energy&fuels

Steam–Coal Gasification Using CaO and KOH for *in Situ* Carbon and Sulfur Capture

Nicholas S. Siefert,*^{,†,‡} Dushyant Shekhawat,[§] Shawn Litster,[‡] and David A. Berry[§]

[†]National Energy Technology Laboratory (NETL), United States Department of Energy (U.S. DOE), Pittsburgh, Pennsylvania 15236, United States

[‡]Department of Mechanical Engineering, Carnegie Mellon University, Pittsburgh, Pennsylvania 15213, United States

[§]National Energy Technology Laboratory (NETL), United States Department of Energy (U.S. DOE), Morgantown, West Virginia 26507, United States

ABSTRACT: We present experimental results of coal gasification with and without the addition of calcium oxide and potassium hydroxide as dual-functioning catalyst-capture agents. Using two different coal types and temperatures between 700 and 900 °C, we studied the effect of these catalyst-capture agents on (1) the syngas composition, (2) CO_2 and H_2S capture, and (3) the steam-coal gasification kinetic rate. The syngas composition from the gasifier was roughly 20% methane, 70% hydrogen, and 10% other species when a CaO/C molar ratio of 0.5 was added. We demonstrated significantly enhanced steam-coal gasification kinetic rates when adding small amounts of potassium hydroxide to coal when operating a CaO-CaCO₃ chemical looping gasification reactor. For example, the steam-coal gasification kinetic rate increased 250% when dry mixing calcium oxide at a Ca/ C molar ratio of 0.5 with a sub-bituminous coal, and the kinetic rate increased 1000% when aqueously mixing calcium oxide at a Ca/C molar ratio of 0.5 along with potassium hydroxide at a K/C molar ratio of 0.06. In addition, we conducted multi-cycle studies in which CaCO3 was calcined by heating to 900 °C to regenerate the CaO, which was then reused in repeated CaO-CaCO₃ cycles. The increased steam-coal gasification kinetics rates for both CaO and CaO + KOH persisted even when the material was reused in six cycles of gasification and calcination. The ability of CaO to capture carbon dioxide decreased roughly 2-4% per CaO-CaCO₃ cycle. We also discuss an important application of this combined gasifier-calciner to electricity generation and selling the purge stream as a precalcined feedstock to a cement kiln. In this scenario, the amount of purge stream required is fixed not by the degradation in the capture ability but rather by the requirements at the cement kiln on the amount of $CaSO_4$ and ash in the precalcined feedstock.

1. INTRODUCTION

There are multiple coal power plant designs with CO_2 capture and sequestration $(CCS)^{1-7}$ that can meet the United States Environmental Protection Agency (U.S. EPA) proposed limitations on greenhouse gas (GHG) emissions.⁸ These designs include the following general types:⁴ (1) conventional pulverized coal combustion with CCS (PCC-CCS) using amine-based solvents for post-combustion capture, (2) conventional integrated gasification combined cycle with CCS (IGCC-CCS) using physical solvents operating near room temperature for pre-combustion capture, (3) advanced integrated gasification combined cycle with CCS (adv. IGCC-CCS) using O_2 separation membranes as well as warm gas, pre-combustion capture of H_2S and CO_{21} (4) oxycombustion of coal or chemical looping combustion of coal using a transition-metal redox cycle that generates a near pure stream of CO_{2i} and (5) chemical looping gasification using a calcium oxide-carbonate cycle, in which a pure stream of CO₂ is generated in the calcination step. $^{9-15}$

While the calcium looping gasification process is not nearly as developed as the conventional PC–CCS and IGCC–CCS processes, there are reasons why the calcium looping gasification process could achieve a lower levelized cost of electricity than the conventional PC–CCS and IGCC–CCS processes. These reasons include the following: (1) the high methane content of the gas from the gasifier may allow for

© XXXX American Chemical Society

integration with existing natural gas combined cycle power plants^{16,17} while meeting proposed U.S. EPA regulations on GHG emissions; (2) there will likely be less equipment required because acid gas capture, methanation, and water-gas shift all occur in the gasifier;¹⁸ (3) the solid bleed stream from this CaO–CaCO₃ process could likely generate revenue as a precalcined feedstock to cement kilns, potentially decreasing the GHG emissions of both power plants and cement kilns;⁹ and (4) a CaO–CaCO₃ process should be fairly fuel flexible, being capable of handling fuels such as coal, biomass, and even high-halogen-content plastics.¹⁹

Calcium oxide has been a well-studied coal gasification catalyst because of the abundance of calcium carbonate as well as its ability to both catalyze reactions and capture acid gases inside of a coal gasifier. For example, the use of CaO to aid in the gasification of coal was first patented in 1867.²⁰ Carbon dioxide capture and regeneration by calcium oxide have been studied and reviewed by many previous groups, such as Stamnore and Gilot,²¹ Florin and Harris,²² Liu et al.,²³ and

Received: December 31, 2012 Revised: February 26, 2013

Special Issue: Accelerating Fossil Energy Technology Development through Integrated Computation and Experiment

Table 1. (a) Dry Weight Percentage and Dry, Non-ash Elemental Percentage of the Main Components of the Pittsburgh No. 8 Bituminous Coal and Wyodak-Anderson Sub-bituminous Coal and (b) Ash Composition on a Weight Percentage

(a) dry weight percentage and dry, non-ash elemental percentage of the main components of the Pittsburgh no. 8 bituminous coal and Wyodak-Anderson sub-bituminous coal

sub-bituminous coar										
coal	C (wt %)	H (wt %)	O (wi	: %)	N (wt %)	total	S (wt %)	ash ((wt %)
Pittsburgh no. 8	2	73.1	4.7	7.	8	1.5		2.2		9.1
Wyodak-Anderson	1 (58.3	4.9	16.	4	1.0		0.6		3.8
		C (mol %)	Н ((mol %)	O (mol %	6)	N (mol %)		organic S (m	ol %)
Pittsburgh no. 8		53.5		41.1	4.3		0.9		0.2	
Wyodak-Anderso	on	48.8		41.7	8.8		0.6		0.1	
			(b) ash	composition on a	weight perce	ntage				
coal	$\begin{array}{c} Na_2O + K_2O \\ (wt \%) \end{array}$	CaO (wt %)	MgO (wt %)	BaO + SrO (wt %)	$ \begin{array}{c} Fe_2O_3 \\ (wt \%) \end{array} $	Al_2O_3 (wt %)		SiO ₂ (wt %)		SO ₃ (wt %)
Pittsburgh no. 8	2.1	2.6	1.3	0.0	19.5	25.2	1.2	45.9	0.0	2.0
Wyodak-Anderson	Nyodak-Anderson 2.3 15.1 3.		3.6	0.9	10.2	15.5	1.2	1.2	22.0	

Dean et al.⁹ While CaO can capture HCl, H₂S, and CO₂, only CO_2 can easily be regenerated by increasing the temperature and/or decreasing the pressure. Gasification processes using calcium oxide addition have typically been studied when there has been a need to produce a syngas with high methane or hydrogen content. For example, the goal of the CaO acceptor process by Consol Energy from the 1960s to the 1980s¹⁰ was to generate a high content of methane and a low content of carbon dioxide. The goal of some more recent chemical looping fluidized-bed gasifiers, such as the HyPr-RING¹¹ and the calcium looping process (CLP),¹²⁻¹⁴ has been to generate a near pure stream of hydrogen. The HyPr-RING process is a pilot-plant-scale reactor system, whose gasification reactor operates at 650 °C, 3.0 MPa, and a molar CaO/carbon ratio of ~0.8 while generating a syngas of roughly 91% H_2 and 9% CH_4 , on a dry molar basis. The CLP at The Ohio State University¹²⁻¹⁵ is a two-fluidized-bed reactor process, whose goal is to generate near pure hydrogen.

Similar to calcium oxide, alkali hydroxides are both a catalyst for steam–coal gasification and a sorbent for capturing HCl, H_2S , and CO_2 .^{24,25} There has also been a long history of using alkali hydroxides and alkali carbonates to enhance the kinetics of steam–coal gasification.^{26–28} The history of catalytic coal gasification as of 1984 was reviewed by Wood and Sancier.²⁹ In comparison to catalytic gasification of coal using alkali carbonates and hydroxides, there are a number of advantages and disadvantages of using calcium oxide. One advantage of calcium oxide as the *in situ* capture agent for acid gases is that calcium species remain in the solid phase, which minimizes the interaction of the catalyst/capture with the ceramic or steel walls of the reactor compared to a process using molten alkali hydroxides. However, because calcium oxide and calcium carbonate are solids at typical gasifier temperatures, alkali earth oxides are not as good at being catalysts as alkali hydroxide catalysts, as was reported in our previous work.²⁴

Our goal here is to take advantage of the positives of both alkali hydroxides and alkali earth oxides while mitigating their associated negatives. We present experimental results from fixed-bed coal gasification with calcium oxide addition and CaO regeneration in a calcination reactor. The results show that small amounts of alkali hydroxides and calcium oxide make an effective catalyst–capture combination when mixed with liquid water and coal prior to entering the gasifier. To measure degradation in the reuse of regenerated CaO, we also present results when the calcined material is reused in multiple CaO– CaCO₃ cycles. These experimental results could later be used

to optimize the design and operation of a $CaO-CaCO_3$ cycle that sells the mostly CaO bleed stream as precalcined feedstock to a cement kiln to reduce the GHG emissions of both the power plant and the cement kiln.

2. EXPERIMENTAL SECTION

2.1. Materials. We ran steam-coal gasification experiments using two different coal types to study the effect of calcium oxide (Alfa Aesar, Ward Hill, MA) and potassium hydroxide (Alfa Aesar, Ward Hill, MA) addition on different coal types. We obtained coal samples from the Argonne National Laboratory Premium Coal Bank,³⁰ whose website contains the full information on the coals used, such as particle distribution, elemental analysis, and proximate analysis. The coal types were a high-volatile bituminous coal (Pittsburgh no. 8, 100 mesh) and a sub-bituminous coal (Wyodak-Anderson, 100 mesh). These two coals represent the two main types of non-lignite coals currently used in the U.S.: a medium-sulfur eastern bituminous coal and a low-sulfur western sub-bituminous coal. In Table 1, we list the coal composition on a weight basis, including ash (mostly silica aluminates), as well as on a molar basis (without ash). We focus mostly on the Wyodak-Anderson coal from Wyoming because its low ash, low sulfur, and high reactivity make it an ideal fuel for low-temperature calcium oxide looping gasification. The sulfur in the Wyodak-Anderson coal is 27 wt % pyritic, 5 wt % sulfatic, and 68 wt % organic. The sulfur in the Pittsburgh no. 8 coal is 63 wt % pyritic and 37 wt % organic. As for a dry proximate analysis, the Wyodak-Anderson coal is 45 wt % volatile matter and the Pittsburgh no. 8 coal is 38 wt % volatile matter. The ash composition of the coal is shown in Table 1b on a weight basis, with basic ash components on the left and acidic components on the right.

2.2. Experimental Design and Procedures. A reactor was constructed out of Incoloy 800HT and was designed to withstand temperatures up to 900 °C and pressures up to 2.1 MPa. This pressure was chosen because of its proximity to the pressure of the combustor of a modern gas turbine, such as the GE 6FA (1.6 MPa). Figure 1 shows a drawing of the reactor as well as a schematic of the experimental layout. The dimensions of the 99.8% alumina crucible (CoorsTek, Golden, CO) inside of the reactor were 23 cm tall, 2.5 cm outer diameter, and 1.9 cm inner diameter. The steam tube was made out of 1.3 cm diameter 316 stainless-steel tubing. The furnace heater was a Series 3110 tube furnace by Applied Test Systems (Butler, PA). Water vapor and tars were condensed prior to the mass spectrometer (Pfeiffer OmniStar, Asslar, Germany). Argon was used as a carrier gas because there are no overlaps in the mass spectra with the syngas species of interest. All experiments were conducted in a batchcontinuous process. First, coal and catalyst were added to the reactor; then, the reactor system was sealed; next, the system was pressurized and flushed of air using argon; and then, the furnace temperature was increased while starting the flow argon and water vapor. The water vapor and argon flow rates were 62 and 10 standard cubic centimeters per minute (sccm), respectively, unless otherwise noted. Further



Figure 1. Fixed-bed catalytic reactor and regenerator: (a) reactor vessel and (b) schematic.

details of the reactor and the experimental layout can be found in the study by Siefert et al. $^{\rm 24}$

Before loading the ceramic crucible, the fresh coal and catalyst were mixed together dry outside of the crucible. Next, the stainless-steel steam tube was inserted into the ceramic crucible. The dry-mixed catalyst and coal were poured inside of the ceramic crucible, outside of the steam tube. For those cases in which there was the addition of water, we then added 30 g of deionized water and mixed the coal and catalyst inside of the ceramic crucible. The crucible was then placed inside of the Incoloy 800HT reactor, and finally, the system was sealed. For those cases with water addition, the water was evaporated before the experiment began by heating the system to 200 °C. For those cases in which the catalyst was reused for a number of cycles, the material from the previous run was removed from the ceramic crucible after allowing the reactor to cool back to room temperature. The material was weighed to make sure that all material had been recovered. The weight was always within $\pm 5\%$ of the expected weight because of the previous material plus the new ash material in the coal added in the previous experiment. During cooling, dry air was passed over the bed of CaO to prevent the formation of Ca(OH)₂. After collecting the catalyst and ash material from the previous run, we ground the material until all of the material passed through a 20-mesh sieve (841 μm

2.3. Syngas Product Analysis. In this section, we detail the process for how we converted the compositions versus time data from the mass spectrometer into average gas compositions as well as into a coal gasification kinetic rate. The real-time gas composition data from the mass spectrometer was converted into a production-averaged gas composition through the following procedures: (1) determine the flow rate of each component of the syngas by multiplying the known inlet flow rate of argon by the ratio of the gas composition of the syngas species to the gas composition of the argon; (2) integrate the flow rate of each syngas species from the start of the reaction until 60% coal conversion; and finally, (3) divide the total flow of each gas species by the total non-argon gas flow. The equation for the production average gas composition, PAGC_µ of the syngas species *i* is given by

$$PAGC_{i}(t) = \frac{\int_{0}^{t} \dot{\eta}_{Ar} \left(\frac{c_{i}(t)}{c_{Ar}(t)}\right) dt}{\sum_{i} \int_{0}^{t} \dot{\eta}_{Ar} \left(\frac{c_{i}(t)}{c_{Ar}(t)}\right) dt}$$
(1)

where \dot{n}_{Ar} is the flow rate of argon and $c_i(t)$ is the concentration of species *i* at a particular time, *t*.

To measure coal conversion, we used the data from the mass spectrometer to determine the change in the chemical oxygen demand (COD) of the coal, where COD is the amount of oxygen above that already in the coal that is required to oxidize the carbon to CO_2 and hydrogen to H₂O.³¹ Using the COD remaining in the coal to define coal conversion was crucial because we were not able to obtain realtime weight balance or carbon/hydrogen/oxygen balance. For example, it was not possible to obtain a real-time carbon balance because we were capturing carbon dioxide inside of the gasifier. Because we were condensing out water vapor before the mass spectrometer, it was not possible to obtain a real-time hydrogen or oxygen balance. However, as discussed in a prior work,²⁴ it is possible to carry out a COD balance because CO₂ and H₂O have no COD. In that prior work, we defined the reduction charge to be the number of moles of electrons that could be supplied to the anode electrode of an electrochemical cell. The units of reduction charge are moles of e-, and the value of the reduction charge of an element or a molecule is equal to 4 times the COD of the element/molecules when the COD is given in units of moles of O_2 .

To determine the reduction charge of a molecule, we assigned the following values to each element in a molecule: C = +4; H = +1; O =-2; N = 0; Ar = 0; S = -2 (+6); Li = Na = K = +1; Cl = -1; and Ca = +2. Note that we have assigned a reduction charge value of -2 to sulfur in the gasifier. It should be noted that in an oxidizing environment the redox state of sulfur should actually be +6 because the end redox state of sulfur in the environment is $SO_3(g)$ and $H_2SO_4(aq)$. Using the values of reduction charge listed above, we calculated the reduction charge of gas-phase molecules as follows: H_2 = 2; CO = 2; $H_2O = CO_2 = H_2S = 0$; $CH_4 = 8$; $C_2H_4 = 12$; and C_2H_6 = 14. If molecular oxygen had been added, it would have been assigned a value of $O_2 = -4$. These values are the values of the number of electrons generated from the electrochemical half-cell reaction that involves 1 mol of the reactant and its complete oxidation, and these values are the same values of z used in the denominator of the Nernst equation for electrochemical cells when the reaction involves 1 mol of the fuel on the anode and if the cathode electrode were in contact with oxygen and/or air. Using the same elemental values above, we calculated the reduction charge of the solid-phase species in the gasifier as follows: $Ca(OH)_2 = CaO = CaCO_3 = CaS = CaCl_2 = KOH = K_2S =$ $K_2CO_3 = KCl = 0.$

Using the coal analysis presented earlier in Table 1, each 5 g sample of dry Pittsburgh no. 8 coal is composed of 0.31 mol of C, 0.25 mol of H, 0.025 mol of O, 0.005 mol of N, and 0.003 mol of S. By assigning a value of reduction charge to each element in the coal, we obtained a value of 1.43 mol of e^- for every 5 g of Pittsburgh no. 8 coal. Each 5 g sample of dry Wyodak-Anderson coal is composed of 0.29 mol of C, 0.25 mol of H, 0.05 mol of O, 0.004 mol of N, and 0.001 mol of S. We obtained a value of 1.31 mol of e^- of reduction charge for every 5 g of Wyodak-Anderson coal.

Just as there are conservation equations for each element in a chemical reaction, there is a conservation equation for the reduction charge. The reduction charge conservation equation can be calculated by adding together the conservation equations associated with each element, multiplied by the value of z assigned to each element. The reduction charge conservation equation is the following:

$$\frac{\partial (\text{RCR})_{\text{system}}}{\partial t} = \sum_{i}^{\text{inlet}} \widehat{\text{RC}}_{i} \dot{n}_{i} - \sum_{i}^{\text{exit}} \widehat{\text{RC}}_{j} \dot{n}_{j}$$
(2)

where RCR is the reduction charge remaining, \widehat{RC} is the molar reduction charge, and \dot{n} is the flow rate of species entering or exiting the system. For our system, the reduction charge balance equation is the following:

$$\frac{\partial (\text{RCR})_{\text{coal}}}{\partial t} = -(2\dot{n}_{\text{H}_2} + 2\dot{n}_{\text{CO}} + 8\dot{n}_{\text{CH}_4} + 14\dot{n}_{\text{C}_2\text{H}_6} + 12\dot{n}_{\text{C}_2\text{H}_4})$$
(3)

Note that, in going from eq 2 to eq 3, the left-hand side of the equation goes from the reduction charge in the system to the reduction charge in the coal because the reduction charge of all of the solid-phase elements is zero, except for the coal. Although to do this, we had to assign a value of -2 to sulfur. Note also that, in going from eq 2 to eq 3, the inlet term on the right-hand side of the equation is zero because the only inputs are water vapor and argon.

Here, to define a lump kinetic rate of steam—coal gasification, we first had to calculate the reduction charge remaining in the coal as a function of time. To calculate a normalized reduction charge remaining, we integrated eq 3 with time and divided by the original reduction charge in the coal. This yielded the definition of normalized reduction charge remaining (NRCR) for our system.

NRCR(t) =

$$1 - \frac{\int_{0}^{t} (2\dot{n}_{H_{2}} + 2\dot{n}_{CO} + 8\dot{n}_{CH_{4}} + 14\dot{n}_{C_{2}H_{6}} + 12\dot{n}_{C_{2}H_{4}})dt}{4n_{C} + n_{H} - 2n_{O} - 2n_{S}}$$
(4)

To determine the lump kinetic rate of steam–coal gasification, we fit an exponential curve through the plot of NRCR versus time from NRCR \approx 100 to 40%. We wanted to make sure that all experiments would be compared on an equal basis. We chose the value of 40% based on the fact that, in a CaO–CaCO₃ cycle, typically 20–40% of the carbon is left ungasified to provide the enthalpy required to operate the calcium oxide regenerator (i.e., calciner).³² Also, 40% NRCR was the largest value of conversion reached by all data sets. It should be noted that the lumped kinetic rate includes both steam–coal gasification reactions as well as coal pyrolysis reactions.

2.4. CaO Regeneration and Calculation of CO₂ Captured. In this section, we detail the process for how we converted the data from the mass spectrometer during the regeneration (i.e., calcination) step of the cycle into both a kinetic rate of CO₂ desorption as well as a value for the total desorption of CO2. After each gasification experiment with CaO, the following steps occurred: the flow rate of steam was turned off; the pressure was released back to 0.1 MPa; and the reactor temperature was raised to 900 $^\circ\text{C}.$ It took roughly 20 min for the temperature to go from 700 to 900 °C. During the CO₂ desorption phase of the CaO-CaCO₃ cycle, we maintained the same flow of argon (10 sccm) as in the gasification phase. After 90 min of calcination, 200 sccm of air was added for an additional 30 min. While this does not represent what would occur at a commercial facility, we followed this process to study the release of CO₂ from the calcium carbonate in the absence of oxygen, so that we could directly measure CO₂ release from the calcium carbonate rather than having to separate this amount from the amount of CO₂ generated via combustion of the remaining coal. To measure the flow rate of CO₂ released from the calcium carbonate, we multiplied the argon flow rate (10 sccm) by the ratio of the CO₂ gas composition to the argon composition plus one half of the ratio of CO gas composition to the argon composition. We counted half of the carbon monoxide composition toward the carbon dioxide release because some carbon dioxide reacts via the reverse Boudouard reaction with any unburnt carbon in the coal because this reaction is spontaneous at temperatures above 700 °C. The reverse Boudouard reaction, $C(s) + CO_2(g) \rightarrow 2CO(g)$, is spontaneous at the temperature of calcination ($\Delta G^{1173 \text{ K}} = -40 \text{ kJ mol}^{-1}$), and therefore, we had to count half of CO generated during this desorption phase toward the total CO2 released from the calcium carbonate. To calculate the total CO₂ released, we integrated the molar flow rates with respect to time to determine the total moles of CO₂ released. Finally, to measure a normalized amount of CO₂ released, we divided this integral by the total moles of CaO added to the gasifier. The equation is given below

NCP (method 1) =
$$\left(\int_{t'}^{t'+90 \text{ min}} (\dot{n}_{\text{CO}_2} + 1/2\dot{n}_{\text{CO}}) dt\right) / n_{\text{CaO}}$$
(5)

where NCP is the normalized capture percentage, t' represents the time at which gasification ends and calcination begins, \dot{n}_i is the molar flow of species *i*, and n_{CaO} is the moles of CaO added to the gasifier at the start of the experiment. It should be noted here that the kinetic rate for CO₂ calcination was on the order of 3 h⁻¹; therefore, 90 min of calcination represents roughly 4 e-folding decay times, and hence, only 2% or less of CO₂ would not have been released by the end of 90 min.

We also compared the values of NCP calculated in this method to an estimate of the CO₂ captured during the steam–coal gasification portion of the experiment. To estimate the amount of CO₂ capture, we subtracted the amount of carbon that leaves the reactor during coal gasification (i.e., the amount of CH₄ + CO + CO₂ + 2C₂HC) from the amount of carbon in the coal that reacts during gasification

NCP (method 2) =
$$\left((1 - \text{NCRC})n_{\text{C}} - \int_{0}^{t'} (\dot{n}_{\text{CO}_{2}} + \dot{n}_{\text{CO}} + \dot{n}_{\text{CH}_{4}} + 2\dot{n}_{\text{C}_{2}\text{H}_{6}} + 2\dot{n}_{\text{C}_{2}\text{H}_{4}})dt \right) / n_{\text{CaO}}$$

(6)

where NCRC is the normalized coal remaining at the end of gasification and $n_{\rm C}$ is the moles of carbon in the 5.0 g of coal added at the beginning of the experiment. It should be noted that method 2 is less exact because it assumes that C, H, and O atoms are gasified at the same rate.

These two methods of calculating the normalized capture percentage provide a verification of our estimates of how much CO_2 was captured during gasification. The values of normalized capture percentage presented in sections 3.5 and 3.6 are the average of the " CO_2 captured" and the " CO_2 released", as estimated by the two methods discussed above. These calculations allow us to measure the amount of CO_2 captured during the gasification phase of each experiment and the degradation in the capture ability after repeated CaO–CaCO₃ cycles.

While it was not possible to conduct a carbon balance for just the gasification portion of the experiment, we were able to conduct a carbon balance analysis across the combined gasification and CaO regeneration portions of the experiment. In the Results, we will be including the carbon balance, which is defined as the total carbon exiting the reactor during the entire experiment normalized by the carbon originally in the coal.

3. RESULTS

3.1. Results during the Startup Phase. Here, we present gas composition and coal conversion during the startup phase of experiments with and without catalyst addition to measure the amount of pyrolysis occurring during startup. These data will be presented as a function of the temperature inside the reactor. Because the temperature inside the reactor increased at an average rate of 11 °C min⁻¹, the results can easily be converted into results versus time. First, we present in Figure 2a the gas composition and coal conversion during the startup phase when there was no steam flowing and no catalyst added with the Wyodak-Anderson coal. Any gas produced during startup is therefore only due to devolatilization reactions (i.e., pyrolysis) or subsequent reaction of released carbon dioxide with the coal to form carbon monoxide. During the startup with no steam and no catalyst, approximately 2% of the reduction charge of coal exits the reactor. The first gas to be released is carbon dioxide, and this process begins around 350 °C. Then, at 400 °C, there is release of carbon monoxide, methane, ethane/ethylene, and hydrogen. The timing of the release of



Figure 2. Gas composition and normalized coal conversion during the temperature ramping startup for 5.0 g of Wyodak-Anderson coal. The reactor volume was initially just solid coal and 100% Ar. (a) No steam and no catalyst, (b) continuous flow of 0.05 g min⁻¹ of water plus 8.2 g of CaO mixed with coal before startup, and (c) continuous flow of 0.05 g min⁻¹ of water plus 8.2 g of CaO and 1 g of KOH mixed with 30 g of water and coal before startup. Note the different scales for each axis (right-hand-side *y*-axis scale for NCC only). The temperature increase inside of the reactor was approximately linear with a ramp rate of 11 °C min⁻¹.

these pyrolysis gases is similar to the timing found by Wen and Dutta,³³ who found that volatile species typically are released from the coal in the following order: H_2O , CO_2 , CO, C_2H_6 , CH_4 , tars/liquids, and H_2 . The CO_2 released comes from decarboxylation of the carboxyl acid groups in the coal. While on a molar basis, carbon dioxide and carbon monoxide are the dominant pyrolysis gases, on a reduction charge basis, methane is the dominant species in the pyrolysis gas because the carbon dioxide that exits the reactor has no reduction charge. When

the temperature reaches 700 $^{\circ}$ C, methane makes up roughly 75% of the reduction charge leaving the reactor.

In Figure 2b, we present the gas composition and coal conversion during the startup phase of an experiment with 5.0 g of Wyodak-Anderson coal, 8.2 g of CaO, 62 sccm steam flow $(0.05 \text{ g min}^{-1})$, and 10 sccm of argon flow. The reactor volume is initially just solid coal and 100% Ar until roughly 500 °C. There is no noticeable increase in the composition of carbon dioxide at 350 °C or carbon monoxide at 400 °C. It is possible that the CaO was capturing the carbon dioxide and preventing the carbon dioxide gas from reacting with the coal to form carbon monoxide. The presence of steam as well as 0.5 mol of CaO per mole of carbon in the coal causes the gas composition to be very different in these first two cases. When there is no calcium oxide and steam, the gas has large quantities of carbon dioxide; however, when there is calcium oxide and steam, the gas composition is mostly hydrogen and methane. As seen in Figure 2b, at 650 °C, there is a rapid increase in the composition of hydrogen, which is being generated by a combination of steam-coal gasification, water-gas shift, and pyrolysis reactions. However, by 700 °C, in both panels a and b of Figure 2, roughly the same amount of reduction charge has left the reaction during the startup phase of the experiment. This suggests that CaO does not speed up the pyrolysis reactions and suggests that the effect of CaO is to capture CO₂ released directly from the coal as well as to capture CO that has been water-gas-shifted to form CO₂ and H₂.

In Figure 2c, we present the gas composition and coal conversion during the startup phase of an experiment with 5.0 g of Wyodak-Anderson coal, 8.2 g of CaO, and 1 g of KOH, with a continuous flow of 62 sccm (0.05 g min⁻¹) of steam and 10 sccm of argon. The reactor volume is initially just solid coal and 100% Ar until roughly 300 °C. In Figure 2c, we can see the clear positive effect of mixing the coal, catalyst, and water. In all of the experiments conducted with CaO/KOH and water, there was hydrogen production at temperatures at least 100 °C lower than for the pyrolysis or the case of adding calcium oxide that has only been dry mixed with the coal. Similar to the case with just CaO addition, there was virtually no CO₂ in the startup gas stream. However, by 600 °C, 9% of the reduction charge had already been released.

3.2. Flow Rates and NRCR during the Gasification Phase. Here, we present the flow rate and NRCR versus time for steam-coal gasification of 5.0 g of Wyodak-Anderson subbituminous coal at 700 $^\circ C$ and 2.1 MPa. The following cases are presented in Figure 3: (a) coal without catalyst, (b) coal with 8.2 g of CaO mixed dry, and (c) coal with 8.2 g of CaO and 1.0 g of KOH mixed with 30 g of water prior to entering the gasifier. We first discuss the results in Figure 3, showing the flow rate versus time of each of the syngas components. There was an increase in flow rates with the addition of calcium oxide (Figure 3b) compared to no catalyst (Figure 3a), and there was an even larger increase in flow rates with the addition of calcium oxide and potassium hydroxide (Figure 3c) compared to no catalyst (Figure 3a). There is also a noticeable change in the gas composition when adding calcium oxide to the reactor. As expected, the H_2 concentration increases and the CO_2 concentration decreases when adding enough CaO to capture 50% of the carbon in the coal. As seen in panels b and c of Figure 3, the flow rate of carbon dioxide increases with time after there is partial saturation of the calcium oxide; then, the flow rate hits a maximum and decreases along with all of the syngas species as the coal is consumed. In panels a and b of



Figure 3. (Left) Flow rate of the syngas components from steam-coal gasification experiments at 700 $^{\circ}$ C and 2.1 MPa using 5 g of Wyodak-Anderson coal and a water flow rate of 0.05 g/min. (Right) NRCR of the coal versus time for the same experiments. (a) No catalyst, (b) 8.2 g of CaO mixed dry with coal, and (c) 8.2 g of CaO and 1.0 g of KOH mixed with the coal as well as 30 g of water prior to entering the gasifier.

Figure 3, there is a large spike in syngas production near t = 0, and this is due to pyrolysis reactions that occur during startup and early in the gasification phase. This effect is more noticeable in the case without catalyst than in the cases with catalysts because the catalysts increase the steam—coal gasification reaction rates.

Figure 3 also shows the NRCR in the coal as a function of time. This is a measure of how much COD is left in the coal, and it goes to zero when all of the carbon and hydrogen in the coal have reacted. In the graphs on the right, it is easy to see the large increase in coal conversation when using CaO and KOH mixed with 30 g of water compared to dry mixing just CaO or using no catalyst with the coal. Another item to highlight in panels b and c of Figure 3 is that NCRC versus time data show signs of two separate exponential fits. In other words, there appears to be two distinct reactions occurring with different time scales. The faster kinetics at earlier times is a clear indication that both pyrolysis and steam-coal gasification are occurring at earlier times, whereas at later times, the pyrolysis reactions are complete and only steam-coal gasification reactions are occurring. The evidence for pyrolysis reactions only at the beginning of the experiment includes the observation that the ethane flow rate decreases much faster than the flow rate of hydrogen. Ethane is a coal pyrolysis product and is not a steam-coal gasification product.

3.3. Effect of the Temperature: Coal without Catalyst.

In the following two sections, we convert the data versus time into product-averaged gas composition and a kinetic rate of coal gasification at temperatures between 700 and 900 °C. In Table 2a, we present the experimental gas composition and kinetic rate of coal conversion for Wyodak-Anderson sub-bituminous coal without a catalyst as a function of the temperature. In Table 2a, we also present the simulated chemical equilibrium gas composition using HSC Chemistry 6 (Outotec Solutions, Espoo, Finland). To model Wyodak-Anderson coal in HSC Chemistry 6, we used a mixture of species with the same ratio of C/H/O as given in Table 1. We can model coal this way because, for a given input of ratios of C/H and C/O, the output gas composition from a chemical equilibrium simulation is independent of the molecules used to make up the ratios of C/ H and C/O. All of the experiments presented in this section and in the next section were repeated 3 times at each temperature. The data in the tables are the average composition to 60% conversion, the kinetic rate to 60% conversion, and the standard deviation of the conversation rate of the three realizations at that temperature. For the Wyodak-Anderson coal, there was an approximately 3-fold increase in the coal conversion rate between 700 and 900 °C. At 900 °C and 2.1 MPa, the conversion rate of the Wyodak-Anderson coal was $0.63 h^{-1}$. For comparison, the conversion rate of the graphite Table 2. Product-Average Gas Composition, Kinetic Rate of Coal Gasification, and Standard Deviation of the Kinetic Rate to 60% Coal Conversion for Steam–Coal Gasification at a Pressure of 2.1 MPa at Temperatures between 700 and 900 °C for (a) Wyodak-Anderson Coal without a Catalyst–Capture Agent and (b) Pittsburgh No. 8 Coal without a Catalyst–Capture Agent^a

(a) Wyodak-Anderson sub-bituminous coal without a catalyst–capture agent													
temperature (°C)	H ₂	(%)	%) CH_4 (%) C_2H		C ₂ H	IC (%) CO ₂ (%)		2 (%)	CO (%)		H_2S (ppm)	rate (h^{-1})	standard deviation of the rate (h^{-1})
900	45	(54)	14	(5)	1.5	(0.0)	22	(10)	17	(32)	692	0.63	±0.21
800	47	(53)	16	(8)	2.0	(0.0)	23	(18)	(18) 12 (20) 679 0.37				± 0.14
700	38	(58)	20	(8)	3.0	(0.0)	28	28 (27) 12 (8)		722	0.21	± 0.05	
				(b)	Pittsbu	rgh no. 8	bitumi	nous coa	l withou	it a cata	lyst–capture aş	gent	
temperature (°C)	H ₂	(%)	CH	4 (%)	C ₂ H	IC (%)	CC	02 (%)	CC) (%)	H_2S (ppm)	rate (h^{-1})	standard deviation of the rate (h^{-1})
900	36	(45)	21	(11)	3.6	(0.0)	16	(5)	23	(38)	3576	3576 0.82 ±0.2	
800	32	(47)	28	(14)	4.2	(0.0)	17 (15) 19 (24) 2830 0.51		±0.15				
700	36	(57)	27	(9)	5.2	(0.0)	17	(26)	14	(8)	5763	0.19	± 0.05

^aExperimental values are shown on the left side of a column, and HSC Chemistry 6 numerical chemical equilibrium simulations are shown on the right side of a column in parentheses.

Table 3. Product-Average Gas Composition, Kinetic Rate of Coal Gasification, and Standard Deviation of the Kinetic Rate to 60% Coal Conversion for Coal Gasification at a Pressure of 2.1 MPa at Temperatures between 700 and 900 °C for (a) Wyodak-Anderson Coal with 8.2 g of CaO and (b) Pittsburgh No. 8 Coal with 8.7 g of CaO^a

(a) Wyodak-Anderson sub-bituminous coal with CaO/C of 0.5:1								
temperature (°C)	H ₂ (%)	CH ₄ (%)	C ₂ HC (%)	CO ₂ (%)	CO (%)	H ₂ S (ppm)	coal conversion rate (h^{-1})	normalized CO ₂ capture (%)
900	65 (61)	18 (25)	2.1 (0.0)	5.6 (4.0)	9.5 (10.0)	40 (2)	1.0	65
800	66 (67)	19 (21)	2.8 (0.0)	3.7 (2.8)	8.4 (8.5) 12	26 (3)	0.9	70
700	70 (68)	18 (30)	3.3 (0.0)	0.7 (0.7)	7.9 (1.1)	8 (3)	0.7	79
(b) Pittsburgh no. 8 bituminous coal with CaO/C of 0.5:1								
temperature (°C)	H ₂ (%)	CH ₄ (%)	C ₂ HC (%)	CO ₂ (%)	CO (%)	H ₂ S (ppm)	coal conversion rate (h ⁻¹)	normalized CO ₂ capture (%)
900	49 (56)	21 (14)	2.6 (0.0)	7.1 (320) (2	27) 22	24 (1)	1.3	60
800	50 (55)	25 (34)	3.6 (0.0)	4.4 (1 B) (1	10) 9	97 (2)	0.9	68
700	51 (64)	26 (35)	4.8 (0.0)	3.6 (1.11)5	(1)	17 (12)	0.4	74
an 1 1	,	.1 1 6	.1 6					

"Experimental values are shown on the left side of a column, and HSC Chemistry 6 numerical chemical equilibrium simulations are shown on the right side of a column in parentheses.

under a similar temperature, pressure, and steam flow rate was only 0.014 h^{-1} .

In Table 2b, we present the experimental gas composition and kinetic rate of coal conversion for Pittsburgh no. 8 bituminous coal without a catalyst as a function of the temperature. Using HSC Chemistry 6, in Table 2b, we also present the calculated gas composition assuming that there is complete chemical equilibrium. To model Pittsburgh no. 8 coal, we used a mixture of species with the same ratio of C/H/O as given in Table 2. Because HSC Chemistry 6 is a chemical equilibrium calculator, the equilibrium composition is only a function of the temperature, total pressure, and ratio of C/H/ O. There was a 4-fold increase in the coal conversion rate between the range of 700 and 900 °C. As expected from the chemical equilibrium simulations, at increased temperatures, there was an increase in the carbon monoxide composition and a decrease in the carbon dioxide composition. In parts a and b of Table 2, there was a large difference between the experimental and simulated compositions of methane and higher hydrocarbons. A more accurate ability to predict the chemical composition would require knowledge of both the pyrolysis reactions and the rate of breakdown of pyrolysis molecules inside of the gasifier.

As the temperature increased in both the chemical equilibrium simulations and the experimental results in Table 2, there was an increase in the carbon monoxide composition

and a decrease in both methane and carbon dioxide compositions. However, because a chemical equilibrium simulation cannot account for pyrolysis product gases that are kinetically limited from reacting before leaving the reactor, there was a large difference between the experimental and simulated compositions of methane and higher hydrocarbons. It should be noted that, in Table 2, "C₂HC" represents the total ethane and ethylene in syngas. Consistently throughout the experiments, the measured ratio of ethane to ethylene was approximately 2; however, we only present the sum of ethane plus ethylene because of the similarity of the two species. While there were changes in the gas composition between 700 and 900 °C, the ratio of the total carbon to the total moles of reduction charge in the syngas did not vary significantly. At 700 and 900 °C, the ratio of the number of moles of C to the moles of e⁻ of reduction charge for the Wyodak-Anderson coal was 0.22, and at 800 °C, this ratio was 0.20. For comparison, this ratio is approximately 0.125 for natural gas and 0.29 for Lurgi dry ash oxy-gasification of lignite without CO₂ capture.³⁴

It is also important to note that, given the C/H/O/S ratios in Table 1, the chemical equilibrium dry gas composition of H_2S should be on the order of 1000 ppm for Wyodak-Anderson coal and 2000 ppm for Pittsburgh no. 8 if all of the organic sulfur in the coal is converted to gaseous products at the same rate as the hydrogen and carbon in the coal. As seen in Table 2, the experimental H_2S gas composition from the Pittsburgh no. 8 coal was between approximately 2800 and 5800 ppm and that from the Wyodak-Anderson coal was approximately 700 ppm. The experimentally measured H_2S gas compositions in both the Wyodak-Anderson and Pittsburgh no. 8 coals were fairly close to the expected values using HSC Chemistry 6.

3.4. Effect of the Temperature: Coal with CaO Mixed Dry. We continue with the analysis of steam-coal gasification experiments as a function of the temperature of the reactor but now discuss experiments in which calcium oxide is mixed with the coal prior to being added to the reactor. In Table 3a, we present the experimental gas composition and kinetic rate of coal conversion for 5.0 g of Wyodak-Anderson sub-bituminous coal (100 mesh) with 8.2 g of fresh CaO (100 mesh) as a function of the temperature. In Table 3a, we present the simulated gas composition using HSC Chemistry 6 assuming that there is complete chemical equilibrium. There was a roughly 40% increase in the coal conversion rate between the range of 700 and 900 °C. This increase for the same difference in temperatures was significantly less than without a catalyst. As expected from the chemical equilibrium simulations, at increased temperatures, there was an increase in both the carbon monoxide and carbon dioxide compositions and a decrease in hydrogen composition. For example, there was a slight increase in the ratio of moles of carbon to moles of e⁻ of reduction charge with an increasing temperature (0.10 at 700 °C, 0.11 at 800 °C, and 0.12 at 900 °C), which was calculated using the Wyodak-Anderson results in Table 3a. Because the pyrolysis gas products are kinetically limited from reaching equilibrium, there was a large difference between the experimental and simulated compositions of higher hydrocarbons. There was also a large difference between the amount of H₂S that exits the reactor and that calculated assuming chemical equilibrium. As opposed to the case without the addition of CaO, there was more H₂S measured than predicted by chemical equilibrium calculations.

In Table 3b, we present the experimental gas composition and kinetic rate of coal conversion for 5.0 g of Pittsburgh no. 8 bituminous coal and 8.7 g of CaO as a function of the temperature. Using HSC Chemistry 6, in Table 3b, we also present the calculated gas composition assuming that there is complete chemical equilibrium and 100% coal conversion. There was a 3-fold increase in the coal conversion rate between the range of 700 and 900 °C. This increase for the same range in temperatures was only slightly less than without a catalyst. There was less carbon dioxide capture by the calcium oxide addition when operating with Pittsburgh no. 8 coal than when operating with Wyodak-Anderson coal, but this was to be expected because of the higher sulfur content and slightly higher ash content of the Pittsburgh no. 8 coal. As expected from the chemical equilibrium simulations, at increased temperatures, there was an increase in the carbon monoxide and carbon dioxide compositions and a decrease in the hydrogen composition. In Table 3a, we also present the percentage of the CaO that converts into CaCO₃. This amount decreases with increased temperatures. Because the Gibbs free energy of forming calcium carbonate increases with an increasing temperature, CaO will not be able to capture as much carbon dioxide at higher temperatures. As was the case for the Wyodak-Anderson sub-bituminous coal, there was a large difference between the experimental and simulated compositions of methane, higher hydrocarbons, and hydrogen sulfide.

We next estimated the activation energy for steam-coal gasification using the results presented in Tables 2 and 3. By assuming that the gasification of the coal follows an Arrhenius rate equation, we estimated the value of the effective activation barrier for gasification both with and without the addition of calcium oxide. These values are listed in Table 4. We found that

Table 4. Effective Activation Barrier Energy in kJ mol⁻¹ for Both Coal Types with and without the Addition of Calcium Oxide on a 0.5:1 Molar Ratio of CaO/Carbon in the Coal

effective activation barrier energy	no catalyst (kJ mol ⁻¹)	dry mixed lime (kJ mol ⁻¹)
Pittsburgh no. 8	62 ± 13	52 ± 15
Wyodak-Anderson	55 ± 11	15 ± 8

the effective activation barrier is lower for the lower rank coal, and as expected, calcium oxide addition lowered the effective activation barrier. The error bars in Table 4 represent the standard derivation in the estimation of the effect activation barrier based off of the nine experiments (three experiments at each of the three temperature values) that went into the calculation of the slope of the rate constant versus temperature.

Before discussion of experimental results from repeated CaO–CaCO₃ cycles, it should be highlighted that the Wyodak-Anderson coal would make a better choice than Pittsburgh no. 8 coal for repeated CaO–CaCO₃ cycles for the following reasons: (1) the kinetic rate of steam–coal gasification was slightly higher at 700 °C; (2) the normalized capture percentage was slightly higher; and most importantly, (3) there is less sulfur and silica aluminates in the coal, which, as we will discuss in section 4.2, has a large impact on the amount of makeup CaCO₃ required to meet requirements to sell the purge stream to a cement kiln. For these reasons, we chose to use only the Wyodak-Anderson coal in the CaO–CaCO₃ cycle degradation discussed in the next two sections.

3.5. Cycle Degradation of Calcium Oxide Only. Here, we discuss results of repeated CaO-CaCO₃ cycles. The steps in this experimental process were discussed in section 2.4 and are elaborated here. After each regeneration/calcination step in the cycle, the material was removed from the ceramic crucible and mixed with the fresh coal before being added back into the reactor. There was no addition of fresh CaO into the process after the beginning of cycle 1. We present results on the degradation of the regenerated calcium oxide to capture carbon dioxide and hydrogen sulfide. In Table 5, we present the following: (1) the syngas composition during gasification, (2) the first-order coal conversion rate to 40% reduction charge remaining, (3) the percentage of the calcium oxide that captures CO_2 , and (4) the first-order release rate of the calcium carbonate during regeneration/calcination. The results in Table 5 represent an average of two experiments, where each experiment was conducted out to six cycles of gasification/ carbonation and regeneration/calcination. For example, the material mixed with the 5.0 g of fresh coal in cycle 2 was the material recovered from the regeneration (calcination) phase of cycle 1. The amount of material recovered after each cycle increased from \sim 8 to \sim 10 g between cycles 1 and 6 because of the ash in the coal. The weight recovered was consistent with the material being mostly CaO rather than $Ca(OH)_2$.

The trends with increasing cycle number are as follows: (a) the coal gasification rate did not significantly change; (b) the capture percentage decreased 2.4% after each cycle with a

Tabl	e 5.	Resul	ts versus	Cyc	le Num	ber f	for	5.0	g	of	Wyo	odal	c-Anc	lerson	Coal	and	Initial	ly	8.2	g (of	CaC)"
------	------	-------	-----------	-----	--------	-------	-----	-----	---	----	-----	------	-------	--------	------	-----	---------	----	-----	-----	----	-----	----

	H ₂ (%)	CH ₄ (%)	C ₂ HC (%)	CO ₂ (%)	CO (%)	H ₂ S (ppm)	coal conversion rate (h^{-1})	normalized CO ₂ capture (%)	CO_2 release rate (h^{-1})
cycle 1	82	10	1.3	3.0	3	6	0.7	79	2.7
cycle 2	80	11	1.4	3.4	5	16	0.7	78	3.6
cycle 3	82	11	1.7	3.6	4	8	0.7	70	3.3
cycle 4	81	11	1.3	3.7	3	25	0.6	74	2.5
cycle 5	81	10	1.2	4.7	3	42	0.7	73	3.1
cycle 6	76	11	1.3	7.4	4	40	0.6	67	3.2

^{*a*}Gasification occurred at 2.1 MPa and 700 °C. CaO regeneration occurred at 0.1 MPa and 900 °C, and CaO was then reused in the next cycle with fresh coal. Results include syngas composition during gasification, the first-order coal conversion rate out to 40% reduction charge remaining, the percentage of the calcium oxide that captures CO_2 , and the first-order release rate of the calcium carbonate during regeneration (calcination).

Table 6.	Results	5.0 g	r of W	vodak-Anderson	Coal. 8.	2 g of	CaO	. and 30	g of H ₂ O"
					,			,	A / / / / / / /

	H ₂ (%)	CH ₄ (%)	C ₂ HC (%)	CO ₂ (%)	CO (%)	H ₂ S (ppm)	coal conversion rate (h ⁻¹)	normalized CO ₂ capture (%)	$\begin{array}{c} \mathrm{CO}_2 \ \mathrm{release} \ \mathrm{rate} \ (\mathrm{h}^{-1}) \end{array}$	carbon balance (%)
cycle 1	72	18	4.7	0.2	5.0	1	1.1	78	2.2	95
^{<i>a</i>} Gasificati	ion occu	urred at 2	2.1 MPa an	d 700 °C	C, and C	aO regener	ration occurred at 0.1	MPa and 900 °C.		

			66.0 11	C TT O TTA
Table 7. Cycle Results with 5.0 g	g of Wyodak-Anderson	Coal and Initially 8.2	g of CaO and I g	of KOH"

	H ₂ (%)	CH ₄ (%)	C ₂ HC (%)	CO ₂ (%)	CO (%)	H ₂ S (ppm)	coal conversion rate (h ⁻¹)	normalized CO ₂ capture (%)	$\begin{array}{c} \text{CO}_2 \text{ release rate} \\ (h^{-1}) \end{array}$	carbon balance (%)
cycle 1	73	16	3.9	0.2	7.0	21	2.3	79	3.0	93
cycle 2	74	16	3.1	0.7	6.8	2	1.9	75	3.2	91
cycle 3	75	13	3.0	0.8	7.8	5	2.0	74	3.5	103
cycle 4	77	13	2.9	0.8	5.4	28	2.6	74	2.4	93
cycle 5	69	17	3.7	1.8	8.2	9	2.2	70	2.4	100
cycle 6	67	14	2.7	5.6	11	2	2.1	60	2.7	93

^{*a*}Gasification occurred at 2.1 MPa and 700 °C. CaO regeneration occurred at 0.1 MPa and 900 °C, and CaO was then reused in the next cycle with fresh coal. Results include syngas composition during gasification, the first-order coal conversion rate out to 40% reduction charge remaining, normalized capture percentage during gasification, CO_2 release rate during calcination, and overall carbon exiting reactor during gasification and calcination normalized by carbon in input coal.

standard deviation of $\pm 4.2\%$; (c) there was a slight increase in the sulfur composition; and (d) there was not a significant change in the CO₂ release kinetic rate. Because there was less CO_2 capture by the calcium oxide with an increasing cycle number, this shows up in the syngas composition as higher values of carbon dioxide and lower values of hydrogen, but there was no significant change in methane, ethane, or carbon monoxide composition. It should also be noted that the average degradation rate per cycle that we measured is consistent with the results from prior studies (as summarized in the study by Weimer et al.¹⁸). The silica aluminates and the sulfur in the ash can react with CaO to form species that cannot capture carbon dioxide, as will be discussed further in section 4. If these reactions are not kinetically limited, the ash in the coal could account for a degradation of roughly 3% per cycle and the sulfur in the coal could account for a degradation of roughly 1% per cycle, for a combined degradation of roughly 4% per cycle. Therefore, we conclude that the cause of the degradation in the capture ability is likely the sulfur and the silica aluminates in the ash. Though, it should be noted that we cannot rule out other degradation methods, such as sintering of the calcium oxide.

In Table 6, we present a single-cycle experiment in which fresh lime and the Wyodak-Anderson coal were mixed with 30 g of water prior to coal gasification. This single cycle test was repeated 3 times, and the average values from the three realizations are shown in Table 6. One noticeable effect of mixing the coal and CaO aqueously before the experiment was that the amount of hydrocarbons in the syngas increased significantly compared to an exactly similar experiment but without aqueous mixing of the coal and CaO. There was also a slight increase in the gasification kinetics when CaO was mixed aqueously with the coal compared to the results in Table 5 without H₂O addition prior to gasification (1.1 versus ~0.7 h⁻¹.) While the addition of water increased the kinetic rate, we discuss in the next section a way to further increase the steam– coal gasification kinetics.

3.6. Cycle Degradation of Calcium Oxide and Potassium Hydroxide. In the next set of experiments, we studied the effect of adding a small amount of potassium hydroxide to the coal and calcium oxide to increase the rate of reaction. We conducted these experiments because the steamcoal gasification kinetic rates using only CaO, as seen in Tables 5 and 6, were only on the order of 1 h^{-1} . This is not particularly fast compared to gasification rates in oxygen-blown gasifiers, <1 s⁻¹. Therefore, to increase the kinetic rate and, hence, decrease the reactor size for a given required flow rate of syngas, we evaluated the impact of adding 1 g of KOH to 8.2 g of CaO added at the start of a set of six cycles. In addition, to further to improve the capability of KOH to catalyze reactions with coal, we have mixed CaO and KOH with the coal and 30 g of water. Mixing alkali or alkali earth catalyst with coal and water has been shown by previous authors $^{35-38}$ to increase the ability of the alkali to catalyze steam-coal gasification because the alkali and alkali earth species can ion exchange with protons from carboxylic acid and hydroxyl groups in the coal. In particular, CaO plays in important role inside the gasifier in keeping the

potassium in an active form, so that the alkali species is free to catalyze reactions with the coal.³⁹ In section 4, we will discuss further how CaO keeps potassium in an active form. In the experiments presented in this section, the gasification and regeneration steps were conducted exactly the same as in Table 5, except 1.0 g of KOH added before the first cycle and the fresh coal and regenerated material from the previous cycle were mixed with 30 g of water before being added to the reactor.

Table 7 shows results, similar to Table 5, in which a series of six CaO gasification/CaCO₃ calcination cycles were performed to measure the degradation in the ability of regenerated catalysts and capture agents to catalyze steam-coal gasification and to capture carbon dioxide and hydrogen sulfide. In Table 7, we present the syngas composition during gasification, the firstorder coal conversion rate out to 40% reduction charge remaining, the percentage of the calcium oxide that captures CO₂, the first-order release rate of the calcium carbonate during regeneration (calcination), and overall carbon balance. As in Table 5, each data point represents an average of two experiments, where each experiment was taken out to six cycles. With increasing cycle number, the trends were the following: (a) decreasing hydrogen and increasing carbon dioxide and carbon monoxide, (b) no significant decrease in the ability to capture H_2S_1 (c) no significant change in the kinetic rate, and (d) a slight decrease in the CO_2 release rate during the regeneration phase. The CO₂ capture percentage decreased an average of 3.8% after each cycle, with a standard deviation of $\pm 3.5\%$. The average measured carbon balance across the 12 experiments in Table 7 was 96%, and the standard deviation was 10%, which means that the expected value for the carbon balance (100%) falls within the 1 standard deviation of the average measured value for the carbon balance.

In comparison to the results in Table 5, there were clear advantages of adding 1 g of KOH with the calcium oxide before the first experiment and mixing the regenerated catalyst aqueous with the fresh coal before each experiment. There was a roughly 3-fold increase in the coal gasification conversion rate than when only the regenerated calcium oxide was drymixed with the coal. The 1.0 g of alkali hydroxide represents a K/C molar ratio of 0.06. This value of \sim 2.2 h⁻¹ is close to the value of 1.9 h⁻¹ that we measured in a previous work²⁴ using the same pressure, coal type, temperature, and steam flow rate but using a 1:1 molar ratio of alkali hydroxide/carbon when the Wyodak-Anderson coal and catalyst were dry-mixed before loading into the reactor. This value of \sim 2.2 h⁻¹ is well above the value of 0.34 h^{-1} that we measured in a previous work²⁴ under the same conditions but with the dry mixing of a ~0.25:1 molar ratio of alkali/carbon (when the alkali was either in the form of alkali carbonate or alkali hydroxide). This value of ~ 2.2 h^{-1} was also well above the value of 1.0 h^{-1} when mixing CaO with coal aqueously. We therefore conclude that the reason for the significantly improved kinetics was a combination of using an alkali hydroxide and aqueously mixing the catalyst with the coal. Using only 1 g of potassium carbonate or only aqueously mixing CaO with the coal did not achieve the large value of kinetics measured when using CaO + KOH mixed with the coal and water.

4. DISCUSSION AND ANALYSIS

In general, there are two factors that limit the number of times that material could be reused in the $CaO-CaCO_3$ cycle: (1) degradation in the capture capability after repeated cycles and

(2) for the particular case of selling the bleed stream, limits in the $CaSO_4$ and ash content specified by the cement kiln. We discuss these topics in the next two sections, which will explain the rationale behind only collecting data out to six cycles in previously discussed figures.

4.1. CO_2 Capture and CaO Degradation Mechanisms. As was seen in Tables 5 and 7, the capability to capture carbon dioxide decreases with an increasing cycle number. In Table 8,

Table 8. Gas- and Solid-Phase Chemical Reactions Inside of the Gasifier with *in Situ* Capture of Acid Gases

reaction	$\Delta H^{1000 \text{ K}}$ (kJ mol ⁻¹)	$\Delta G^{1000 \text{ K}}$ (kJ mol ⁻¹)
$CO_2(g) + CaO(s) \rightarrow CaCO_3(s)$	-169	-23
$\begin{array}{l} CaCO_3(s) + SiO_2(s) \rightarrow CO_2(g) + \\ CaSiO_3(s) \end{array}$	+79	-68
$\begin{array}{l} {\rm CaCO}_3(s) + {\rm Al}_2{\rm SiO}_5(s) \rightarrow {\rm CaAl}_2{\rm SiO}_6(s) + \\ {\rm CO}_2(g) \end{array}$	+101	-60
$CaO(s) + H_2S(g) \rightarrow CaS(s) + H_2O(g)$	-60	-61
$CaO(s) + FeS(s) \rightarrow CaS(s) + FeO(s)$	-11	-11
$\begin{array}{l} CaSiO_3(s) + H_2S(g) \rightarrow CaS(s) + SiO_2(s) + \\ H_2O(g) \end{array}$	+30	+30
$\begin{array}{l} \text{CaAl}_2\text{SiO}_6(s) + \text{H}_2\text{S}(g) \rightarrow \text{CaS}(s) + \\ \text{Al}_2\text{SiO}_5(s) + \text{H}_2\text{O}(g) \end{array}$	+8	+21
$\begin{array}{l} \text{CaSiO}_3(s) + 2\text{HCl}(g) \rightarrow \text{CaCl}_2(s) + \\ \text{H}_2\text{O}(g) + \text{SiO}_2(s) \end{array}$	-122	-15
$\begin{array}{l} 2 \mathrm{KOH}(s) + \mathrm{CO}_2(g) \rightarrow \mathrm{K}_2 \mathrm{CO}_3(s) + \\ \mathrm{H}_2 \mathrm{O}(g) \end{array}$	-189	-91
$\begin{array}{l} CaCO_3(s) + 2KOH(s) \rightarrow K_2CO_3(s) + \\ CaO(s) + H_2O(g) \end{array}$	-20	-68
$K_2S(s) + CaCO_3(s) \rightarrow K_2CO_3(s) + CaS(s)$	-34	-52
	+143	+14
$\begin{array}{l} 2KCl(s) + CaCO_3(s) \rightarrow K_2CO_3(s) + \\ CaCl_2(s) \end{array}$	+141	+122
$\begin{array}{l} K_2SiO_3(s) + CaCO_3(s) \rightarrow K_2CO_3(s) + \\ CaSiO_3(s) \end{array}$	+16	-48
$\begin{array}{l} K_2CO_3(s) + SiO_2(s) \rightarrow K_2SiO_3(s) + \\ CO_2(g) \end{array}$	+87	-58

we present a list of the chemical enthalpy and Gibbs free energy for important gas/solid phase reactions in the coal gasifier. To minimize space, we have not shown chemical reactions that are combinations of the reactions below. Note that the values of ΔH and ΔG are given at 1000 K and for all gases at partial pressures of 0.1 MPa. The reaction enthalpies and Gibbs free energies of the reactions were calculated using HSC Chemistry 6.

We draw the following conclusions from the equilibrium thermodynamic data listed in Table 8. First, it is thermodynamically favored for calcium oxide and calcium carbonate to chemically react with the silica aluminates in coal ash and to lose its capability to capture either CO_2 or H_2S . Second, calcium silicate can still be used to capture strong acid gases, such as hydrogen chloride, but the preferred state of chloride in the gasifier is potassium chloride, which was shown not to be catalytic by previous researchers.³⁸ Abotsi et al.³⁸ showed that potassium hydroxide, carbonate, and sulfide are active catalysts, whereas potassium silicate and chloride are inactive because of their stronger ionic bonds and higher melting temperatures.

Using the data in Table 8 as well as data from HSC Chemistry 6 not listed in Table 8 also at 1000 K and 0.1 MPa, we have ranked the thermodynamic stability of various solid states of calcium and potassium. For calcium, the ranking from least to most stable is the following: $Ca(OH)_2 < CaO < CaCO_3$

< CaS < CaSiO₃ < CaCl₂. For potassium, the ranking from least to most stable anion is slightly different from calcium: $K_2O <$ $KOH < K_2S < K_2CO_3 < K_2SiO_3 < KCl$. For any given anion, we found the following ranking as far as which cation was more stable: CaCO₃ < K₂CO₃; K₂S < CaS; K₂SiO₃ < CaSiO₃; and $CaCl_2$ < KCl. Therefore, for the case of thermodynamic equilibrium in the gasifier when there is more Ca than K, we can state the following: (1) carbon dioxide will first be captured by potassium before it is captured by calcium; (2) hydrogen sulfide will be captured by calcium; (3) alumina silicates in the ash will deactivate calcium rather than potassium; and (4) chlorides in the fuel, if present, will deactivate the potassium rather than the calcium. From this information, we can conclude that, from a thermodynamic point of view, the sulfur and alumina silicates in the coal will be able to decrease the capture capability of the catalysts; however, sulfur and alumina silicates in the coal will not be able to convert potassium cations into a non-catalytic solid because the sulfur and alumina silicates prefer thermodynamically to be bound with calcium cations. Because the degradation of the calcium oxide as a result of the interaction with the sulfur and alumina silicates, there would be a limit to the number of cycles that the regenerated material can be used, and this means that a purge stream of roughly 2-4% of the material would be have to be removed and replaced by fresh calcium carbonate. However, as we will see in the next section, if the bleed stream is to be sold to a cement kiln, then there will be more stringent limitations on the number of cycles that the material can be reused.

4.2. Application to Co-generation of Cement Kiln Feedstock. In this section, we elaborate on one particular application of the CaO–CaCO₃ cycle in which the bleed stream is sold to a cement kiln as a precalcined feedstock. This is a particularly interesting application because selling the purge stream exiting the regenerator to a cement kiln would provide additional revenue, create less waste, and reduce GHG emissions from the cement kiln.⁴⁰ As will be shown in this section, in such a CaO–CaCO₃ process, the major limitation on the amount of material that can be recycled will likely be set by the sulfur and ash limitations imposed by cement kilns on precalcined feedstock. Figure 4 illustrates what this process shown is similar to that patented by Hippo and Sheth⁴¹ and assigned to GreatPoint Energy, Inc. (Cambridge, MA). As



Figure 4. Process flow diagram of the CaO/CaCO₃ cycle with the addition of potassium hydroxides to increase reaction kinetics.

Figure 4 shows, the purge stream would likely occur after the regenerator because the mostly CaO purge stream could be sold as precalcined feedstock to a cement kiln rather than placing the purge stream after the gasifier and removing material as calcium carbonate.

For such an application, it is important to estimate the amount of makeup CaO and KOH that would be required to sell the bleed stream as input into a cement kiln. The amount of makeup $CaCO_3$ and KOH (or K_2CO_3) and, hence, the amount of bleed stream will be a function of the limitations on the amount of $CaSO_4$ and ash that a cement kiln can accept in its precalcined feedstock. If there is sub-stoichiometric $O_2(g)$ sent to the regenerator, then $SO_2(g)$ is a possible product leaving the calciner.¹⁰ However, if there is excess oxygen during CaO regeneration, CaS converts into CaSO₄ and will not release $SO_3(g)$ because the ΔG for $SO_3(g)$ release from $CaSO_4$ at 900 °C is +196 kJ mol⁻¹. Therefore, CaSO₄ will accumulate in this cyclic process unless there is purge stream that removes as many moles of sulfur as are captured inside the gasifier. Weimer et al.¹⁸ discussed these limitations in a paper on their CLP, which they called lime-enhanced gasification (LEGS) of brown coal, which is a process that occurs at pressures around 3.0 MPa and temperatures less than 800 °C. They analyzed the amount of purge stream required to meet requirements at typical cement kilns for <10 wt % CaSO₄ and <30 wt % ash, where ash here means alumina silicate, chloride, iron, titanium, and phosphorus composition of the solid mixture. They analyzed the case of a German brown coal with a similar ash content but a higher sulfur content than the Wyodak-Anderson subbituminous coal analyzed here. They determined that meeting the sulfur requirement would require a higher purge rate than the purge rate based off of the ash limitation.

Assuming the limitations listed in the study by Weimer et al.¹⁸ of less than 10 wt % CaSO₄ and less than 30 wt % ash as well as using the data collect in this paper, we calculated the maximum number of cycles that the catalyst-capture agent material could be reused and, hence, the purge stream fraction required. First, we calculated the case if the ash content was the limiting case. If one ignores the sulfur content, then the purge fraction of calcium oxide and, hence, the makeup fraction of calcium carbonate should be roughly 11% of the amount of total calcium oxide going around the process. To meet the requirement that the silica, alumina, and iron contents of the purge stream are less than 30% of the solids mixture, the calcium oxide can only go through roughly nine cycles on average before being purged. Second, if one considers only the sulfur content, then the purge fraction of calcium oxide and, hence, the makeup fraction of calcium carbonate should be roughly 18% of the amount of total calcium oxide going around the process. Therefore, to meet the requirement that the CaSO₄ content of the purge stream is less than 10% of the solids mixture, the calcium oxide can only go through roughly six cycles on average before being purged. This means that, as in the case of the brown coal case studied by Weimer et al.,¹⁸ the sulfur limit is more restrictive than the ash limit.

An ideal fuel for such a $CaO-CaCO_3$ cycle would be very low in sulfur content, so that the bleed stream could be sold to a cement kiln as a precalcined feedstock without creating large bleed streams. This sulfur limitation is the main reason why we only collected results out to six cycles using the 0.6 wt % sulfur Wyodak-Anderson coal and why we did not collect data with the 2 wt % sulfur Pittsburgh no. 8 coal.

5. CONCLUSION

We have experimentally demonstrated a fixed-bed CaO-CaCO₃ process for turning coal into a syngas that is roughly 15% CH₄, 75% H₂, 3% C₂H₄₋₆, 6% CO, and 1% CO₂. The ratio of carbon to reduction charge for this syngas is 0.09 (mol of C/ mol of e^{-}), less than this ratio for methane, 0.125 (mol of C/ mol of e⁻). Because of the presence of pyrolysis gases, such as ethane, this syngas composition is not in chemical equilibrium, and this means that chemical equilibrium simulations of CaO-CaCO₃ processes in a fixed/moving-bed gasifier will drastically underestimate the amount of hydrocarbons in the syngas. Our results showed a 3-fold increase in the steam gasification kinetic rate when a small amount of potassium hydroxide was added along with CaO. At a commercial scale, this would likely mean that there could be a roughly 3-fold decrease in the size of the gasifier compared to the case of dry mixing coal and the regenerated calcium oxide. To measure steam-coal gasification rates, we developed a reduction charge (i.e., COD) balance approach that allows for a rate constant to be measured even though one cannot conduct carbon, hydrogen, or oxygen balance because of in situ CO₂ capture and water vapor condensation prior to the mass spectrometer. In addition, we conducted multi-cycle studies, in which CaO was calcined by heating to 900 °C and reused in repeated CaO-CaCO₃ cycles. The increased steam-coal gasification kinetics rates for both CaO and CaO + KOH persisted even when the material was reused in six cycles of gasification and calcination.

AUTHOR INFORMATION

Corresponding Author

*Telephone: (412) 386-4404. E-mail: nicholas.siefert@netl. doe.gov.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank the NETL Strategic Center for Coal for their support of this research. In particular, we thank Tristan McQuain, Jack Ferrel, Richard Bergen, David Ruehl, and William Grimes for their expertise during the operation of the gasifier.

REFERENCES

(1) Herzog, H. J. Greenhouse Gas Control Technol., Proc. Int. Conf., 5th 1999, 101–106.

- (2) Johnson, T. L.; Keith, D. W. Energy Policy 2004, 32, 367-382.
- (3) Rubin, E. S.; Chen, C.; Rao, A. B. Energy Policy 2007, 35, 4444–4454.
- (4) Rubin, E. S.; Mantripragada, H.; Marks, A.; Versteeg, P.; Kitchin, J. Prog. Energy Combust. **2012**, *38*, 630–671.
- (5) Davison, J. Energy 2007, 32, 1163-1176.

(6) Kunze, C.; Spliethoff, H. Fuel Process. Technol. 2010, 91, 934-941.

(7) Hammond, G. P.; Akwe, S. S. O.; Williams, S. *Energy* 2011, 36, 975–984.

(8) United States Environmental Protection Agency (U.S. EPA). Standards of Performance for Greenhouse Gas Emissions for New Stationary Sources; U.S. EPA: Washington, D.C., 2012; EPA-HQ-OAR-2011-0660; FRL-RIN 2060-AQ91.

(9) Dean, C. C.; Blamey, J.; Florin, N. H.; Al-Jeboori, M. J.; Fennell, P. S. Chem. Eng. Res. Des. 2011, 89, 836–855.

(10) Curran, G. P.; Fink, C. E.; Gorin, E. Adv. Chem. Ser. 1967, 141– 165.

(11) Kuramoto, K.; Ohtomo, K.; Suzuki, K.; Fujimoto, S.; Shibano, S.; Matsuoka, K.; Suzuki, Y.; Hatano, H.; Yamada, O.; Shi-Ying, L.;

Harada, M.; Morishita, K.; Takarada, T. Ind. Eng. Chem. Res. 2004, 43, 7989–7995.

(12) Fan, L. S.; Li, F. X.; Ramkumar, S. Particuology 2008, 6, 131–142.

(13) Ramkumar, S.; Fan, L. S. Energy Fuels 2010, 24, 4408-4418.

(14) Ramkumar, S.; Iyer, M. V.; Fan, L. S. Ind. Eng. Chem. Res. 2011, 50, 1716-1729.

(15) Fan, L. S.; Zeng, L.; Wang, W. L.; Luo, S. W. Energy Environ. Sci. **2012**, *5*, 7254–7280.

(16) Chiesa, P.; Lozza, G.; Mazzocchi, L. J. Eng. Gas Turbines Power 2005, 127, 73.

(17) Wu, J.; Brown, P.; Diakunchak, I.; Gulati, A.; Lenze, M.; Koestlin, B. Advanced gas turbine combustion system development for high hydrogen fuels. *Proceedings of the ASME Turbo Expo 2007: Power for Land, Sea and Air*; Montreal, Canada, May 14–17, 2007.

(18) Weimer, T.; Berger, R.; Hawthorne, C.; Abanades, J. C. Fuel 2008, 87, 1678–1686.

(19) Cheng, S.-I. Integrated gasification process. U.S. Patent 4,353,713, Oct 12, 1982.

(20) Squires, A. M. In *Fuel Gasification*; American Chemical Society (ACS): Washington, D.C., 1967; Advances in Chemistry, Vol. *69*, Chapter 14, pp 205–229.

(21) Stamnore, B. R.; Gilot, P. Fuel Process. Technol. 2005, 86, 1707–1743.

(22) Florin, N. H.; Harris, A. T. Chem. Eng. Sci. 2008, 63, 287-316.

(23) Liu, W.; An, H.; Qin, C.; Yin, J.; Wang, G.; Feng, B.; Xu, M. *Energy Fuels* **2012**, *26*, 2751–2767.

(24) Siefert, N.; Shekhawat, D.; Litster, S.; Berry, D. *Energy Environ. Sci.* **2012**, *5*, 8660–8672.

(25) Kamo, T.; Takaoka, K.; Otomo, J.; Takahashi, H. Fuel **2006**, 85, 1052–1059.

- (26) Nishiyama, Y. Fuel Process. Technol. 1991, 29, 31-42.
- (27) Pereira, P.; Somorjai, G. A.; Heinemann, H. Energy Fuels **1992**, 6, 407–410.

(28) Hirsch, R. L.; Gallagher, J. E.; Lessard, R. R.; Wesselhoft, R. D. Science **1982**, 215, 121–127.

- (29) Wood, B. J.; Sancier, K. M. Catal. Rev. 1984, 26, 233-279.
- (30) Vorres, K. S. Energy Fuels 1990, 4, 420-426.
- (31) Berguerand, N.; Lyngfelt, A. Fuel 2008, 87, 2713-2726.
- (32) Xu, X.; Xiao, Y. H.; Qiao, C. Z. Energy Fuels 2007, 21, 1688-1694.

(33) Wen, C. Y.; Lee, E. S.; Dutta, S. Coal Conversion Technology; Addison-Wesley Pub. Co.: Reading, MA, 1979.

(34) Probstein, R. F.; Hicks, R. E. *Synthetic Fuels*; Dover Publications: Mineola, NY, 2006.

- (35) Li, C. Z. Fuel 2007, 86, 1664–1683.
- (36) Stojanowska, G.; Jones, J. M. J. Energy Inst. 2005, 78, 126-138.

(37) Yamashita, H.; Nomura, M.; Tomita, A. Energy Fuels 1992, 6, 656-661.

(38) Bota, K. B.; Abotsi, G. M. K.; Sims, L. L. Energy Fuels 1994, 8, 937-942.

(39) Wang, J.; Yao, Y.; Cao, J.; Jiang, M. Fuel 2010, 89, 310-317.

(40) Rodriguez, N.; Alonso, M.; Abanades, J. C.; Grasa, G.; Murillo, R. *Greenhouse Gas Control Technol., Proc. Int. Conf., 9th* **2009**, *1*, 141–148.

(41) Hippo, E. J.; Sheth, A. C. Mild catalytic steam gasification process. US 2007/0000177 A1, June 1, 2006.