

The Effect of Potassium Carbonate on
the Gasification of Illinois No. 6 Coal

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Catalyzed coal gasification can lead to reduced gasifier size and lower gasification temperatures which give greater thermal efficiencies. Therefore, an investigation of the steam gasification of a bituminous coal under moderately high pressures was conducted. The primary objective of the study was to determine the influence of an alkali metal carbonate catalyst on the kinetic parameters of the gasification reaction.

The coal chosen for the study was an Illinois No. 6 coal and this material was gasified both with and without the addition of potassium carbonate. Experiments were carried out at temperatures between 700 and 900°C and at a pressure of 2.17 MPa (21.4 atm). The partial pressures of steam, carbon dioxide and hydrogen were also varied during the investigation. The carbon gasification rate was modeled using an unreacted, shrinking-core model and kinetic constants and activation energies were determined.

Experimental Methods

The apparatus used to gasify the coal was a high-pressure, tubular, fixed bed reactor with an external heat supply. One of the unique features of this apparatus was its charging system. A 10 g sample of coal was held at a temperature near ambient in a pressurized vessel located above the reactor. Actuation of a ball valve allowed the sample to fall into the reactor, commencing the experimental run.

The apparatus was able to gasify a sample of coal with steam, or mixtures of steam and H_2, N_2 , or CO_2 . Carbon gasification rates were determined from the product gas flowrate and composition. The essential features of the apparatus are shown in Fig. 1.

The reactor and coal charging vessel were constructed from type 316 stainless steel. The reactor body was a 21-inch (53.3 cm) long, 3/4-inch schedule 160 tube with an outside diameter of 1.050 in. (26.7 mm) and an inside diameter of 0.614 in. (15.6 mm). A 0.125-in. (3.2 mm) thick porous stainless steel disc was located inside the tube, 6.5 in. (16.5 cm) from the bottom. This disc supported the bed of coal inside the reactor.

The coal charging vessel, a cylindrical funnel-shaped container with a volume of approximately 50 cm³, was connected to the top of the reactor by a vertical 3/4-inch schedule 160 tube with an inside diameter of 0.464 in. (11.8 mm). At the bottom of this vessel was a ball valve. Charging the reactor was accomplished by opening the valve by means of a pneumatic actuator. The coal then fell a distance of 11 in. (27.9 cm) into the reactor.

The heat necessary to generate steam and gasify the coal was supplied externally through electric resistance heaters. There were three separate electrical heating circuits. These supplied the gas preheater and steam vaporizer, the reactor furnace, and the bottom flange heater.

Water for steam generation was delivered to the system by a high-precision

metering pump. The water used was high purity, liquid chromatography solvent grade material. The flowrate of the other gases supplied to the reactor were controlled by means of two electronic thermal-type mass flow controllers.

After exiting the reactor, the hot product gases and unreacted steam were filtered using glass wool to remove tar and liquid products. The gases were then cooled to condense excess steam, the pressure of the cooled gases was reduced to atmospheric, and they were then analyzed. A quadrupole mass spectrometer was used to determine the product gas compositions. The flowrate of product gas was determined with a wet test meter.

All of the material used in this study was Illinois No. 6 coal. Its proximate and ultimate analyses, free swelling index, and heating value are listed in Table 1. The coal had been previously pulverized, and particles with sizes between 0.297 mm and 0.149 mm (50 x 100 U.S. mesh) were retained.

The catalyst used in this investigation was anhydrous reagent quality potassium carbonate. The catalyzed samples used in the gasification experiments were produced by solution impregnation of the raw coal with K_2CO_3 in an autoclave at 285°C and 7.0 MPa with the product being dried by flash evaporation. The uncatalyzed samples were subjected to mild oxidative pretreatment. This was necessary to prevent agglomeration of coal in the fixed-bed reactor.

An experimental run was carried out in the following manner. Appropriate conditions of reaction temperature and reactant gas partial pressure were selected. The flowrates of nitrogen and carbon dioxide or hydrogen were adjusted to meet these specifications as measured by timed readings of the wet test meter. Steam flow was commenced by adjusting the water metering pump. Finally the ball valve was opened and the coal entered the reaction zone.

During the first five minutes of the run, the flow of products was rapid due

Table 1. Analyses of Illinois No. 6 coal.

	Moisture free coal	Moisture and ash free coal
Proximate analysis (wt. %)		
Volatile matter	40.5	46.5
Fixed carbon	46.5	53.5
Ash	13.0	--
Ultimate analysis (wt.%)		
Hydrogen	4.7	5.4
Carbon	67.7	77.8
Nitrogen	1.1	1.3
Sulfur	3.8	4.3
Oxygen	9.8	11.2
Ash	13.0	--
Heating Value	12307 Btu/lb (28619 kJ/kg)	14148 Btu/lb (32900 kJ/kg)
Free swelling index	3.5	3.5

to the devolatilization of the coal and the time at every one-quarter revolution of the wet test meter (0.0125 cu ft, 354 cm³) was recorded. After five minutes, the volume reading of the wet test meter was recorded at 3-minute intervals. Discrete values of the concentration of each gas were also read from a digital display and recorded by the operator at intervals of 2.5 minutes, beginning at 5 minutes.

The length of time of each experiment varied. In the experiments conducted at 800°C and 900°C, the 10 g coal sample was usually allowed to react until 80-90% conversion of carbon had been achieved. At 700°C, the experiments were terminated after approximately two hours.

At the end of the experiment, flow of water to the steam vaporizer and flow of gases were terminated. All heaters were shut down, and the reactor furnace was opened. When the apparatus was cool, the reactor was depressurized and opened. The char and ash were withdrawn and weighed. All condensate was drained from the trap and the volume of water recorded. The tar filter was removed and weighed immediately.

Results

In this study, the influence of the following parameters on the steam gasification rate of Illinois No. 6 coal was investigated: the presence of K₂CO₃ as a catalyst; the partial pressures of steam, CO₂ and H₂; and reaction temperature. The total pressure of the system was held at a constant value of 2.17 MPa (21.4 atm) throughout the study. The total flowrate of gases into the reaction zone was also kept fixed in each experiment at some value between 980 and 1020 sccm. Variation of the reactant gas composition was accomplished by increasing the mass flowrate of steam, CO₂ or H₂ and simultaneously decreasing the mass flowrate of the inert carrier gas, nitrogen. Nitrogen was both a diluent and a carrier gas for product removal.

Runs were made at 700, 800 and 900°C with the pretreated coal and coal impregnated with 10 wt.% K₂CO₃. The effect of CO₂ concentration on the gasification rate of K₂CO₃-impregnated coal was studied at a constant steam partial pressure in a series of 6 runs. An additional 6 runs were made with a mixture of steam, N₂, and H₂ of constant composition to evaluate the magnitude of hydrogen inhibition of the steam gasification rates. Runs were made at each of the three temperatures, 700, 800 and 900°C, with both the pretreated coal and coal impregnated with 10 wt.% K₂CO₃.

Using the data of each experiment, a number of calculations were performed. The gasification rate and carbon conversion were calculated from a balance of carbon-containing reaction products. The extent of reaction of the steam was determined from a balance of hydrogen-containing or oxygen-containing products. Reactant and product gas partial pressures were computed at the reactor inlet and outlet. From these partial pressures, the apparent equilibrium constants of the water-gas shift, carbon-steam, and carbon-H₂ reactions were calculated. Finally, product gas sums and overall material balances were determined for each experiment.

Gasification rate

The carbon gasification rate was generally high initially, decreased rapidly and then slowly decreased throughout the remainder of the run. Fig. 2 shows typical results obtained at 700°C with a catalyzed coal sample. The initial peak in the curve seemed to be caused by devolatilization of the coal, which was followed by gasification of the base carbon in the sample.

To obtain a quantitative measure of the reaction rate, the shrinking, unreacted-core model for the case of complete gasification of a spherical, solid particle under conditions of chemical reaction rate control was used to describe the carbon

conversion-time data.* The integrated form of the equation based on this model is

$$1 - (1 - X_c)^{1/3} = \frac{k C_s^n t}{\rho_p R}$$

where X_c = carbon conversion

k = reaction rate constant

C_s = concentration of gaseous reactant at particle surface

n = reaction order

ρ_p = molar density of particle

R = initial radius of particle

t = time

In general, the model did not fit the initial data where devolatilization was occurring, but a good fit was obtained over the range of carbon conversions from 0.3 to 0.8. Applying the model to data from all the runs over the range of conversions from 0.3 to 0.7 using linear regression analysis gave correlation coefficients of 0.98 or larger except for two runs where the coefficients were 0.95 and 0.91.

To determine the reaction order with respect to steam concentration, n , a multiple linear regression analysis was performed on the data from the gasification experiments where only steam and nitrogen were used. Within the standard error of the estimate, the overall reaction order was one for both K_2CO_3 -catalyzed and uncatalyzed steam gasification.

Assuming first order kinetics and using the Arrhenius expression, the frequency factor and activation energy were calculated for both catalyzed and uncatalyzed steam gasification of Illinois No. 6 coal. The derived reaction rate parameters are summarized in Table 2. As expected, the overall activation energy was somewhat lower for catalyzed gasification.

Apparent Equilibrium Constants

The value of the apparent water-gas shift equilibrium constant, $K_S = (p_{CO_2})(p_{H_2})/(p_{H_2O})(p_{CO})$, tended to decrease from the time of peak gasification rate until devolatilization was complete. From the time devolatilization was complete until the carbon had completely gasified, the value observed was approximately constant. The value of K_S for each experiment, over the time for which it was approximately constant, is compared in Fig. 3 with a literature value of K_S over the range of temperatures from 700°C to 900°C.

Table 2. Arrhenius parameters for steam gasification of Illinois No. 6 coal.

Material Gasified	Parameter	Estimate	Standard error of estimate	Correlation Coefficient
10% K_2CO_3 -impregnated coal	Activation energy	133.7 kJ/mol (31.7 kcal/mol)	13.8 kJ/mol (3.3 kcal/mol)	0.931
	Frequency factor, min ⁻¹	1.32×10^8	4.5	
Oxygen-pretreated coal (uncatalyzed)	Activation energy	151.5 kJ/mol (36.2 kcal/mol)	6.3 kJ/mol (1.5 kcal/mol)	0.986
	Frequency factor, min ⁻¹	2.94×10^8	2.1	

*For a derivation of the model, see Levenspiel, O. 1972. Chemical Reaction Engineering. 2nd ed. Wiley, New York.

The values of K_S fall both above and below the theoretical curve. Some deviation is due to the sensitivity of K_S to errors in calculation of product gas partial pressures. At 700°C, the gasification rate was slow and steam conversion was slight. Therefore, equilibrium of the water-gas shift reaction may not have been reached. At 800°C and 900°C apparent values of K_S for both catalyzed and uncatalyzed gasification are closer to the theoretical curve than were the values at 700°C. If a 20% margin of uncertainty is assumed, the K_S values of most experiments at 900°C indicate the attainment of water-gas shift equilibrium.

In contrast, the carbon-steam and carbon- H_2 reactions did not appear to be in thermodynamic equilibrium. Neither equilibrium constants reached a consistent value at any time during the burnoff of the carbon and both values were at least an order of magnitude smaller than their theoretical value during the char gasification period.

Influence of CO_2 on the gasification rate

To determine the effect of CO_2 partial pressure, a series of 5 runs was made at constant steam flowrate while varying the CO_2 concentration. These runs were carried out with 10 wt.% K_2CO_3 -impregnated coal at 800°C and the CO_2 partial pressure was varied from 97 kPa (0.96 atm) to 576 kPa (5.68 atm) using a constant steam pressure of 1.35 MPa (13.3 atm).

The calculated kinetic constants for these runs were generally somewhat lower than the value determined with pure steam. However, the deviation was within the expected range introduced by experimental errors. Therefore, the only conclusion that may be drawn from this set of experiments is that CO_2 concentration, over the range used, exerted a relatively small effect on the steam gasification rate of K_2CO_3 -impregnated coal when compared with the effects of steam concentration and temperature.

Influence of H_2 on the reaction rate

Runs were made at 700, 800 and 900°C with both 10 wt.% K_2CO_3 -impregnated coal and untreated coal. All 6 runs were done with the same hydrogen and steam partial pressures, namely 428 kPa (4.22 atm) and 1.69 MPa (16.7 atm), respectively.

Hydrogen inhibited the steam gasification rate of both coal samples. The results of the experiments with the K_2CO_3 -impregnated coal showed that the magnitude of this inhibition decreased with increasing temperature for the catalyzed reaction. Comparison of the k values obtained with and without H_2 present show that the ratio of $k_{H_2O/H_2}/k_{H_2O}$ increased from 0.13 at 700°C to 0.38 at 900°C. The ratio of the k values was higher for uncatalyzed coal and did not change systematically. This ratio was 0.51 at 700°C, 0.27 at 800°C and 0.47 at 900°C. At atmospheric pressure, the inhibition of the carbon-steam reaction by hydrogen is expected to decrease with increasing temperature because of the relative magnitudes of the elementary activation energies. At higher pressures, the trend is probably more complicated, since the reaction steps leading to CH_4 production are significant. CH_4 generation rates were approximately the same in the char gasification periods for reactions both in pure steam and in the steam/ H_2 mixture. CH_4 represented a greater percentage of the total product gas in the experiments with the steam/ H_2 mixture than in those with pure steam.

Conclusions

The overall gasification reaction was found to be first order with respect to steam concentration, with the rate being unaffected by CO_2 and inhibited by hydrogen. The variation of gasification rate with carbon conversion was described by the unreacted, shrinking-core model, with the rate constants for runs catalyzed by K_2CO_3 being about four times those for uncatalyzed runs. The activation energies for the

catalyzed and uncatalyzed runs were 134 and 152 kJ/mol, respectively. The principal products of both catalyzed and uncatalyzed steam gasification were H_2 and CO_2 . The water-gas shift reaction reached equilibrium for most experiments at $900^\circ C$ and some at $800^\circ C$, with the presence of K_2CO_3 having little effect on the approach to equilibrium.

Acknowledgement

The experimental portion of the study was carried out with the cooperation and financial support of the United States Department of Energy, using the facilities of the Pittsburgh Energy Technology Center in Bruceton, Pa. Mr. John W. Courts assisted in the operation of the experimental apparatus.

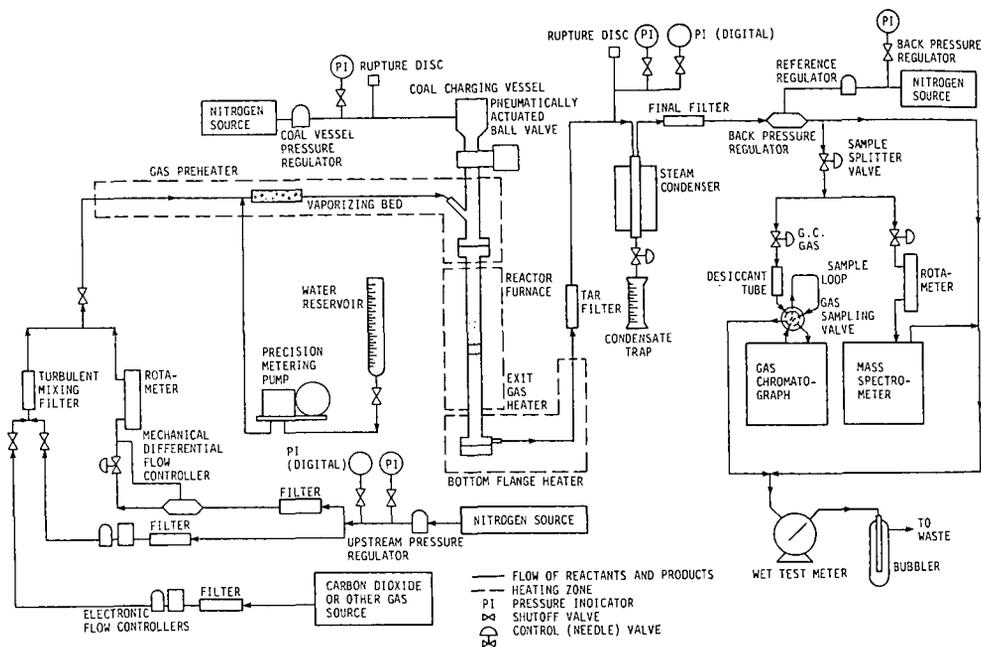


Figure 1. Flow diagram for experimental apparatus

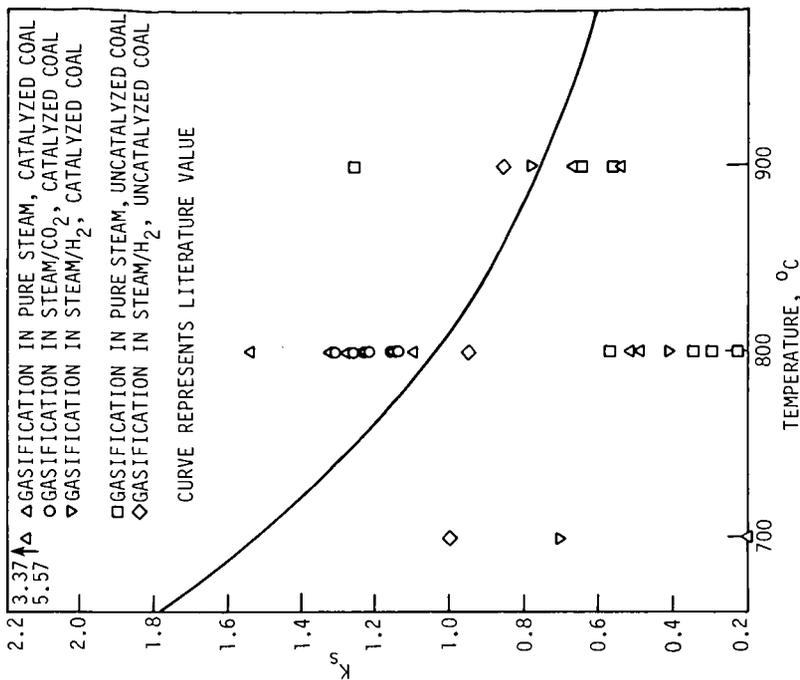


Figure 3. Approach of product gases CO , CO_2 , H_2 , and H_2O to thermodynamic equilibrium of the system: $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$

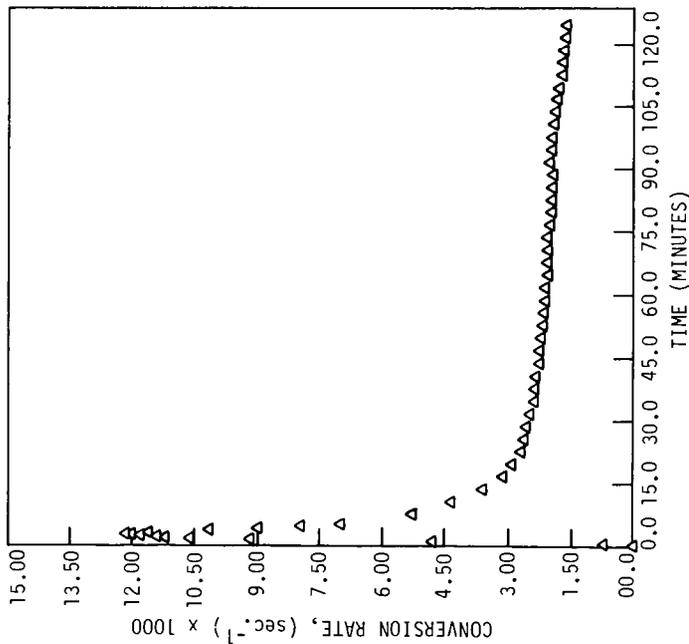


Figure 2. Rate of carbon conversion versus time; conditions = 700°C , 10 wt. % K_2CO_3 -impregnated coal, and N_2 -steam as reactant gas