Technical Progress Report
"Rate Inhibition of Steam Gasification by Adsorbed Hydrogen"
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Efforts during the ninth quarter of the grant period have focused on completing core matrix experiments and initiating experiments with coal char in addition to Saran char. Experimental progress was delayed somewhat during this quarter, as the turbomolecular pump on the mass spectrometer vacuum system malfunctioned and had to be replaced. That resulted in a one-month shutdown of the apparatus. During that time, progress was made on preparation of theses, manuscripts for publication, and proposals for future funding.

Results and Discussion

The final results of adsorbed hydrogen concentration following gasification versus fractional conversion for Saran char are given in Figure 1. New results this quarter include reactions to intermediate levels of conversion (20-30%) and correction of hydrogen content for char "aging" in several samples. We can now state conclusively that surface hydrogen concentration following gasification exclusively depends only conversion and not on gasification conditions such as gas composition or pressure. Surface hydrogen concentration initially increases very rapidly to about $10 \text{ cm}^3/\text{g}$ at 1% carbon conversion, and then slowly increases out to $90 \text{ cm}^3/\text{g}$ at 70% conversion, the highest levels we have measured.

The results of an experiment in which reactant gas concentration was cycled from 40% $\text{H}_2\text{O}/60\%$ argon to 40% $\text{H}_2\text{O}/60\%$ H_2 and back is given in Figure 2. Results of this experiment are given by triangles in Figure 2; the rate curve for a sample gasified uninterrupted in steam is given for reference as circles in the Figure. The large dropoff in rate upon introduction of hydrogen, and the subsequent recovery when hydrogen is removed, is a good illustration of hydrogen inhibition and clear evidence that reverse oxygen exchange is the dominant mode of hydrogen inhibition at conversions above 1%. The adsorbed hydrogen concentration following this experiment fell on the curve with other points in Figure 1.

Initial results of gasification with unannealed and annealed coal char are given in Figure 3; results for unannealed and annealed Saran char are also given for comparison. Unannealed coal char gasification (Figure 3a) and Saran char gasification (Figure 3b) in 40% $\text{H}_2\text{O}/60\%$ argon was conducted at 725°C and 3.1 Mpa total pressure. Coal char gasification rate is about one-half that of the Saran char, but the trends in conversion are similar for both. Surprisingly, the primary gasification product from coal char is CO_2 , whereas the primary product from Saran char is CO . We suspect that the ash in coal is acting as a shift catalyst and driving the shift reaction to CO_2 ; this catalytic activity of coal ash has been reported in the literature.

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Gasification rate curves of annealed coal char (Figure 3c) and annealed Saran char (Figure 3d) again show that the annealed coal char gasification rate is about one-half that of Saran char, and the primary product with coal char is CO_2 versus CO for Saran char. The shape of the rate versus conversion curves are markedly different for annealed and unannealed chars. For unannealed chars, the rate is initially very high and declines rapidly over the first 2-3% of carbon conversion, after which it levels out. This suggests that very reactive carbon is present on the unannealed chars which quickly reacts upon exposure to steam. For the annealed material, the rate is initially low and increases with conversion. Remembering that annealed chars have essentially been stripped of heteroatoms and active sites annealed, it is not surprising that initial reactivity is low and builds up as carbon is converted and more active sites are formed. The rate of the annealed char is a very small fraction of the unannealed material: if we take an activation energy of 55 kcal/mol for the reaction; the annealed char rate is about 5% that of unannealed char.

We have measured adsorbed hydrogen concentration on the annealed coal char sample following reaction and found the value to be $11 \text{ cm}^3/\text{g}$, much lower than that determined for Saran char. We are in the process of further characterizing the coal char surface area and adsorbed hydrogen content to ascertain if behavior between Saran and coal chars are similar.

Two other achievements during the past quarter are noted. First, we replaced the outer ceramic tube on our 1500°C reactor because it showed signs of wear. We were surprised to see that the background signals of N_2 , H_2O , and H_2 in the mass spectrometer during sample outgassing in the reactor were almost an order of magnitude lower with the new tube. Clearly there was a defect in the old tube that allowed leakage of air at elevated temperatures. We now look forward to high quality TPD results of oxygen complexes on char surfaces during upcoming oxidation studies.

Second, we have had ultimate analyses of annealed Saran char and annealed coal char conducted by Galbraith Laboratories. Results of these ultimate analyses are given in Table 1 on the attached page; we have included the analyses of unannealed chars for comparison. The key result is that there was no detectable hydrogen or nitrogen present on the annealed char samples. It also appears that there is some uncertainty in carbon content for the annealed coal char, as the sum of ash and carbon add to significantly more than 100%.

In conclusion, we are continuing to progress through the grant objectives, and during the coming quarter will focus on further reactions with annealed coal char. We will also initiate the oxidation portion of the grant, in looking to reverse the effects of hydrogen inhibition by oxidizing the carbon to remove adsorbed hydrogen. Some of these experiments will be conducted with deuterium to clearly ascertain the fate of adsorbed hydrogen upon exposure to oxygen.

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Ultimate Analysis of Chars (wt% dry basis)				
	Coal char	Annealed coal char	Saran char	Annealed Saran char
C	75.3	87.2	96.4	97.8
H	0.5	<0.01	0.5	<0.01
N	1.3	<0.1	1.0	<0.1
S	3.6	1.4	0.4	<0.1
Ash	17.3	15.0	0.1	0.4
O (by diff.)	2.0	<0.1	1.6	1.8

Figure 1: Adsorbed Hydrogen Concentration on Annealed Saran Char Following H₂O/H₂ Gasification at 0.3 - 3.1 MPa

Figure 2: H₂O/H₂ Gasification Rate of Annealed Saran Char at 1.0 MPa, Step Changes in Reactant Gas Composition

Figure 3.