CATALYTIC EFFECT ON THE GASIFICATION OF A BITUMINOUS ARGONNE PREMIUM COAL SAMPLE USING WOOD ASH OR TACONITE AS ADDITIVE

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ABSTRACT

Illinois #6 from the Argonne Premium Coal Sample Program was gasified with and without catalyst added. Catalyst loading effects and the effect of catalysis on screen fractions were studied using K_2CO_3 as the catalyst. The reactivity increased significantly with each 2.8 wt% of additional potassium as potassium carbonate until there was 11.3 wt% potassium. The reactivity increased slightly with 14 wt% potassium and again slightly with 17 wt% potassium present. The order of the reaction with respect to carbon approached zero with the higher catalyst loading. Wood ash with its high potassium (12 wt%) and calcium content (47 wt%) was shown to be as good a catalyst as the K_2CO_3. Taconite, an iron ore from northeastern Minnesota, is plentiful, relatively inexpensive, has the required characteristics for bed material, and may be a potential catalyst. In this test series, however, it exhibited only slight catalytic effects.

Beulah-Zap lignite from the Argonne Premium Sample Program was gasified with and without wood ash additive as a basis for comparison with Illinois #6 reactivities.

INTRODUCTION

Catalyzed and uncatalyzed steam gasification of low-rank coals (LRCs) to produce hydrogen-rich gas streams is a well-known process and is in commercial use today in this country (Dakota Gasification Plant, Beulah, North Dakota) and abroad. The successful process produces synthesis gas from which methane is produced to supplement clean-burning natural gas supplies. Besides augmenting transportable energy supplies, gasification provides a means of controlling undesirable emissions from coal utilization processes. Sulfur from the gasified coal is contained within the plant and is a by-product of the process. Steam gasification offers a means of utilizing high-sulfur (noncompliance) coals in such a way as to entrain and remove sulfur gasses before they are released to the atmosphere. As environmental standards become more rigid regarding sulfur emissions, gasification as a means of utilizing higher sulfur content coals may become more attractive.

Low-rank coals make good gasification feedstock due to inherent catalysts in the form of salts of alkali and alkaline earth elements and due to their reactive organic functionalities. These components give LRCs first order carbon reactivities of > 2 hr^{-1} at 750°C (1). Raw low-rank coals have consistently been shown to have higher reactivities in the gasification process than bituminous coals. Gasification of bituminous coals could become feasible if the reactivity of those coals with their greater carbon content/lb could be increased. Catalysis brought about by alkali and alkaline earth additives has been shown to increase the reactivities of these coals (2,3). Cost and availability of catalytic materials is a major concern when catalysis is required. As a result, reactivity, and supplies of inexpensive potential additives needed to increase that reactivity, becomes a primary consideration in selecting gasification feedstock. Several plentiful, naturally occurring materials (minerals) are available, including nahcolite, trona, halite, limestone, dolostone, potash, saltpeter, and sunflower seed hulls; most of which have been investigated as catalysts (4,5). The first three mentioned minerals are rich in sodium, the next two are rich in calcium, and the last three are rich in potassium, all of which are known to be good catalysts for the coal gasification reaction. Potassium and sodium have proven to be the best catalysts of this group. The advantage of using sodium is that its mineral deposits are much more common than potassium mineral deposits, making the former less expensive. The major disadvantage of sodium is the agglomeration of particles and the ash fouling that it causes. Although it is more expensive, potassium appears to cause less operational problems. Therefore, if a source can be found that is less expensive than sources now available, and if recycling of the potassium can be made possible, potassium will become the best choice of catalyst from the alkali-alkaline earth materials mentioned above. Wood ash which typically has a high potassium content may be such a catalyst.

Transition metals have also been shown to catalyze the coal gasification reaction. Taconite, a metal ore from Minnesota, is plentiful, inexpensive, and rich in iron, making it a candidate for a gasification additive.

This paper reports the results of a bench-scale study of steam-char rate enhancement conferred to Illinois #6 from the Argonne Premium Coal Sample Program by the presence of potassium carbonate (K_2CO_3), wood ash, or taconite. An Argonne sample of Beulah-Zap lignite was gasified and reported on for comparison.

EXPERIMENTAL

The coals tested were Illinois #6 (Herrin seam) and Beulah-Zap (Beulah-Zap seam) from the Argonne Premium Coal Sample Program. They were received in 10-gram lots in sealed vials and were used directly from the vials without further preparation, other than catalyst addition. Unused sample was stored under inert gas in sealed 20-mL scintillation vials. Proximate and ash analysis are shown in Table 1.

Ten weight percent dry catalyst was admixed with each coal to be tested. Dispersal of the catalyst was accomplished by shaking the coal-additive mixture vigorously in closed vials for ca. ten minutes. The catalysts were prepared by combustion in air. Hardwood (cottonwood and aspen) ash was prepared in a small batch. The cottonwood/aspen ash was the remnants of a domestic fireplace fire. The plywood ash was provided by Northwood Panelboard Co, Solway, Minnesota.

Approximately 40 milligrams of coal or coal/catalyst material is loaded onto the pan of the DuPont 951 thermogravimetric analysis microbalance module. The quartz tube enclosing the pan and serving as the reaction chamber is secured by a knurled nut to the balance housing. The reaction chamber is purged with an ambient pressure argon flow at ca. 160 cm^3/min. The sample is heated at ~100°C/min to the target temperature at which point the $H_2O_{(g)}$ flow is introduced through the side arm of the quartz tube, and argon flow is reduced to ca. 60 cm^3/min. The reaction was carried out at 700°, 750°, and 800°C. Total gas effluent can be collected in a gas bag for analysis by GC. Weight, time, and temperature are stored by the DuPont 1090 data station for later data reduction.

RESULTS AND DISCUSSION

Illinois #6 and Beulah-Zap lignite from the Argonne Premium Coal Sample Program were gasified with and without catalyst added. As shown in Table 2, the uncatalyzed bituminous coal char had typical low reactivities with steam in the 700°-800°C temperature range when compared with those of low-rank coal. The uncatalyzed Beulah-Zap reactivities at each of the three temperatures were 40-50 times greater than those of the Illinois #6. However, in the presence of only 1-2 wt% added potassium, the difference was reduced to < ten times and with 5 wt% added potassium, < 2 times.

Catalyst loading effects and the effect of catalysis on screen fractions of Illinois #6 were studied using K_2CO_3 as the model catalyst. The reactivity increased significantly with each 2.8 wt% of additional potassium as potassium carbonate, until there was 11.3 wt% potassium as shown in Figure 1. As potassium concentrations were increased to 14 wt% and 17 wt%, the reactivity increased only slightly. As the catalyst loading was increased, the dependence on carbon concentration decreased. The order of the reaction with respect to carbon approached zero with the higher catalyst loading, as shown in Figure 2.

Illinois #6 was sieved to get size fractions for reactivity testing. The fractions collected were +60 mesh (>0.250 mm), -60x100 mesh (0.250>p>0.149 mm), -100x140 mesh (0.149>p>0.105 mm), -140x200 mesh (0.105>p>0.074 mm), and -200x325 mesh (0.074>p>0.044 mm). Figure 3 shows the reactivity as a function of those sieve fractions.

Hardwood ash with its high potassium (12 wt%) and calcium content (47 wt%) was shown to have promise as a catalyst. Increased reactivity brought about by dry wood ash was slightly less than that of an equivalent amount of K_2CO_3, but the application of dried aqueous extract of the ash containing 39 wt% potassium did provide an equivalent increase in reactivity. Taconite, an iron ore from northeastern Minnesota, is plentiful, relatively inexpensive, and has the required characteristics for a bed material, and may be a catalyst for the coal char-steam reaction. In this test series, however, it exhibited only slight catalytic effects.

Illinois #6 agglomerated when heated to the gasification temperatures. However, addition of K_2CO_3 to the coal resulted in no observable agglomeration. A similar effect was noted on addition of the hardwood ash as a reaction catalyst, whereas addition of the ash from a plywood plant did not prevent agglomeration. Table 3 shows the elemental analyses of the ash from the coal with 10 wt% additive. The softening and collapsing of pores during agglomeration and subsequent decrease in surface area is at least partially responsible for the low reactivity of the coal. The addition of potassium carbonate and the hardwood ash resulted in decreased agglomeration as well as an increase in reactivity, whereas the ash from the plywood facility had little effect on either.

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TABLE 1

PROXIMATE AND ASH ANALYSES OF ILLINOIS #6 BITUMINOUS AND BEULAH-ZAP LIGNITE FROM THE ARGONNE PREMIUM COAL SAMPLE PROGRAM

	Illinois #6 Raw (TGA)		Beulah-Zap Raw (TGA)	
Sample	AR	MF	AR	MF
Moisture, wt%	9.41	--	32.66	--
Volatiles, wt%	34.75	38.36	30.19	44.83
Fixed C, wt%	41.08	45.35	30.67	45.54
Ash, wt%	14.76	16.29	6.49	9.64

XRF Analysis of Coal Ash

	Ill. #6		Beulah-Zap	
Element	% of Ash	% of Coal	% of Ash	% of Ash
Silicon	20.43	3.33	8.88	0.86
Aluminum	9.68	1.58	5.35	0.52
Iron	12.59	2.05	5.88	0.57
Titanium	0.60	0.10	0.42	0.04
Phosphorous	0.09	0.01	0.31	0.03
Calcium	5.64	0.92	16.72	1.63
Magnesium	0.72	0.12	6.27	0.61
Sodium	0.00	0.00	4.01	0.39
Potassium	2.41	0.39	0.33	0.03
Sulfur	2.72	0.44	6.37	0.62

TABLE 2

REACTIVITIES OF UNCATALYZED AND CATALYZED COAL CHAR WITH STEAM*

	Illinois #6					Beulah-Zap		
Catalyst	None	K_2CO_3	A[1]	B[2]	C[3]	Tac.	None	A[1]
				k, hr^{-1}				
Temp, °C								
700	0.06	--	--	--	--	--	2.30	3.64
750	0.15	4.36	--	--	3.01	0.41	7.76	8.67
800	0.33	--	0.35	0.54	--	--	14.61	10.41
E_a, kcal/mol	5.57						38.53	

* Assumed 1st order with respect to carbon.
[1] A Provided by Northwood Panelboard Co.
[2] B Residue from combustion of cottonwood/aspen.
[3] C Aqueous extract of hardwood ash.

TABLE 3

XRF ANALYSES OF ASH FROM COAL +10WT% CATALYST, wt%

			w/Ill. #6		w/B-Zap
XRFA Results	Ill. #6	B-Zap	Ash B	Ash A	Ash A
Silicon	3.33	0.86	4.49	5.04	2.58
Aluminum	1.58	0.52	1.95	1.97	1.77
Iron	2.05	0.57	2.26	2.22	2.27
Titanium	0.10	0.04	0.14	0.12	0.11
Phosphorous	0.01	0.03	0.07	0.06	0.02
Calcium	0.92	1.63	3.88	3.39	1.26
Magnesium	0.12	0.61	0.59	0.46	0.16
Sodium	0.00	0.39	0.12	0.07	0.01
Potassium	0.39	0.03	1.12	1.07	0.50
Sulfur	0.44	0.62	0.63	0.57	0.50
Total %	8.94	5.30	15.26	14.97	9.18

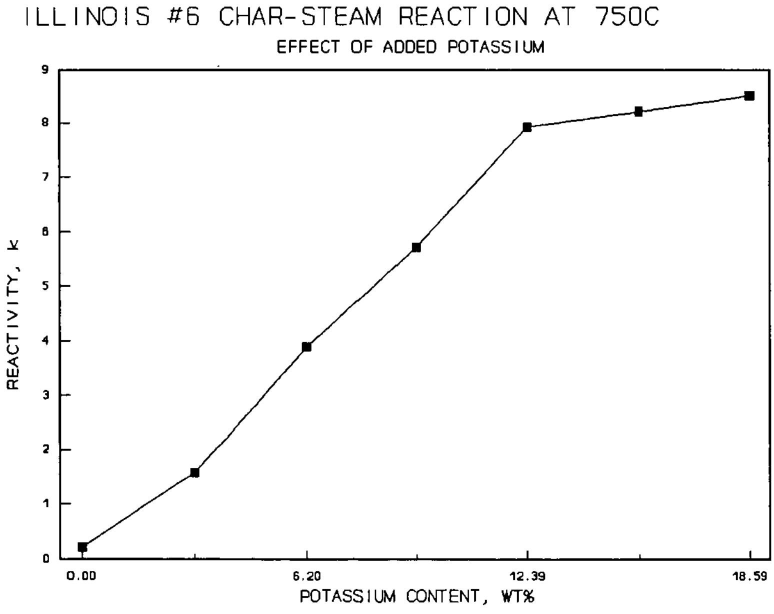

Figure 1. Effect of K_2CO_3 catalyst loading on Illinois #6 char-steam reactivity at 750°C.

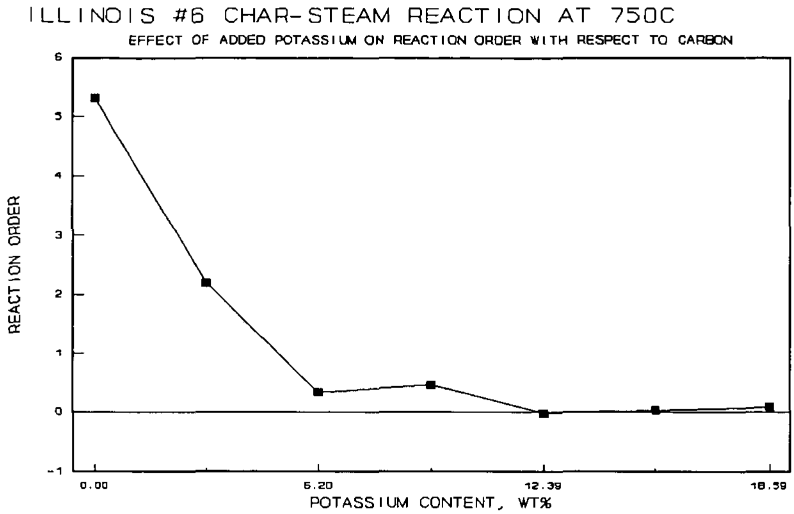

Figure 2. Effect of potassium loading on order of Illinois #6 char-steam reaction with respect to carbon.

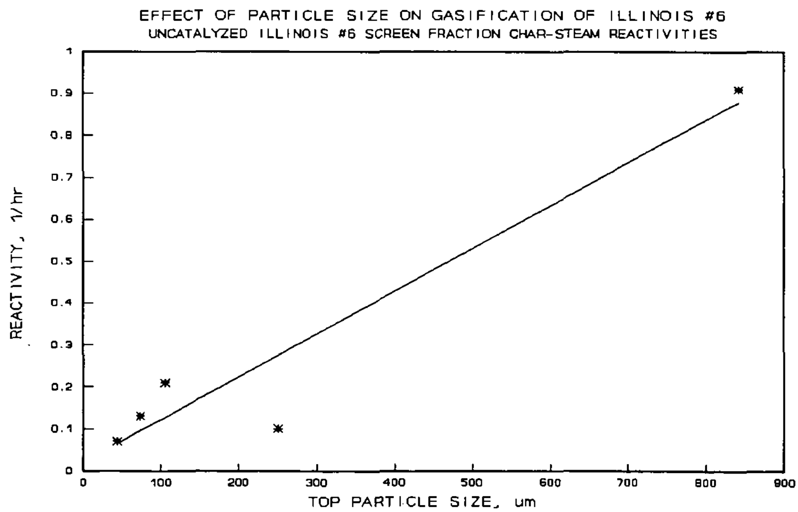

Figure 3. Effect of exclusion of particle size on Illinois #6 char-steam reactivity.