Catalytic CO₂ gasification of a Powder River Basin Coal

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ABSTRACT

CO₂ gasification of Wyodak low-sulfur sub-bituminous coal from the Powder River Basin (PRB) of Wyoming was conducted in a fixed-bed laboratory gasifier at atmospheric pressure with Na₂CO₃, an inexpensive catalyst widely available in Wyoming. The sodium effect on the coal pyrolysis and the sodium forms existing during the char gasification were investigated using thermo-gravimetric analyses (TGA) and X-ray diffraction (XRD) analyses, respectively. Sodium was found to decrease the tar production and promote the char condensation during the pyrolysis. The interaction between added sodium and the minerals in Wyodak coal were observed during the char gasification. Grain, integrated, and random pore models were employed to fit the kinetic data obtained under both non-catalytic and catalytic

conditions. The apparent activation energies of the coal-CO₂ gasification without and with use of the catalyst (3 wt. % Na) are ~91 kJ/mol and ~64 kJ/mol, respectively, a 30% decrease. Thus, Na₂CO₃ is a promising catalyst for the PRB coal-CO₂ gasification.

Keywords: CO₂; coal gasification; Na₂CO₃; XRD; kinetic model

1. INTRODUCTION

Due to their large domestic coal resources, increasing dependence on international energy resources has made coal to liquid (CTL) technology development more attractive in China, the United States, Australia, and India. In the U.S., Wyoming is well known for its abundance of coal, especially in the Powder River Basin region, which meets about 40% of U.S. coal demand. Thus people are highly interested in using Wyoming coal as a potential feedstock for producing liquid fuels.

CTL can be realized through both direct and indirect processes, and coal gasification is the first and most important step in the all the indirect CLT processes [1-4]. CO₂ can be produced from several processes in the indirect CTL plant, such as coal combustion and water gas shift (WGS), in which CO₂ streams are at high temperatures. Emitting the high-temperature CO₂ into atmosphere not only causes environmental issues but also wastes energy resources. On the other hand, using the high-temperature CO₂ as a gasifying agent could create a win-win scenario for environmental protection and improved CTL energy utilization.

For the slow reaction kinetics, research groups have investigated the catalytic CO₂ gasification of coal, and evaluated the performance of various catalysts, such as alkali chlorides, sulfates, nitrates and carbonates [5-11]. The negative effects of Cl⁻, SO₄²⁻ and NO₃⁻ on the quality of syngas and the life spans of gasifiers cannot be ignored [2, 3]. Produced largely in Wyoming, Na₂CO₃ is promising by contrast, as the harmful impacts of CO₃²⁻ are much less than those of Cl⁻, SO₄²⁻ and NO₃⁻. Ye et al. [5] found that Na₂CO₃ could considerably accelerate CO₂ gasification of a South Australian low-rank coal at atmospheric pressure and temperatures between 714 °C and 892 °C. Suzuki et al. [6] studied the CO₂ pulsed gasification of Yallourn coal char loaded with Na₂CO₃ and proposed the following redox cycles as the CO₂ gasification mechanism

The data collected by Shinya Yoshida et al. [7] demonstrated that the rate of CO₂ gasification using Na₂CO₃ was 3.3 times higher than without the use of Na₂CO₃.

Although many studies associated with Na₂CO₃-catalyzed CO₂ gasification technologies have been undertaken, supplemental work still needs to be done. This includes the characterization of sodium effect on the Wyodak coal pyrolysis, the analyses of sodium forms during the char gasification, and the quantitative comparison of gasification kinetic models with the use of the catalyst. Accordingly, this research was designed to make progress in these areas.

2. EXPERIMENTS

2.1 Materials

The raw Wyodak coal from the Wyoming Powder River Basin was ground and particles smaller than 74 μm (80 wt.% passed through a 200 mesh screen) were used in this work. Other reagents included Na_2CO_3 as the catalyst (dense soda ash, 99.8%, FMC Inc.), CO_2 as the gasifying agent (UHP, US Welding), and N_2 as the carrier gas (UHP, Praxair).

An incipient wetness impregnation method (IWIM) was used to mix Na_2CO_3 with the coal particles [1-3]. The resulting Na-coal mixtures were air-dried at 98 $^\circ\text{C}$ until no further decrease in mass was observed; the mixtures were then stored in an air-tight receptacle to prevent further changes in moisture content and loss of volatile matter. The weight percentage of sodium added in the coal was calculated on a dry and ash-free coal basis (DAF). The coal sample without catalyst was also prepared using only distilled water by IWIM.

2.2 Coal characterization

Thermo-gravimetric analyses (TGA Instruments SDT Q600 apparatus) were used to evaluate the mass loss of coal samples during pyrolysis under both non-catalytic and catalytic conditions. Around 40 mg coal sample was loaded onto a ceramic capped alumina sample holder, and was heated at 30 $^\circ\text{C}/\text{min}$ to 120 $^\circ\text{C}$ in N_2 stream with a flow rate of 100 ml/min. After 20min of isothermal equilibration, the sample continued to be heated at 10 $^\circ\text{C}/\text{min}$ to

the maximum pyrolysis temperature of 900 °C, then held at this temperature for another 10 minutes for isothermal equilibration.

X-ray diffraction (XRD) analyses were performed on powdered coal samples in a Rigaku Smartlab X-ray diffraction system. Analyses were conducted using a Cu K α 1 line (1.5406 Å) operating at 40 kV/40 mA, with 2θ ranging from 20° to 80° with 0.020° steps and a time/step of 0.05s. The collected 0.05–0.10g samples for XRD tests were taken before and after pyrolysis, after 30-min gasification, and after complete gasification.

2.3 Gasification

Gasification experiments were carried out in a fixed-bed reactor at ambient atmospheric pressure (~75 kPa at the elevation of Laramie in Wyoming). A 1/2" (13 mm) diameter stainless steel tube was used as the reactor, and the coal sample (5.48 g with 0 wt.% Na on dry basis; 5.82 g with 3 wt.% Na on dry basis) was loaded in the middle of the reactor and fixed by ceramic wool. Initially, N₂ was introduced into the apparatus to purge the system. Then a tubular furnace (Thermolyne 21100) was used to heat the reactor at 10 °C/min to desired gasification temperatures within a N₂ stream at a flow rate of 4.1 ml/min. After that, the gasifying agent, CO₂, was introduced into the system at a flow rate of 180 ml/min. Heating tapes were used to preheat the entering gases and keep the products at desired temperatures, which were monitored by thermocouples. Tar in the products was separated through a water-cooled condenser and collected into a vial. Then, the cleaned syngas passed through a desiccant-filled tube for further water removal. Finally, the syngas entered the micro gas chromatograph (micro GC) (Agilent 3000A), which was equipped with two micro-

columns (MolSieve 5A PLOT and 4 m PoraPlot U) and two calibrated thermal conductivity detectors (TCD). The micro GC detected the composition of the syngas every 3.7 minutes. Extra syngas was vented into the fume hood. All of the collected data were recorded with a computer connected to the micro GC.

The sample preparation, sample loading and aging of the reactor could bring uncertainty into the gasification results. For this reason, all the possible measures were taken to minimize the uncertainties of all the reported results. These measures include calibrating mass flow controllers and Micro GCs prior to each gasification test, and repeating the gasification tests under the same conditions for at least three times. Statistical analyses were conducted for all obtained data and all the error bars were reported.

2.4 Inlet CO₂ flow rate determination

CO₂ was used as the gasifying agent in this work. The suitable CO₂ flow rate under the given gasification conditions needed to be established. Several CO₂ flow rates, from 30 ml/min to 180 ml/min, were chosen in the initial gasification tests with 3 wt.% Na at 900 °C. The high CO₂ flow rate led to short reaction times. When increasing to 180 ml/min, the CO₂ flow rate showed little effect on coal gasification time. Clearly, the effect becomes less obvious when CO₂ flow rate continues to increase, especially when it is higher than 180 ml/min, and thus more CO₂ introduced to gasifier could not be consumed or higher CO₂ concentrations in the outlet/produced gas were observed. With these factors in mind, a CO₂ flow rate of 180 ml/min was chosen for coal gasification in this work.

3. RESULTS AND DISCUSSION

3.1 Sample characterization

The proximate and ultimate analysis results of the raw Wyodak coal are shown in Table 1. Char samples after the coal pyrolysis with and without sodium at 700 °C, 800 °C and 900 °C were collected; their ultimate analyses are shown in Table 2.

Figure 1 shows the XRD spectra of raw Wyodak coal and the coal with 3 wt.% Na. Kaolinite and SiO₂ were found in the raw Wyodak coal, according to Figure 3(a). The reference patterns for kaolinite and SiO₂ are powder diffraction files (PDF) # 78-2109 and # 85-0794, respectively. Coal is composed of many basic structural units bridged with bonds. The basic structural units consist of condensed polynuclear aromatic and alkyl side chain/functional groups. There are also some low molecular aliphatic compounds and inorganic minerals that exist independently in the gaps between the basic structural units. The inorganic minerals would combine together or with the adjacent atoms to form more stable compounds at high temperatures [2]. Figure 1b shows that no distinct peak for Na₂CO₃ was observed in the spectrum of the coal mixture prepared by IWIM. Part of Na₂CO₃ could be decomposed during the sample preparation, in which Na⁺ would combine with the carboxylic and phenolic groups in coal [5].

3.2 Sodium effect on the coal pyrolysis

Figure 2 shows the TGA results of raw Wyodak coal, the coal with 3 wt.% Na, and pure Na₂CO₃, respectively. The residue weight percentages were calculated on dry ash- and

catalyst-free basis after the isothermal equilibration at 120 °C. Results show that the residue weight percentage of the coal sample loaded with Na₂CO₃ was lower than that under non-catalytic conditions in the temperature range of 120-740 °C. The mass loss of Na₂CO₃ above 860 °C had little effect on the result of the sample with 3 wt.% Na. To clearly demonstrate the effect of sodium on the coal weight loss, the plot of the sample weight loss rate as a function of temperature was inserted in Figure 2. The mass loss rate is defined as:

$$r = -\left(\frac{1}{W_{daf}} \frac{dm}{dT}\right) \quad (E1)$$

where r is the rate or fractional weight per time; W_{daf} is the initial sample weight on dry ash- and catalyst-free basis; and m is the instantaneous mass of the sample at temperature T . The insert in Figure 2 indicates that sodium could lead to a change in the mass loss rate at ~650 °C. Puente et al. found that when pyrolysis temperature exceeded ~550 °C, the coal char would undergo ring condensation with the evolution of secondary gases, mainly CO and H₂ [12-14]. Thus, the plot suggested that sodium promoted the char condensation at ~650 °C. The evidence was reinforced by the differences in the generation rates of H₂ and CO under non-catalytic and catalytic conditions, as shown in Figures 3a and c. The plots of mass loss rates were inserted into the corresponding figures for comparison purpose. With 3 wt% sodium, the peaks of CO and H₂ generation rates at ~780 °C shifted to ~660 °C, which correspond to the second peak of the weight loss rate obtained with 3 wt.% Na at ~650 °C. Additionally, the ultimate analysis of char on DAF basis shown in Table 2 also proves that the char obtained from 3 wt.% Na coal at 700 °C had lower hydrogen and oxygen but higher carbon contents than those without sodium.

Figure 3a shows that the generation rate of H₂ increased with the addition of sodium

in the primary pyrolysis in the temperature range of 470- 600 °C. During pyrolysis, hydrogen stabilizes the small molecular fragments, and then these fragments would be released as tar or light hydrocarbons [12]. With less hydrogen, the fragments are inclined to combine together and remain in the char, as shown in Figure 4. Thus, the increase in H₂ generation rate during the primary pyrolysis indicates that sodium impeded the evolution of tar and light hydrocarbons, such as the generation rate of CH₄ (light hydrocarbons) shown in Figure 5b. This may also explain the phenomenon that the mass loss rate of coal with 3 wt.% Na was lower at ~550 °C, as shown in Figure 4. Figures 3c and 3d show that sodium decreases the generation rates of CO and CO₂ at ~430 °C. The possible reason is that sodium reacts with the –OH or –COOH in coal, as indicated below [15]

The reactions increased the stability of the oxygen-containing groups, and thus blocked the release of CO or CO₂. Sodium does not reduce the CO yield during the char condensation, as the evolution of CO in this period mainly resulted from the elimination of ether linkage [12].

3.3 XRD analyses of sodium forms in the char gasification

Figure 5 and Figure 6 show the XRD spectra of raw Wyodak coal samples gasified at 900 °C, as well as the coal samples with 3 wt.% Na gasified at 700 °C, 800 °C and 900 °C after pyrolysis, after 30min gasification, and after complete gasification. Ca₂Al₂SiO₇, Fe₂MgO₄ and SiO₂ were found in the raw Wyodak coal ash after gasification at 900 °C (Figure 5a(3)). The main elements (e.g. Si, Ca, Al, Fe and Mg) were in line with the

elemental analysis of the Wyodak coal ash [2]. Coal gasification with Na_2CO_3 has been widely studied and the mechanism is proposed as R(1) and R(2), or the following reactions [16-19]:

However, no Na, Na_2O or Na_2CO_3 was observed in the XRD spectra. Sodium is supposed to be highly mobile and redistributes rapidly in the coal matrix as the char gasifies [20-22]. The dissociative sodium is thought to form new active sites by bonding with oxygen-containing functional groups in char [20, 23] that do not gather together in the crystalline phase. On the contrary, calcium, aluminum, iron and silicon from the inorganic minerals in coal are not regarded as highly mobile under 900 °C [1, 24]. They combine with the atoms in the minerals and the mobile sodium adjacent to them [18, 25], and crystallize to form a number of new phases (e.g. cristobalite, anorthite, nepheline) in char gasification [26, 27], as shown in Figure 5 and 6.

In the XRD spectra for samples with 3 wt.% Na (Figures 5b, 6a, and 6b), sodium was observed in form of aluminosilicate or calcium silicate. On the other hand, the peaks of SiO_2 observed in the spectra for samples without sodium (Figure 5a) weakened or disappeared altogether in the spectra with sodium, confirming that SiO_2 combined with sodium during the catalytic gasification. The reaction routes generally were as follows:

These are detrimental to catalytic coal gasification, as sodium participates in forming non-catalytic compounds [25, 28].

The composition of sodium aluminosilicate was altered with the reaction time during char gasification, as shown in Figures 5b, 6a and 6b. For example, in Figure 6a, sodium exists in the form of $\text{Na}_6\text{Al}_4\text{Si}_4\text{O}_{17}$ ($3\text{Na}_2\text{O} \cdot 2\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) after pyrolysis. After 30 min gasification, the sodium was found in the form of NaAlSiO_4 ($\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$). Then, $\text{Na}_{1.75}\text{Al}_{1.75}\text{Si}_{0.25}\text{O}_4$ ($7\text{Na}_2\text{O} \cdot 7\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) was observed in the spectra of the sample collected at the end of gasification. This indicates that some sodium escaped from the aluminosilicate during char gasification, while at the end of gasification a quantity of sodium participated in the formation of sodium aluminosilicate. The mineralized sodium during pyrolysis can be reactivated in char gasification phase as follows [18]:

It was also observed that the composition of sodium aluminosilicate and calcium silicate varied with gasification temperature. For example, sodium aluminosilicate was found in the coal ash after gasification at 700 °C (Figure 5b(3)) in the form of $\text{Na}_6\text{Al}_4\text{Si}_4\text{O}_{17}$ ($3\text{Na}_2\text{O} \cdot 2\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) rather than $\text{Na}_{1.75}\text{Al}_{1.75}\text{Si}_{0.25}\text{O}_4$ ($7\text{Na}_2\text{O} \cdot 7\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) in that obtained at 800 °C (Figure 6a(3)). $\text{Na}_4\text{Ca}_4\text{Si}_6\text{O}_{18}$ was found in the coal ash obtained from the gasification at 800 °C (Figure 6a(3)), while $\text{Na}_{15.6}\text{Ca}_{3.84}\text{Si}_{12}\text{O}_{36}$ was present in the coal ash obtained at 900 °C (Figure 6b(3)). The elevated temperature was thought to lead to a compact structure containing sodium aluminosilicate and calcium silicate.

The peaks at 31.423°, 45.035° and 55.943° for CaS [29, 30] cannot be ignored in the

XRD spectra. The possible means of CaS formation during coal pyrolysis can be indicated by the follow reactions [30]:

CO_2 is believed to be the oxidizing agent of certain mineral phases present in the coal, such as pyrrhotite and oldhamite (CaS) [31]. Thus the peaks for CaS in the spectra were weakened or disappeared during char gasification with CO_2 . It is possible that the CaS reacted with CO_2 , forming CaO [32] and then Ca_2CO_3 , as shown in Figures 5b(2), 6a(2) and 6b(2).

3.4 Kinetics in char gasification

3.4.1 Kinetic models

Char gasification with CO_2 is a heterogeneous gas-solid reaction. The pore structure and surface area of the solid particle changed as the char was consumed during gasification, which would indicate the need to vary the gasification rate. The gasification rate can be demonstrated by the following general model [33]:

$$\frac{dx}{dt} = k(T, P_{\text{CO}_2}) f(x) \quad (\text{E2})$$

where k is the reaction rate constant based on the reaction temperature (T) and the partial pressure of CO_2 (P_{CO_2}), x is the fractional conversion of carbon, and $f(x)$ is the structure factor. The $f(x)$ changed in the different kinetic models with different assumptions.

Shrinking core model (SCM) has often been considered as fitting the kinetic data collected in coal gasification [1, 3, 34]. As a kind of porous substance, the pore surface area

of coal greatly exceeds its external particle surface area. However, gas-solid reactions (e.g. $\text{CO}_2 + \text{C} \rightarrow 2\text{CO}$) inside the coal pores could be inhibited by mass transfer in coal gasification. As a result, the reactant gas (e.g. CO_2 or steam) is consumed either on the exterior of the coal particle or within the pores close to the particle exterior surface [34]. Subsequently, the reaction moves from the surface into the particle through a layer of ash and catalyst to the interface of the shrinking, unreacted core, and then progresses toward the center of the coal particle [35]. In this case, the kinetic data of coal gasification can be modeled with SCM. The structure factor $f(x)$ of SCM is as follows [34, 36, 37]:

$$f(x) = \frac{S_0(1-x)^m}{1-\varepsilon_0} \quad (\text{E3})$$

where S_0 is the initial reaction surface, ε_0 is the initial porosity, and m is a shape factor that depends on the shape of the assumed grains (for spheres $m = 2/3$, for cylinders $m = 1/2$, and for flat plate $m = 0$) [37]. Grain model [25] was developed with the assumption that a char particle is an aggregation of smaller grains that are spheres of uniform size, and the chemical reaction between the gas and the grain obeys SCM. In this case, the shape factor is $m = 2/3$, and the gasification rate can be expressed as follows [31]:

$$\frac{dx}{dt} = k_g (1-x)^{2/3} \quad (\text{E4})$$

where k_g is the reaction rate constant for the grain model.

However, the char particle cannot always be spherical, but will more likely be the integration of several shapes. Thus the shape factor m is used to replace the exponent in the grain model and becomes a model with two parameters, namely the integrated model (IM),

which can be written as [36]:

$$\frac{dx}{dt} = k_i (1-x)^m \quad (\text{E5})$$

where k_i is the reaction rate constant for the integrated model and m is the shape factor, which has also been used as the reaction order by some researchers [36, 37].

Bhatia and Perlmutter [38] developed the random pore model (RPM), which takes into account the pore structure and its evolution during char gasification. They assumed that the internal surfaces of the pore structure also served as reaction interfaces, and the cylindrical pores of uneven diameter enlarged as the internal surfaces eroded with the progress of the reaction, eventually merging together [31, 38]. According to the model, the structure factor can be written as [31]:

$$f(x) = \frac{S_0(1-x)\sqrt{1-\psi \ln(1-x)}}{1-\varepsilon_0} \quad (\text{E6})$$

ψ is a dimensionless structural parameter, which can be written as [31, 39]:

$$\psi = \frac{4\pi L_0(1-\varepsilon_0)}{S_0^2} \quad (\text{E7})$$

where L_0 , ε_0 and S_0 represent the initial pore length, porosity and specific surface area. The gasification rate can be expressed as [37]:

$$\frac{dx}{dt} = k_{rp} (1-x)\sqrt{1-\psi \ln(1-x)} \quad (\text{E8})$$

where k_{rp} is the reaction rate constant for the random pore model. According to the

assumption, RPM can predict the occurrence of maximal rate during gasification, which exists over the range $2 \leq \psi \leq \infty$ [36, 40].

3.4.2 Reaction rate constant calculations

The gasification rate vs. carbon conversion under both non-catalytic and catalytic (3 wt. % Na) conditions during char gasification are exhibited in Figure 7, and fitted by grain model (Figure 7a), integrated model (Figure 7b) and RPM (Figure 7c), respectively. According to the nonlinear fitting, the rate constants and parameters at different conditions were obtained and listed in Table 3.

It was observed that the gasification rates without catalyst were high, and decreased sharply at the beginning of the reaction at 700 °C and 750 °C, while those with catalyst did not show similar trends at the same temperatures. The reason for this is that char devolatilization may account for part of the carbon loss at the beginning of gasification without catalyst at 700 °C and 750 °C, and that the devolatilization rate may have declined quickly as gasification proceeded. When gasifying with catalyst, the ring condensation which led the char devolatilization was promoted by the added sodium and was almost finished before 700 °C, as discussed in section 3.2. Thus char devolatilization had little effect on carbon loss at the beginning of gasification with sodium. The participation of char devolatilization in carbon loss brings an adverse effect to the model fitting, especially the random pore model. As shown in Figure 8, the obtained structure parameter ψ is negative according to the data fitting for the reaction at 700 °C and 750 °C, which contradicts E7. In this case, $\psi = 0.01$ was selected in the model to fit the gasification data obtained at 700 °C

and 750 °C. Another problem is that RPM tries to find a maximal rate during the data fitting in some cases, while the trend of the detected gasification rate does not obey the calculated trend, as shown in Figure 8. As the maximal rate exists over the range $2 \leq \psi \leq \infty$, either $\psi = 1.9$ or 1.99 was chosen in the model fitting for those cases.

Figure 7 shows that the integrated model and modified random pore model perform better than the grain model in data fitting under both non-catalytic and catalytic conditions. However, all three models perform worse in data fitting under catalytic conditions at 850 °C and 900 °C than they do under non-catalytic conditions at the same temperatures. This indicates that the catalyst has an effect on the gasification rates at 850 °C and 900 °C. Adding the catalyst factor C into E2, the gasification rate can be written as:

$$\frac{dx}{dt} = k(T, P_{CO_2}) f(x) \cdot C \quad (E9)$$

Supposing that the concentration of active sites formed by the catalyst on the reaction interfaces does not vary during gasification, the catalyst factor C would remain constant. In this case, the original models perform well in the data fitting. However, the catalyst factor cannot always be constant, as it depends on the catalyst properties, reaction temperature, carbon conversion and certain other elements. Popa et al. [2] studied the iron-catalyzed gasification of coal by steam and found that there is an induction period before the catalyst becomes active when gasification begins, which indicates the low concentration of active sites at the beginning of the reaction. Zhang et al. [37] studied the catalyzed gasification of coal char and carbon with CO_2 , and found that the reactivity of gasification with calcium exhibited a maximum in the low conversion range ($x < 0.2$), while gasification with

potassium had a maximum in the high conversion range ($x > 0.6$). As the original RPM could not reconcile theory and experimental data in these cases, they proposed an extended RPM to fit the experimental data obtained from catalytic gasification, as indicated below [37]:

$$\frac{dx}{dt} = k_{rp} (1-x) \sqrt{1-\psi(1-x)} (1+(cx)^p) \quad (\text{E10})$$

where c and p are empirical constants.

As discussed in section 3.3, sodium also had a reactivation process at the beginning of char gasification; thus, the concentration of active sites formed by sodium would increase with reaction time. With the char gasifying, the sodium-to-carbon ratio rose due to the loss of carbon. As the high mobility of sodium, the free sodium was assumed to rapidly redistribute in the char matrix and form new active sites by bonding with oxygen-containing functional groups [20]. Thus the downward trend of the gasification rate with the carbon conversion would be alleviated with sodium compared to raw coal as shown in Figures 7b and 7c. Data fitting under catalytic conditions at 700 °C and 750 °C was not affected by the sodium, as shown in Figures 7a(2), 7b(2) and 7c(2). The possible reason for this is that the mobility of sodium relies heavily on the reaction temperature, and would therefore be limited at relatively low temperatures. As the catalytic factor C is affected by several factors, such as reaction time, carbon conversion and reaction temperature, the experiment in this work was not sufficient to describe it. Thus the expression of the catalytic factor C is not given in this work.

3.4.3 Activation energy calculations

The activation energies of char gasification can be quantitatively evaluated by

Arrhenius law:

$$k = A \exp\left(-\frac{E_a}{RT}\right) \quad (\text{E11})$$

where A is the pre-exponential factor, E_a is the activation energy, R is the ideal gas constant, and T is the reaction temperature. Taking the log of both sides of E2 leads to

$$\ln k = -\frac{E_a}{RT} + \ln A \quad (\text{E12})$$

Using the data shown in Table 3, the kinetic constants A and E_a can be obtained by the slope and intercept of the plot of $\ln k \sim 1,000/T$, respectively, as shown in Figure 9. The fitting results A and E_a are listed in Table 4.

Due to the poor performance of the grain model in data fitting, the results obtained by the integrated model and modified RPM are more reliable. Thus the activation energy obtained from non-catalytic char gasification with CO_2 was determined to be ~ 91 kJ/mol. The result corresponds to the work of Kwon et al. [41], who studied the reaction kinetics of char- CO_2 gasification at atmospheric pressure using four coals with different ranks, and found that the activation energies of samples varied from 79.0 to 155.5 kJ/mol. With the addition of sodium, the activation energy for the char- CO_2 gasification was reduced to ~ 64 kJ/mol. The addition of Na_2CO_3 promoted the reaction kinetics of Wyodak coal gasification with CO_2 .

5. CONCLUSION

Coal gasification with CO_2 could not only provide a new way for the value-added use of CO_2 , but also improve the thermal efficiency of gasification and thus the overall energy efficiency of CTL. Na_2CO_3 , a mineral widely available in Wyoming, can promote char condensation and affect the generation rates of H_2 , CO , CO_2 and CH_4 during Wyodak coal

pyrolysis period. Sodium aluminosilicate and sodium calcium silicate were observed during char gasification, and their composition changed with temperature and gasification time. Integrated model was proved to fit the kinetic data well collected during char gasification. 29.7% of activation energy reduction was realized with the use of sodium during char gasification. The addition of Na_2CO_3 can promote the kinetics of Wyodak coal gasification with CO_2 .

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Table 1.

Proximate Analysis	As Received (wt. %)	Moisture Free (wt. %)	DAF (wt. %)
Moisture	17.81	-	-
Ash	7.17	8.72	-
Volatile matter	36.56	44.48	48.73
Fixed carbon	38.46	46.80	51.27
Total	100.00	100.00	100.00
Ultimate Analysis			
Moisture	17.81	-	-
Hydrogen	2.80	3.40	3.72
Carbon	59.17	71.99	78.87
Nitrogen	0.76	0.93	1.01
Sulfur	0.35	0.43	0.47
Oxygen	11.95	14.54	15.93
Ash	7.16	8.71	-
Total	100.00	100.00	100.00
Heating Value, (Btu/lb)	9,538	11,604	12,713
(kJ/kg)	22,185	26,991	29,570

Hydrogen and oxygen values reported do not include hydrogen and oxygen in the free moisture associated with the samples.

Table 2.

wt.% (dry basis)	0 wt.% Na			3 wt.% Na		
	700°C	800°C	900°C	700°C	800°C	900°C
C	81.53	82.87	83.85	78.11	78.09	78.43
H	1.69	0.98	0.59	1.18	0.68	0.42
N	1.51	1.46	1.40	1.46	1.61	1.56
S	0.36	0.32	0.37	0.25	0.30	0.33
Ash	10.30	11.01	11.61	15.35	16.04	16.61
O	4.61	3.36	2.18	3.56	3.27	2.72

wt.% (DAF basis)	0 wt.% Na			3 wt.% Na		
	700°C	800°C	900°C	700°C	800°C	900°C
C	90.89	93.12	94.86	92.38	93.01	93.98
H	1.88	1.1	0.67	1.39	0.81	0.5
N	1.68	1.64	1.58	1.73	1.92	1.87
S	0.4	0.36	0.42	0.29	0.36	0.39
Ash	--	--	--	--	--	--
O	5.14	3.78	2.47	4.21	3.9	3.25

Table 3.

Model		Grain model		Integrated model			Random pore model		
Catalyst	T (°C)	$k_g (*10^{-4} s^{-1})$	R^2	$k_i (*10^{-4} s^{-1})$	m	R^2	$k_{rp} (*10^{-4} s^{-1})$	ψ	R^2
0 wt. % Na	700	0.3593	0.8422	0.4478	1.0308	0.9057	0.4400	0.0100	0.9055
	750	0.6904	0.9080	0.8492	1.0030	0.9700	0.8459	0.0100	0.9702
	800	1.3576	0.9907	1.4316	0.7558	0.9967	1.4195	0.6667	0.9925
	850	2.3883	0.9985	2.3910	0.6687	0.9985	2.2719	1.2953	0.9968
	900	3.1697	0.9887	3.0237	0.5803	0.9949	2.8168	1.9000	0.9942
3 wt. % Na	700	1.3215	0.9951	1.2917	0.6271	0.9967	1.2392	1.3738	0.9842
	750	2.0719	0.9928	2.0064	0.6098	0.9960	1.8604	1.7629	0.9918
	800	3.5924	0.9803	3.3541	0.5373	0.9939	3.1642	1.9900	0.9857
	850	4.4648	0.9598	4.1235	0.5088	0.9820	3.9668	1.9900	0.9773
	900	5.1099	0.9655	4.7702	0.5330	0.9811	4.5499	1.9900	0.9834

Table 4.

model	Grain model		Integrated model		Random pore model	
factor	0 wt.% Na	3 wt.% Na	0 wt.% Na	3 wt.% Na	0 wt.% Na	3 wt.% Na
E (kJ/mol)	106.78	66.65	92.72	63.95	89.90	64.38
A (s ⁻¹)	20.02	0.54	4.49	0.37	3.17	0.37
R ²	0.9887	0.9491	0.9873	0.9541	0.9823	0.9567

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Figure 1. XRD spectra of raw Wyodak coal and the coal with 3 wt.% Na. (a) raw Wyodak coal; (b) Wyodak coal with 3 wt.% Na.

Figure 2. Thermo gravimetric analysis (TGA) for pure Na_2CO_3 , raw Wyodak coal and Wyodak coal with 3 wt.% Na [mass of coal: ~40 mg; TGA operation conditions (heating rate: 30 °C/min to 120 °C and 10 °C/min to 900 °C; carrier gas and its flow rate: N_2 , 100 ml/min; maximum pyrolysis temperature: 900 °C)].

Figure 3. Generation rates of H_2 (a), CH_4 (b), CO (c) and CO_2 (d) as a function of temperature during coal pyrolysis [mass of DAF coal: 5 g; CO_2 flow rate: 0 ml/min; N_2 flow rate: 4.1 ml/min; maximum pyrolysis temperature: 900 °C].

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Figure 6. XRD spectra of the coal samples with 3 wt.% Na gasified at 800 °C and 900 °C after pyrolysis, after 30-minute gasification and after complete (a) 3 wt.% Na at 800 °C; (b) 3 wt.% Na at 900 °C; (1) after pyrolysis; (2) after 30 minutes gasification; (3) after complete gasification.

Figure 7. Gasification rate vs. carbon conversion under both non-catalytic and catalytic conditions during the char gasification (a) grain model; (b) integrated model; (c) random pore model; (1) 0 wt.% Na; (2) 3 wt.% Na.

Figure 8. Modification of the parameter ψ in the data fitting using random pore model.

Figure 9. Arrhenius plot of $\ln k \sim 1,000/T$ for the calculation of kinetic constants A and E .

Graphic Abstract:

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9