

## ANION EFFECTS ON CALCIUM CATALYSIS OF LOW-RANK COAL CHAR-STEAM GASIFICATION

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### ABSTRACT

Limestone (primarily  $\text{CaCO}_3$ ) has been shown to be an excellent bed material in a fluidized-bed reactor operated at 700-800°C and atmospheric pressure for the steam gasification of coal. It not only maintains its physical integrity under these conditions but also has shown catalytic effects on a subbituminous coal-steam reaction that are comparable with the effects of an alkali salt. The study reported in this paper concerns the effect, if any, of calcium-associated anions on the reaction kinetics of the coal char-steam reaction. Velva lignite and Wyodak subbituminous coals to which  $\text{CaO}$ ,  $\text{CaSO}_4$ , limestone, or  $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$  had been added, were charred in a thermogravimetric analysis unit (TGA) and then were immediately reacted with steam at the temperature and pressure conditions described above. Both coals showed less catalytic effect for limestone and calcium sulfate than for the other two additives. The rate for the Wyodak char-steam reaction increased steadily over 700-800°C with calcium oxide whereas the Velva rate increased rapidly to the maximum between 700-750°C. Apparent activation energies along with surface analyses of selected samples to determine catalyst dispersion and form will be presented.

### INTRODUCTION

Gasification of coal has been shown by many researchers to be greatly enhanced by the addition of alkali or alkaline-earth compounds to the reaction mixture. In the case of the alkali compounds, the excellent catalytic effect of carbonates, hydroxides and bicarbonates, and the somewhat lesser effect of chlorides and sulfates of potassium and sodium are well documented. However, the reasons for the large differences in catalysis that occur with changes in anion have not been satisfactorily explained, and those reasons have been the focus of only limited study, since the negative aspects of using potassium and sodium minerals as catalysts make them impractical to use under present processing conditions. The major drawback to using potassium is the relatively high cost of its catalytically active minerals. Although sodium compounds are plentiful in mineral deposits (trona, nahcolite, sodium chloride) and therefore relatively inexpensive, the inherent problems, such as fouling and agglomeration, associated with having sodium in a reactor make them unsatisfactory additives. Limestone, largely calcium carbonate, has been shown to have a catalytic effect on the reaction between low-rank coal char and steam at temperatures of 700-800°C and ambient pressure in a continuous process unit (CPU)(1). This mineral is not only inexpensive and causes few reactor problems, but also is, in fact, a viable candidate for bed material in fluidized-bed reactors and is promoted by some researchers as an in-bed sulfur-capture material. The question as to the importance of the carbonate, if any, on the activity of the catalyst was addressed in this study by substituting other calcium compounds for limestone in two previous thoroughly-studied char-steam reactions. The answer to the question was expected to provide some understanding of the effect of the anion on the reactivity of the char-steam reaction.

Table 1 shows the elemental analyses of the ash of the raw coals. Both of the coals reacted had a high calcium content.

## EXPERIMENTAL

Laboratory reactivity testing was carried out at 700, 750, and 800°C and ambient pressure on a DuPont 951 Thermogravimetric Analysis (TGA) module interfaced with a DuPont 1090 Thermoanalyzer data station. Approximately 40 milligrams of -60 x 0 mesh raw coal containing 10 wt% catalyst was devolatilized in vitro, followed immediately by reaction of char carbon with steam as previously reported (2). The reactivity parameter,  $k$ , was calculated for 50% carbon gasification in each test.

Pilot-scale data was obtained from experiments carried out in a nominal 30-lb/hour CPU operating at ambient pressure and temperatures similar to those reported for the TGA experiments (1).

## CALCIUM CATALYST SCREENING

Wyodak subbituminous and Velva lignite char-steam reactions were carried out using four calcium-containing catalysts, calcium oxide, calcium sulfate, limestone, and calcium acetate, at 700, 750, and 800°C and atmospheric pressure. The choice of limestone is obvious (see Introduction). Calcium oxide was chosen because it has been reported to be the predominant species responsible for catalysis of the gasification reaction (3). Calcium acetate was selected since it is water soluble and, upon heating, decomposes into calcium carbonate and acetone. Since calcium sulfate is insoluble and does not readily decompose at the temperatures of this study it was the final choice. The Arrhenius energy of activation,  $E_a$ , and the correlation coefficient,  $r_2$ , for the Arrhenius plot, along with the reactivity parameter of each of the reactions is reported in Tables 2 and 3. In addition,  $k$  values calculated from CPU data are also given for experiments where limestone was used as bed material. There appears to be a significant difference in the catalysis of the Wyodak char-steam reaction among the materials tested.

TABLE 1

XRFA RESULTS OF ASH PREPARED FROM AS-RECEIVED VELVA LIGNITE AND WYODAK SUBBITUMINOUS COALS USED IN HYDROGEN PRODUCTION TESTS

Element	Velva Ash % Elemental	Wyodak Ash % Elemental
Silicon	5.57	11.44
Aluminum	5.00	7.55
Iron	12.73	12.45
Titanium	0.38	0.76
Phosphorous	0.20	0.55
Calcium	25.49	14.80
Magnesium	6.52	3.53
Sodium	0.45	0.92
Potassium	0.00	0.00
Sulfur	4.68	5.47
Oxygen (Diff.)	38.98	42.53
Ash	6.94	9.05

TABLE 2  
 REACTIVITY PARAMETER FOR WYODAK CHAR-STEAM REACTIONS CATALYZED  
 WITH VARIOUS CALCIUM-CONTAINING SUBSTANCES.

TEMP, C°	Uncat.	Limestone		CaO	CaSO <sub>4</sub>	Ca(Ac) <sub>2</sub>
		k, in g/hr/g				
		TGA	CPU			
700	1.33	1.26	1.60	3.80		
750	3.28	3.01	3.53	6.36	2.77	4.33
800	7.33	3.86	38.98	15.74		
E <sub>‡</sub>	35.45	23.35	65.64	29.34		
r <sup>2</sup>	1.00	0.92	0.95	0.97		

TABLE 3  
 AVERAGE REACTIVITY PARAMETER FOR VELVA CHAR-STEAM REACTIONS  
 CATALYZED WITH VARIOUS CALCIUM-CONTAINING SUBSTANCES.

TEMP, °C	Uncat.	Limestone		CaO	CaSO <sub>4</sub>	Ca(Ac) <sub>2</sub>
		k, in g/hr/g				
		TGA	CPU			
700	2.40	4.95	2.24	6.89		
750	4.95	6.84	5.45	8.01	4.75	6.80
800	6.89	6.95	49.13	10.86		
E <sub>‡</sub>	22.05	7.14	63.57	9.38		
r <sup>2</sup>	0.97	0.81	0.96	0.95		

## RESULTS AND DISCUSSION

Dispersion of catalyst over the organic matrix is a major consideration when studying gasification and catalyst effects (4,5).

Each of the catalysts studied was applied by admixing 10 wt% with coal. Impregnation was not used so as to preserve the integrity of the anion on contact with the raw coal. Of the four calcium catalysts chosen, two (acetate and oxide) were soluble in water and two were not. In coal with 30+% moisture, water-soluble catalyst can disperse into water-filled micropores as well as over the moist surface of particles. In addition, the CaO forms a base, Ca(OH)<sub>2</sub>, when dissolved in water enabling it to better penetrate the coal structure. However, since the water-insoluble catalysts (carbonate and sulfate) were applied as <150 um particles, they were limited to a finite number of contact surfaces and were probably excluded from most micropores. The variation in solubility that results in differences in catalyst dispersion accounted for some of the effects noted in the study.

The uncatalyzed char-steam reactions had rate constants,  $k$ , which were slightly higher at 700°C and 750°C for Velva than for the Wyodak char. This was attributed to catalysis caused by the higher inherent calcium content of the Velva coal. The Velva coal has 33% more calcium and magnesium than the Wyodak coal on a mole-of-element/gram-of-coal basis. The inherent sodium content of the Wyodak, albeit small, was more than twice as great as that of the Velva but probably too small to give obvious rate increases. Silicon and aluminum, which are known catalyst killers, were nearly three times and two times as abundant, respectively, in Wyodak as they were in Velva. However, at 800°C the Wyodak  $k$  was slightly higher than that of the Velva, probably because of limitations due to physical effects such as mass transport rather than chemical reactivity (6).

The catalyst effects observed in this study varied between the two coals. The CaO gave reactivities which were similar for the two coals at 700°C and 750°C but was 1.5 times greater for the Wyodak than for the Velva at 800°C. The limestone-catalyzed reactions had reactivities that were two-fold greater for the Velva than for the Wyodak at each temperature. The calcium acetate-catalyzed Velva char-steam reactivity at 750°C was 1.5 times larger than that of Wyodak. The calcium sulfate appeared to have no positive catalytic effect at 750°C with either coal char.

The catalytic effect of the calcium on the char-steam reaction for each coal varied substantially with the associated anion. With the Wyodak coal little positive effect was observed for the limestone at the three temperatures tested, and no positive effect, and perhaps even some inhibition, was observed for the calcium sulfate at 750°C. The calcium oxide doubled the reactivity of the Wyodak, but it must be realized that a 10 wt% loading of this material provides 7 wt% calcium whereas the other catalysts tested contributed <4 wt% of the element. Calcium acetate also increased the reactivity of the Wyodak at 750°C even though 10 wt% provides only 2.8 wt% calcium.

With the Velva coal, limestone exhibited catalysis at the lower two temperatures. Calcium oxide, as with the Wyodak coal, enhanced the reaction at all three temperatures. At 750°C calcium sulfate did not catalyze the reaction but the acetate conferred as much catalysis as the limestone at the same temperature.

The Arrhenius energy of activation,  $E_a$ , varied greatly with calcium catalyst in this suite of tests. Wyodak, even in the presence of additive, had a much higher energy requirement for reaction than the Velva.

A comparison of the rate constants obtained using limestone catalyst on the TGA with those of the Continuous-Process-Unit (CPU) showed good agreement at 700°C and 750°C but lack of agreement at 800°C. The fluidized bed provided for improved heat transfer and mass transport compared to the fixed bed of the laboratory unit. In addition, the temperature of the reported 800°C experiment in the CPU was actually 10 to 15 degrees hotter than that of the bench-scale experiments. The limestone used in this experiment undergoes a thermally induced transition at 800°C as shown by Differential Thermal Analysis (DTA) resulting in what appeared by Scanning Electron Microscope (SEM) to be fragmentation of the limestone particles and the subsequent wider dispersion of catalyst. Thus the difference in rate constants for the two reactors at 800°C was probably due to a relatively large TGA sample size which resulted in transport limitations and the lower TGA reaction temperature. The deviation of the correlation coefficient ( $r^2$ ) from 1.00 could also be an indication of those limitations, although from this study there is no basis for ruling out a change in mechanism.

## CONCLUSIONS

- Calcium catalysis of char-steam reactions of low-rank coals is affected by the associated anion.
- Rate constants determined by TGA are comparable with those obtained with the 30-lb/hr CPU.
- Water-soluble calcium compounds are better low-rank coal reaction promoters than those that are insoluble.
- Calcium inherent to the coal does not necessarily affect catalysis by calcium additives.

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