{max}=908^\circ\text{C}$. It is larger and shifted toward higher temperature compared to the peak for the reaction in Ar due to the char steam gasification. From Figure 4 the third peak for the char with CuO matches up with the coal steam char gasification at the same condition. Both of them have the same maximum carbon conversion rate but the char with CuO peak shifts because combustion takes place in the system and char steam gasification is faster than char CO₂ gasification. The curve of carbon conversion rate for the reaction at 850°C in Ar+H₂O is similar to the one at 950°C but the third peak has a lower maximum rate $R_{max}=0.05 \text{ min}^{-1}$ because the rate of char gasification decreases at lower temperature. The carbon conversion rates of the char gasification have the maximum $R_{max}=0.07 \text{ min}^{-1}$ for the reaction at 850°C and $R_{max}=0.20 \text{ min}^{-1}$ for one at 950°C

SUMMARY AND FUTRUE WORKS

Experimental tests on the reactivity of PRB coal char with oxygen carrier CuO were conducted in inert gas Ar and Ar+H₂O environments and at different temperatures of 850°C and 950°C using a fixed bed reactor. The reactor was connected to a quadropole mass spectrometer (QMS) to quantitatively measure the gas constituents of Ar, CO, CO₂, CH₄, H₂, and H₂O. Upon heating CuO in Ar, oxygen (O₂) was released and CuO was converted to Cu₂O. The oxygen uncoupling was faster and produced higher oxygen concentrations at 950°C compared to at 850°C. The mixture of coal char and CuO in Ar was different with CuO only in Ar. The coal char reduced CuO to Cu₂O and generated CO₂ in the test at 850°C. However, in the test at 950°C CuO was reduced to Cu by char and generated CO along with CO₂. In this study the ratio of coal char to CuO was ~8, meaning that CuO was not enough to convert all of the coal char. The final carbon conversions of char for the test at 950°C ($Y=0.56$) was higher than one for the test at 850°C ($Y=0.29$). In the Ar+H₂O environment, the final carbon conversions increased by 197% for the test at 850°C and 47% for the test at 950°C compared to the tests in Ar only due to char steam gasification. This is an ongoing project. Further experimental testing of coal char with CuO in CO₂ will be conducted in the future. The reactivity of coal char with other oxygen carrier such as iron based oxygen carrier will also be investigated.

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