

ENHANCED COAL HYDROGASIFICATION VIA OXIDATIVE PRETREATMENT

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INTRODUCTION

Coal hydrogasification is not commonly viewed as a competitive route to gaseous fuels and thus has not been studied as extensively as steam gasification. Relative to steam gasification, hydrogasification requires higher pressures to make the reaction thermodynamically favorable; more importantly, hydrogen is presently too expensive to be considered a viable reactant for large-scale coal conversion. Hydrogasification is, however, a useful research tool for improving the understanding of other coal gasification processes. Further, hydrogasification is the primary reaction in at least one coal conversion process, the HYDROCARB process [1], and could be an important means of enhancing methane yields in gasification processes such as that developed by Exxon [2].

The reaction of carbon with pure hydrogen offers a unique opportunity to study the role of oxygen in gasification, since any oxygen present during gasification must be initially associated with the solid. Generally, oxygen is present in bulk carbon and as chemically-bound functional groups on the carbon surface. The desorption of these functional groups as CO or CO₂ may be the rate-limiting step in oxidative gasification; desorption also leaves "nascent", or reactive, sites at which further reaction occurs [3]. Thus, oxidizing the carbon surface prior to conversion should increase the concentration of active sites for gasification.

Exposure to molecular oxygen and immersion in concentrated nitric acid are two common methods of oxidative pretreatment of carbonaceous solids. Partial combustion in oxygen may convert some carbon and open new pore structure, while HNO₃ pretreatment does not significantly alter total surface area or carbon structure [4].

For steam and CO₂ gasification, it has been shown that oxidative pretreatment enhances both catalyzed and uncatalyzed gasification rates. In uncatalyzed gasification, Keleman and Freund [5] determined that prior oxidation of a glassy carbon enhances the dissociative adsorption of O₂ and CO₂ on the surface, thus enhancing gasification rate. In catalyzed gasification, Mims and Krajewski [6] determined that catalyst activity is related to the presence of surface oxygen groups. Keleman et al. [7] and Saber et al. [8] showed that surface oxygen groups have a stabilizing effect on alkali salt catalysts and aid in activating the catalysts. Finally, Ohtsuka et al. [9] found that HNO₃ pretreatment increases the gasification rate by six-fold.

The presence of oxygen also strongly affects hydrogen gasification rates. Cao and Back [10] determined that adding 0.1% oxygen to hydrogen increases the rate of methane formation by an order of magnitude, and Blackwood [11] reported that hydrogasification rate depends on oxygen content of the reacting wood char. Otake and Jenkins

[12] showed that methane formation is directly related to desorption of oxygen complexes as carbon monoxide.

Previous work in our laboratory with model carbons [13,14] illustrated that pretreatment via partial combustion produces up to a two-fold increase in uncatalyzed hydrogasification rate. Also, HNO_3 oxidation results in as much as a three-fold enhancement of the K_2CO_3 -catalyzed rate and a lesser (50%) increase in the uncatalyzed rate. Based on the work of Walker [3], Zoheidi [15] postulated that desorption of oxygen groups occurs during heatup. This desorption creates reactive sites at which hydrogen attacks to form methane. Treptau and Miller [14] used x-ray photoelectron spectroscopy to verify that surface oxygen groups desorb before gasification temperatures are reached.

In this paper, we present initial results of oxidative treatment of coal char for the purpose of enhancing hydrogasification rates and overall conversion of coal to methane. Oxidation both before and during the course of carbon conversion is investigated.

EXPERIMENTAL

A coal char, a demineralized coal char, and a Saran char were used as solid reactants in this study. The coal chars were prepared from an Illinois #6 coal (PSOC 1493), and the Saran char was prepared from Saran (Dow MA 127) resin powder. Ultimate analysis of the three chars are given in Table 1.

The chars were prepared by heating coal or Saran resin in a 4.8 cm ID quartz tube furnace under nitrogen at 100°C/min to 900°C and holding for 30 minutes. A portion of the coal char prepared was then demineralized by contacting repeatedly with concentrated HF and concentrated HCl at 55-60°C, vacuum drying in nitrogen at 110°C, and then reheating under nitrogen to 900°C to remove residual volatiles. A sample of each of the three chars was loaded with 10 wt% K_2CO_3 by drying a slurry of char and K_2CO_3 solution at 90°C for several hours.

Oxidative treatments were performed prior to gasification and following partial gasification in hydrogen by exposing chars to air at 375°C in the quartz tube furnace. For oxidation prior to gasification (preoxidation), approximately five grams of char were oxidized in an air flow of 50cc/min. For oxidation following partial gasification, char samples were removed from the gasification reactor, placed in the quartz tube furnace, and oxidized in stagnant air.

Hydrogasification was conducted in a high temperature, high pressure, differential flow reactor. The pressure vessel, furnace, gas collection system, and gas analysis system are all described in detail by Zoheidi [15] with the exception that a Varian Model 3300 Gas Chromatograph is now used for gas analysis. Samples were gasified at 700-800°C in 500 psi pure hydrogen. Rates were measured by timed collection of product gases.

Char samples were analyzed via several procedures both before and after gasification and oxidative treatment. X-ray photoelectron spectroscopy (XPS) was used to determine the surface concentration of oxygen on samples treated at different temperatures and reactor conditions. A vacuum pretreatment reactor [14] enabled us to heat samples to 1000°C under high vacuum or in the presence of reactant

gases. Samples were transferred to the XPS instrument (PHI Model 5400) using a vacuum transfer vessel to avoid sample contamination.

A high pressure Sartorius microbalance was used to determine the total surface area by carbon dioxide adsorption. Prior to CO₂ introduction, the system was evacuated to a pressure of less than one Torr and samples were heated to 150 °C until no further weight loss was observed. The sample was then cooled to room temperature and carbon dioxide pressure was increased incrementally while the sample weight gain was recorded. The Dubinin-Radushkevitch method [16] was used to calculate the total surface area.

Sample pH was determined as a measure of the type of surface oxygen groups present in a manner similar to the ASTM standard method [17]. The char samples were wetted in a 0.1 molar potassium chloride solution and boiled under reflux for 2 hours. A standard 0.1 molar KCl solution was boiled concurrently with the char suspension. The solutions were then cooled to room temperature and the pH of each measured using a Fisher Scientific Accumet 950 pH/ion Meter. The difference in pH between the sample and the standard determines the nature of the surface oxygen groups: a positive change indicates basic groups and a negative change results from acidic surface groups.

RESULTS

The absolute rates reported in the figures for hydrogasification are based on initial mass of carbon in the sample as determined by ultimate analysis (Table 1). Except for gasification of as-received coal char (Figure 2), all gasification runs were carried out for two hours at steady state conditions. Only steady state data are shown; the absence of data at low conversion is the result of carbon conversion at unsteady state.

The rate of hydrogasification of coal char sharply decreases with conversion, undergoing an eight-fold decrease over the first 20% carbon conversion. Preoxidation of demineralized char at 375°C results in up to a 6.3% wt. loss (Table 2), but it does not result in any significant enhancement in gasification rate (Figure 1) or in the total surface oxygen content as measured by XPS (Table 2). The pH measurements indicate, however, that a greater fraction of the surface oxygen groups, following oxidation, are acidic in nature (Table 2).

Results of oxidative treatment (375°C) following partial gasification are shown for coal char in Figure 2. The intermediate oxidations result in a two- to three-fold enhancement in rate upon further hydrogasification. The observed rate enhancement decays as gasification proceeds and after about 5% conversion, the rate returns to approximately that of the nonoxidized sample. Two oxidation times are presented; however, there does not appear to be any added benefit in long oxidation. A slight weight gain of the chars was recorded from the oxidation.

In Figure 3, the effect of adding K₂CO₃ (10% by weight) to coal char is presented. The presence of the catalyst significantly increases the hydrogasification rate, and intermediate oxidation of the catalyzed char results in about a 50% enhancement in rate. There was significant carbon weight loss upon oxidation (20%) so Figure 3 reports rate versus carbon conversion in gasification.

The results of intermediate oxidation of Saran char are given in Figure 4. Again, approximately a two-fold rate enhancement is observed.

DISCUSSION

In earlier work on model carbons [13,14], we postulated the active sites for methane formation are formed by desorption of oxygen functional groups. This desorption occurs during heatup to gasification temperature; Figure 5 illustrates that upon heating coal char to gasification temperature, all excess surface oxygen has desorbed. Since no oxygen is present in the reactant gas in hydrogasification, active sites can only arise from oxygen groups initially on the surface or in the bulk solid. The active sites from surface groups are consumed as carbon is converted, and gasification rate declines accordingly. This drop in gasification rate is evidenced in all results presented.

Oxidative pretreatment (Figure 1) did not result in a large increase in the gasification rate of coal char. The pretreatment had little effect because the sample was already well oxidized as evidenced by the XPS results in Table 2. Thus, few additional sites were formed via oxidation. Following partial gasification of the char, however, active sites have been consumed and the char is in a reduced state. Oxidation at 375°C then placed new oxygen groups on the carbon surface; these new groups desorb upon reheating to gasification temperature to produce active sites for methane formation. These sites are consumed as reaction proceeds and the rate decays back to that of the nonoxidized sample.

Catalyzed gasification rate enhancement from oxidation is in agreement with the results obtained by Saber et al. [8] and Keleman et al. [5] discussed in the introduction. The added stability of potassium species on the carbon surface during gasification is especially important in the reducing hydrogen environment, and thus the rate enhancement from oxidation may be greater in hydrogen than in oxidizing environments.

Changes in carbon structure and morphology occur during gasification, and thus may account for some of the observed gasification behavior. Since the coal char is heterogeneous, the most reactive carbon gasifies first; thus, the decreases in rate may arise from changes in carbon reactivity as well as loss of active sites. The gasification rate, however, is not related to the total surface area of the chars. While the rate decreases markedly, the total surface area remains essentially constant at $290 \pm 15 \text{ m}^2/\text{g}$ sample for the coal char and $750 \pm 35 \text{ m}^2/\text{g}$ sample for the Saran char over the carbon conversion range of 0% to 34%. Also, the Saran char total surface area was initially twice that of the coal char while its gasification rate was similar to that of the char. Further, total surface did not vary significantly over the course of oxidation, indicating that the rate enhancement resulted from fixation of oxygen groups and not from the opening of new pore structure.

Finally, although preoxidation of the coal char did not significantly increase the amount of surface oxygen, it did change the nature of the oxygen groups. The sample surface pH decreased by a factor of two indicating a one hundred-fold increase in surface

acidity. This fixation of acidic surface groups is characteristic of oxidation at 375°C in air. The importance of the type of oxygen group on the rate enhancement is not clear, but it is currently under investigation.

CONCLUSIONS

Oxidation via exposure to molecular oxygen enhances hydrogasification rate of coal chars and model carbons provided the char surface is not previously oxidized. Oxidation following partial gasification results in a two- to three-fold increase in gasification rate for all chars studied, while oxidation of a char previously saturated with oxygen had little effect. Work continues toward increasing rate enhancement via oxidative treatment and in understanding the importance that different types of oxygen groups have on the extent of enhancement.

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Table 1. ULTIMATE ANALYSIS OF SAMPLES
(Weight % - Dry Basis)

| Element | Demineralized | | |
|-------------|---------------|-----------|------------|
| | Coal Char | Coal Char | Saran Char |
| C | 75.30 | 93.01 | 96.36 |
| H | .53 | .27 | .53 |
| N | 1.34 | 1.62 | 1.04 |
| S | 3.55 | 1.82 | .43 |
| Ash | 17.33 | 2.28 | .08 |
| O (by diff) | 1.95 | .73 | 1.56 |
| Cl | --- | .25 | --- |
| F | --- | .02 | --- |
| | 100 | 100 | 100 |

Table 2. XPS AND pH RESULTS FOR DEMINERALIZED COAL CHAR
(XPS Pretreatment Temperature -->200 °C)

| Char Burnoff (%) | Oxidative Pretreatment Treatment Time at 375°C (hr) | XPS Surface | |
|---------------------|---|-------------|------|
| | | O/C Ratio | pH |
| 0.0 | 0 | .0921 | 0.77 |
| 2.3 | 120 | .0971 | -1.3 |
| 6.3 | 160 | .1036 | -2.8 |

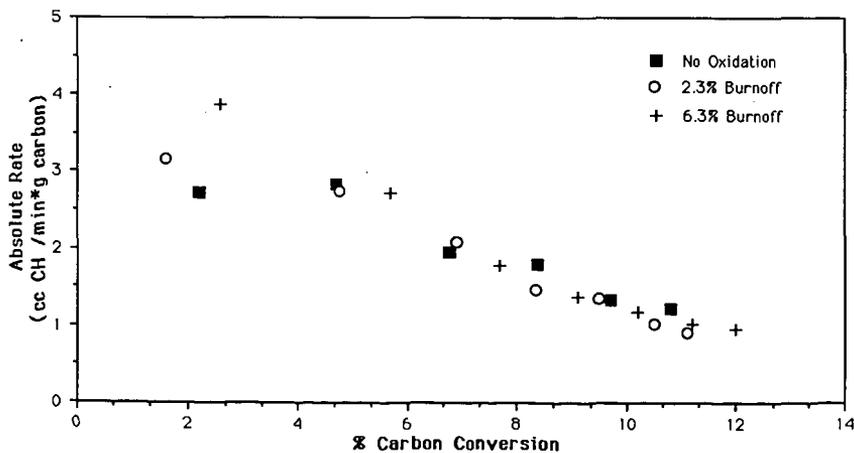


Figure 1. Effect of Preoxidation on Gasification
Rate of Demineralized Coal Char

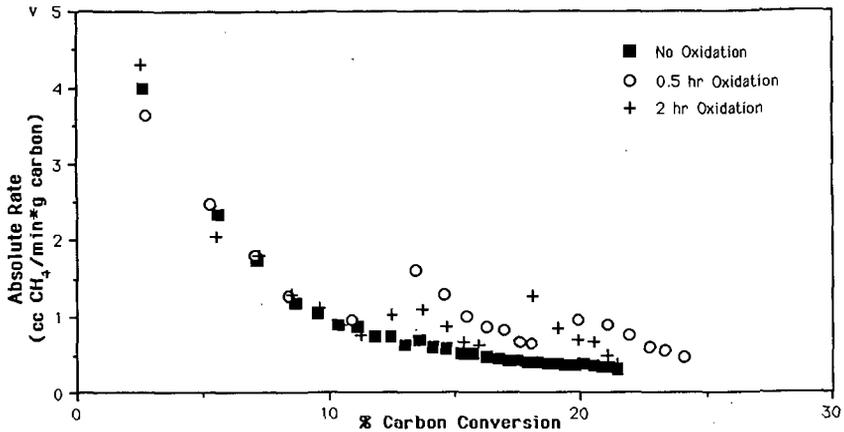


Figure 2. Effect of Two Intermediate Oxidations on the Gasification Rate of Coal Chars

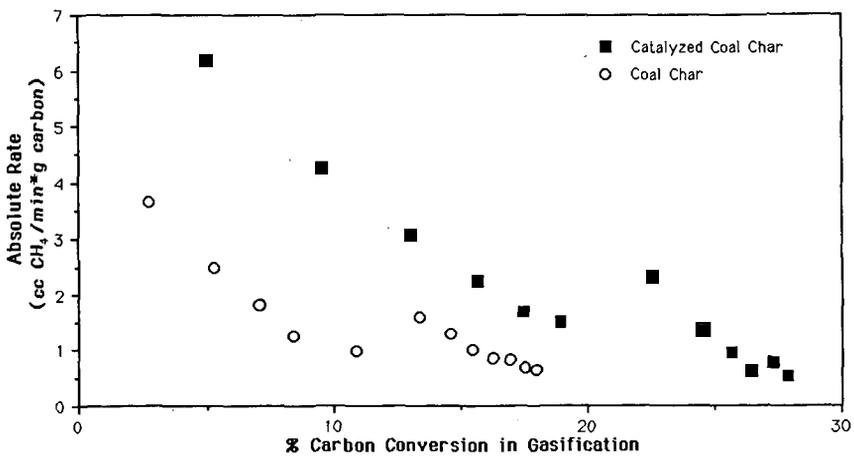


Figure 3. Effect of Intermediate Oxidation on Gasification of K₂CO₃-Catalyzed and Uncatalyzed Coal Char

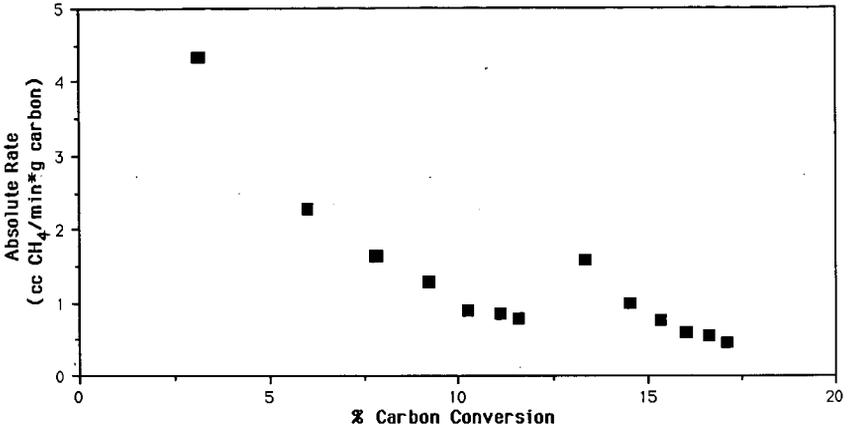


Figure 4. Effect of Intermediate Oxidation on Saran Char

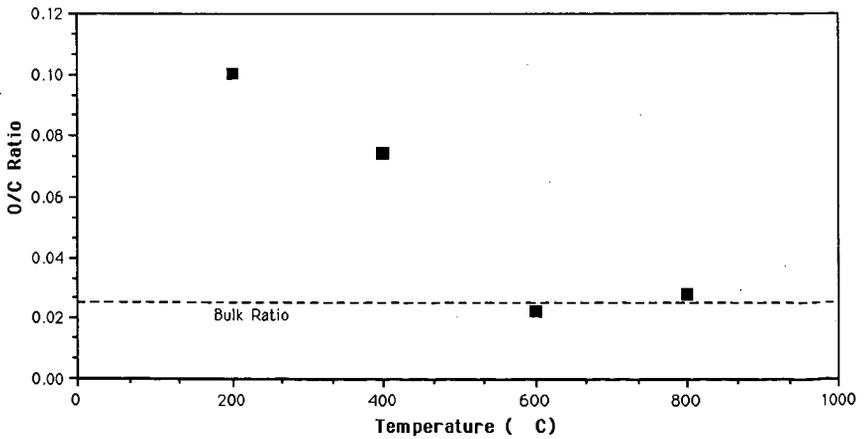


Figure 5. XPS Results for Coal Char Heated to Gasification Temperature