

## CATALYZED GASIFICATION OF COALS AND COAL CHARs

by

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## INTRODUCTION

The alkali metal or alkaline earth oxides, hydroxides, and carbonates have long been known as excellent promoters of the steam and hydrogen gasification reactions, although the catalytic mechanism is not understood. (Reference 1 contains a good review of gasification technology up to 1963.)

Recent work on catalysis is focusing on substantiation and understanding of much of this past work. Some of the most recent findings are:

1. Alkali metal compounds are the most active in promoting increased gasification rates [2,3,4,5,6,7]. A few metals, e.g., Ca, may be as catalytically active as the alkali metals [2,3].
2. Catalyst contacting by impregnation appears to be the most effective [1,7,8,9]. Very little is known about dual catalyst systems [10,11].
3. Studies of catalysis of various carbon systems by Walker et al [12] have pointed out that: a) the chemical state of the catalyst is critically important, b) for pure carbon, substantial catalytic effects are observed with catalyst concentrations in the parts per million range, c) anions play an important role, d) even for pure carbons the mechanism of action of the catalysts is not understood.
4. A kinetic model has been proposed based on the carbon structure becoming more graphitic with increasing extent of reaction [3,4]. Others have noted changes in the carbon structure and activation energy upon gasification [7,9,13,14].

The present work looks at the effect on reactivity of dual catalyst systems, varying catalyst concentrations, catalyst annealing, and catalyst preparation.

## EXPERIMENTAL

The char, obtained from FMC Corporation, was derived from an Illinois No. 6 coal pyrolyzed at 1550°F (for complete analysis see Reference 3). The coals, obtained from Pennsylvania State University, were PSOC 4, a high volatile A bituminous coal from the Elkhorn #3 seam in Deane, Kentucky, and PSOC 106, a high volatile B bituminous coal from the Indiana #1 Block Jefferson Twp.,

Indiana (for complete analysis, see Reference 15). All catalysts were deposited by impregnation from water solutions [4] except where noted, and all catalyst percentages are expressed as weight of the metal.

All experiments were carried out in the high temperature, high pressure thermobalance described earlier [3,4]. Procedures were identical to those in the earlier work.

## RESULTS

Gasification of the FMC char in steam showed that potassium and sodium bicarbonates exhibited the greatest catalytic activity. Similar earlier experiments with this char in hydrogen gave the same results [3]. (The effectiveness of the catalysts can be judged by comparing the time to 90% conversion,  $X_A = .90$ , given in Table 1.) Other work with this char also showed that potassium concentrations on the order of 1 wt. % had little or no effect. This might be expected considering the quantity of metal already present in the char as ash. Increasing the catalyst concentration to 5 wt. % and 10 wt. % gave significantly greater rates of carbon gasification [16].

Gasification rates with caking high volatile bituminous coals at 850°C and 500 psi steam varied approximately with the apparent geometric surface area of the sample. All experiments carried out with these coals were performed under identical conditions so that the comparison of relative catalyst effectiveness would be valid. Dual catalyst experiments with the PSOC coals showed that 5 wt. %  $K_2CO_3$  was more active than mixtures of 5 wt. % potassium plus 5 wt. % of other metals (see Table 1). Potassium carbonate by itself produced methane yields close to the best potassium-cracking catalyst combination  $K_2CO_3-(Al_2O_3)(SiO_2)_3$  and potassium-methanation catalyst combination,  $K_2CO_3-CoCO_3-MoO_3$ .

Annealing these coals in helium at the reaction temperature for 400 seconds with catalyst present gave increased rates. The non-catalyzed PSOC 4 which has a very low ash content, showed no change upon annealing. The non-catalyzed PSOC 106, which has a very high ash content, exhibited significant rate increases upon annealing. Also, annealing the  $K_2CO_3-ZnO$  dual catalyst on PSOC 4 particularly enhanced the rate. Moderate to substantial yields in methane were observed for annealed samples.

In general, impregnation of the catalyst from water solution on the sample was more effective than dry mixing. An exception was tungsten disulfide which

mixed and adhered exceptionally well with the coal in the dry state. This catalyst gave better activity mixed dry than it did upon impregnation. Dry catalyst experiments with sodium sulfide also showed a greater ability to adhere to the coal than sodium sulfate, sulfite, phosphate, and carbonates. The addition of 30 % CO to the inlet H<sub>2</sub>O decreased the catalytic activity for the three dual catalysts tested.

Reactivity of the catalyzed and non-catalyzed PSOC coals was also measured at 650°C and similar catalytic activities were noted for the potassium combinations. Lowering the temperature decreased the volatile yield as expected. Addition of catalysts had little or no effect on volatile yield at 650°C or 850°C. The effect of annealing was also decreased at 650°C. The reactivity with a catalyst present increased modestly with annealing; however, the total methane yield dropped, instead of increasing, as at 850°C. In general, the catalysts reduced total methane production compared to the non-catalyzed coal at 650°C. However, total methane yields from the catalysts at 650°C were the same or greater than the non-catalyzed coal at 850°C.

#### DISCUSSION

Two simple semi-empirical models were used here to fit the data. The first model is that discussed earlier by two of the present authors [4], and the second is a generalized form of a model proposed by Johnson [17].

$$\text{Model 1: } \frac{dx}{dt} = K_1 e^{-bx}(1-x) \quad \text{where } x = \text{fractional conversion of coal, and}$$

$$\text{Model 2: } \frac{dx}{dt} = K_2 (1-x)^n \quad n, b, K_1, K_2 = \text{constant}$$

Each model will fit the data with equal accuracy and there is little evidence to indicate one is more valid than the other. However, some interesting results have been observed. For the non-catalyzed FMC char at 950°C and the non-catalyzed PSOC coals at 650°C, the reaction order appears to be 1st order (n=1) with respect to the mass of carbon present. This is most easily explained by the reaction taking place throughout the entire mass of the sample and has been reported by other investigators for various gas-carbon reactions [13,14,18]. Gasification rates of the non-catalyzed PSOC coals at 850°C varied with apparent sample geometric area. These coals showed very negative b values by model 1, and a shift of n to approximately 2/3 in model 2. Negative values of b indicate that the activation enthalpy is decreasing as conversion proceeds and that the char is becoming easier to gasify. The results

may indicate a surface reaction or catalyst diffusion controlling model. Surface reaction control has been observed by others for steam and oxygen gasification of carbon [14,17,19].

Increasingly more negative values of  $b$  were observed in model 1 as the gasification rate of the catalyzed FMC char increased. There was no obvious trend in the values of  $b$  in model 1 for the catalyzed PSOC coals. Model 2 showed decreases in the value of  $n$  to around  $n=2/3$  for the catalyzed FMC char. Values of  $n$  in model 2 for the catalyzed PSOC coals were very low, possibly indicating a shift to film diffusion control in the Stokes Regime where  $n = 1/3$  [20].

Activation enthalpies calculated for the coals from the 650°C and 950°C data were rather low, again indicating that the gasification reaction was not taking place under pure chemical reaction rate control (for PSOC 4,  $\Delta H_1 = 16.4$  kcal/gmole and  $\Delta H_2 = 11.3$  kcal/gmole; for PSOC 106,  $\Delta H_1 = 19.3$  kcal/gmole and  $\Delta H_2 = 16.6$  kcal/gmole).

The PSOC coals were examined by scanning electron microscopy and electron microprobe analysis for such features as particle structure, catalyst distribution, and structural changes at the catalyst sites as a result of gasification.

The particles of the PSOC 4 coal expanded considerably upon initial gasification. PSOC 106 changed but to a much lesser degree. This metamorphosis produced a highly porous structure in the PSOC 4 coal and a lesser evolved interior in the PSOC 106. Addition of catalysts had no macroscopic effect on this process and remained on the surface of the coal particle.

The use of catalysts to enhance gasification rates could be a significant contribution to present technology. However, economic viability is of paramount importance. Savings from decreases in endothermic heat requirements hopefully could offset catalyst costs. Equilibrium calculations of a 1 to 1 steam to carbon ratio at 500 psi show that the heat of reaction to form the equilibrium composition is reduced from approximately 22.0 kcal/gmole at 900°C to 7.0 kcal/gmole at 650°C. If all of the heat for this reaction were supplied by a 13,000 BTU/lb coal at \$20/ton for a 12,000 ton/day or 250 MM SCF/day gasification plant, that would amount to operational savings of approximately \$33,000/day. To break even, the cost of a catalyst containing 50 wt. % potassium deposited at 10 wt. % potassium on the coal would have to be approximately \$15/ton, assuming no catalyst recovery. Much more

research will be necessary to support catalyst utility. Substantial methane yields from catalysts at 650°C will be necessary. Steam to carbon ratios in our present apparatus are too high (10:1) to be specific about methane production at practical process conditions.

#### SUMMARY

Potassium salts were found to be catalytically more active when used singly than in combination with cracking or methanation catalysts. The gasification rates of the PSOC coals at 850°C were not solely controlled by chemical reaction rates. Increase in rates upon annealing indicate that catalyst diffusion and reaction with the coal (and char) may be limiting the rates in some cases.

TABLE I  
 Steam Gasification of the FMC Char and PSOC 4 and  
 PSOC 106 coal at 500 psi

Run No	Coal	Catalyst	Temp (°C)	Time to 90% Conversion (Seconds)	b	$K_1 \times 10^3$ (l/sec)	n	$K_2 \times 10^3$ (l/sec)	$\text{CH}_4$ produced as mole % of original sample
20222	FMC Char	5% $\text{KHCO}_3$	950	215	-1.50	3.32	.54	5.22	10.0
10225 <sup>a</sup>	"	5% $\text{NaHCO}_3$	940	295	-1.29	2.59	.60	3.77	11.1
30225	"	5% $\text{ZnCl}_2$	950	370	-1.17	2.51	.63	3.49	17.6
20301	"	5% $\text{Ag}(\text{Acet})$	940	400	-1.13	2.57	.62	3.44	9.6
20225	"	5% $\text{UO}_2(\text{NO}_3)_2$	950	535	-0.41	3.17	.79	3.22	18.5
70225	"	5% $\text{CoCl}_2$	940	740	-0.25	2.45	.91	2.59	24.7
40220	"	No Cat.	950	890	-0.00	2.43	1.01	2.45	-
20226	"	5% $\text{Pb}(\text{NO}_3)_2$	950	1000	+0.25	2.43	1.10	2.33	-
20205	PSOC 4	5% $\text{K}_2\text{CO}_3$	850	350	-2.20	1.08	.19	1.81	16.1
50717 <sup>a</sup>	"	$\left( \begin{array}{l} 5\% \text{K}_2\text{CO}_3 \\ 2.5\% \text{CoCO}_3 \\ 2.5\% \text{NiCO}_3 \end{array} \right)$	850	430	-1.40	1.46	.64	2.44	14.7
40710	"	$\left( \begin{array}{l} 5\% \text{K}_2\text{CO}_3 \\ 5\% \text{ZnO} \end{array} \right)$	850	435	-1.56	1.32	.59	2.29	10.8
10203	"	$\left( \begin{array}{l} 5\% \text{K}_2\text{CO}_3 \\ 5\% \text{ZnO} \end{array} \right)^b$	850	530	-2.20	0.78	.19	1.30	15.0
20805-A <sup>c</sup>	"	$\left( \begin{array}{l} 5\% \text{K}_2\text{CO}_3 \\ 5\% \text{ZnO} \end{array} \right)$	850	240	-3.00	0.66	.31	2.24	11.3
10205	"	$\left( \begin{array}{l} 5\% \text{K}_2\text{CO}_3 \\ 5\% \text{W}_2\text{S}_5 \end{array} \right)$	850	440	-2.08	1.11	.24	1.81	13.8
20131	"	$\left( \begin{array}{l} 5\% \text{K}_2\text{CO}_3 \\ 5\% \text{W}_2\text{S}_5 \end{array} \right)^b$	850	560	-2.20	0.77	.32	1.45	13.3
20717 <sup>a</sup>	"	$\left( \begin{array}{l} 5\% \text{K}_2\text{CO}_3 \\ 2.5\% \text{CoCO}_3 \\ 4.0\% \text{MoO}_3 \end{array} \right)$	850	555	-1.86	0.95	.39	1.54	16.1

TABLE I  
continued

Run No.	Coal	Catalyst	Temp (°C)	Time to 90% Conversion (seconds)	b	$k_1 \times 10^3$ (1/sec)	n	$k_2 \times 10^3$ (1/sec)	CH <sub>4</sub> produced as mole % of original sample
20218	"	(5% K <sub>2</sub> CO <sub>3</sub> ) <sup>b</sup> (5% (Al <sub>2</sub> O <sub>3</sub> ) (SiO <sub>2</sub> ) <sub>3</sub> ) <sup>b</sup>	852	540	-1.96	0.90	.34	1.54	20.4
40129	"	10% (Al <sub>2</sub> O <sub>3</sub> ) (SiO <sub>2</sub> ) <sub>3</sub> <sup>b</sup>	850	1220	-2.04	0.28	.34	0.52	16.0
40203	"	10% WS <sub>2</sub>	855	1820	-1.64	0.35	.40	0.52	18.6
60129	"	10% WS <sub>2</sub> <sup>b</sup>	855	1260	-2.36	0.29	.19	0.53	15.2
20708	"	No Cat.	850	1800	-1.56	0.30	.49	0.48	12.5
40802-A <sup>c</sup>	"	"	850	1900	-1.80	0.24	.29	0.35	11.0
20710	PSOC 106	"	850	2360	-0.44	0.55	.89	0.65	8.2
40805-A <sup>c</sup>	"	"	850	1360	-1.19	0.51	.59	0.70	17.0
11017	PSOC 106	No Cat.	650	8100 est.	-1.40	0.70	.99	0.13	10.7
31016	PSOC 4	"	650	7800 est.	-1.40	0.08	1.09	0.16	14.8
11024	"	(5% K <sub>2</sub> CO <sub>3</sub> ) (5% ZrO <sub>3</sub> )	650	805	-1.93	0.63	.34	1.04	11.2
31024	"	(5% K <sub>2</sub> CO <sub>3</sub> ) (2.5% Co <sup>o</sup> CO <sub>3</sub> ) (4.0% MoO <sub>3</sub> )	650	1190	-2.20	0.36	.34	0.69	12.8
31015	"	(5% K <sub>2</sub> CO <sub>3</sub> ) (2.5% Co <sup>o</sup> CO <sub>3</sub> ) (2.5% NiCO <sub>3</sub> )	650	1010	-1.72	0.55	.51	0.96	11.9
31025-A <sup>c</sup>	"	(5% K <sub>2</sub> CO <sub>3</sub> ) (2.5% Co <sup>o</sup> CO <sub>3</sub> ) (2.5% NiCO <sub>3</sub> )	650	910	-1.88	0.53	.42	0.93	8.9

a) estimated final weight

b) dry catalyst preparation

c) annealed in helium at the reaction temperature for 400 seconds.

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