

The Initial Stage of Coal Hydrogenation in the Presence of Catalysts

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Introduction

Several factors are important in the development of an hydrogenation process for the economic conversion of coal to a liquid fuel.^(1,2) These include a better understanding of the structure of coal, the effective use of hydrogen and/or alternate reducing gases and the development of cheaper or more active catalysts.

This paper is concerned with the initial stage of coal hydrogenation, where the reactivity is greatly affected by the chemical structure characteristics of the coal and the conversion per unit of hydrogen consumed is high.^(3,4) Several catalysts are studied and reactivity in an entrained-flow hydrogenation reactor and the chemical structure of the products are determined.⁽⁵⁾

Experimental

Clear Creek, Utah, coal was hydrogenated in a short-residence, entrained-flow reactor.⁽⁵⁾ Zinc chloride, Co-Mo/Al₂O₃, presulfided red-mud and red-mud plus sulfur were used as catalysts. The coal particle size was -100+200 mesh and the catalyst ranged from 6.4% for ZnCl₂ to 10.7% for the other catalysts. The coal was also hydrogenated without catalyst. The temperature ranged from 400° C to 500° C and the hydrogen pressure was held at 1,800 psi. Residence time (8-372 sec) was varied by choice of the tube length (12-36 m). A typical analysis of Clear Creek, Utah, coal is shown in Table 1.

Products were separated by stepwise extraction using hexane, toluene and pyridine. The extraction scheme is shown in Figure 1.

Determination of C, H and N for each product was carried out by a micro method using a Perkin-Elmer 240 CHN Analyzer. Proton NMR spectra were measured at 90 MHz and 300 MHz. Molecular weights were determined by vapor pressure osmometry on Corona Wescan 117 Molecular Weight Apparatus.

Results and Discussion

The yields of hydrogenation products are shown in Table 2. Comparison of the initial stage of hydrogenation for 8-12 sec at 500° C in the presence of different catalysts and without catalyst shows conversions of about 20% for all samples. A catalytic effect on conversion and product distribution is not apparent. This indicates that at least 20% of Clear Creek, Utah, coal converts noncatalytically into liquid and gas. This is similar to the results obtained on Japanese coals^(6,7).

In Figure 2 the effect of temperature and time at 500° C on conversion and product distribution using ZnCl₂ catalyst is shown. The effect of temperature during short residence times of 8 to 12 sec is not large. Conversions increase from 6% to 18% with the increase of temperature from 400° to 500° C. However, the effect of time at 500° C is large. For example, conversions increase from 18% to 35% during the period from 8 to 21 sec. The effect of reactor length on conversion at 500° C

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is also shown in Figure 2, using $ZnCl_2$ catalyst the conversions increase from 18% to 75% with an increase in reactor length from 12 m to 36 m. Using the other catalysts and with no catalyst the conversions are merely ca.20% at 36 m reactor length. This indicates that $ZnCl_2$ is a very active catalyst in the initial stage of hydrogenation.

These results suggest that in this reactor the reaction up to 500° C and 12 sec proceeds noncatalytically except when a very active catalyst is used. About 20% of the coal takes part in the reaction. At 500° C and after 12 sec, the reaction proceeds catalytically and is greatly affected by residence time.

In Figure 3 and 4 the results of ultimate analysis of each product are shown. The H/C atomic ratio decreases with increasing conversion, especially up to 20% conversion. The changes in liquid (oil + asphaltene -I) and asphaltene-II are remarkable. The O,N,S/C atomic ratio increases with conversion up to 20% conversion, and it is nearly constant in spite of the progress of conversion in the reaction beyond 20% conversion. At about 20% conversion the H/C ratio of each product for $ZnCl_2$ catalyst is lower than for other catalysts. This suggests that $ZnCl_2$ catalyzes reactions which decrease the H/C ratio.

Comparison of a typical proton NMR spectra of liquid (oil+asphaltene-I) measured at 90 MHz and 300 MHz shows two new bands in the aliphatic region at 1.5 - 1.8 ppm and 2.0-2.1 ppm in the 300 MHz spectra.⁸⁾ The hydrogen distribution of each product was obtained from NMR spectra. Hydrogens bound to aromatic carbons, H_a , and hydrogens bound to carbons α to aromatic rings, H_α , increase and the hydrogens bound to aliphatic carbons β or further from aromatic rings, H_o , decrease with increasing conversion.

Structural analysis was performed using the equation of Brown and Ladner^(6,7,9) Results of these calculations are shown in Figure 5. The carbon aromaticity, f_a , increases and the aromatic hydrogen-to-carbon ratio of the hypothetical unsubstituted aromatic material, H_{au}/C_a , decreases with the increase of conversion. Up to 20% conversion the changes in liquid (oil + asphaltene-I) and asphaltene-II are significant. The main differences in the chemical structure between liquid (oil + asphaltene-I) and asphaltene-II are the average number of aromatic rings in the unit structure (H_{au}/C_a) and f_a . At about 20% conversion the degree of substitution of ring carbons, σ , of each product using $ZnCl_2$ catalyst is lower, and f_a is higher than those obtained with the other catalysts. This suggests that $ZnCl_2$ catalyzes reactions which decrease σ and increase f_a , e.g., dealkylation. This ability of $ZnCl_2$ may be related to the high activity in the initial stage of hydrogenation.

It is concluded that a continuous distribution exists in the structural units of coal. The units taking part in the noncatalytic reaction up to about 20% conversion are characterized by higher H/C ratio, lower O,N,S/C ratio, higher content of aliphatic hydrogen ($H_\alpha + H_o$), lower f_a and 1-2 aromatic rings. In the catalytic reaction (greater than 20% conversion) the units taking part in the reaction are characterized by lower H/C ratio, higher content of H_a , higher f_a and larger number of aromatic rings.

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Table 1. - Analysis of Clear Creek, Utah, coal

Ultimate analysis (% d.a.f.)				Atomic ratio		Proximate analysis (%)			
C	H	N	O(diff)	H/C	O,N,S/C	Moisture	Ash	Volatile matter	Fixed carbon
76.1	5.5	1.6	16.8	0.87	0.18	0.83	6.50	45.42	47.25

Table 2. Yield of products from hydrogenation

Catalyst	Temp, (°C)	Tube length (m)	Time (sec)	Product distribution (% d.a.f.)							Conversion (% d.a.f.)
				Aqueous phase	Liquid		Total	Residue		Toluene insolubles	
					Oil	Asphal- tene-I		Gas	Asphal- tene-II		
ZnCl ₂	400	36	13	1.7	1.3	0.6	3.6	2.0	0.6	93.8	6.2
	450	36	13	4.0	2.7	3.0	9.7	3.2	2.5	84.6	15.4
	500	12	8	4.2	4.4	3.4	12.0	2.0	3.7	82.3	17.7
		18	21	4.9	7.9	11.2	24.0	3.5	8.0	64.5	35.5
Co-Mo		24	8	3.9	4.8	4.8	13.5	2.9	2.3	81.3	18.7
	500	36	372	7.4	35.1	3.7	46.2	11.0	17.0	25.8	74.2
Presulfided red-mud		36	12	3.3	6.3	4.1	13.7	2.6	2.9	80.8	19.2
	500	36	12	4.5	5.3	6.5	16.3	4.1	2.5	77.1	22.9
Red-mud plus sulfur		36	12	4.3	4.5	7.5	16.3	3.3	2.5	77.9	22.1
	500	36	10	2.9	5.5	5.1	13.6	3.4	3.0	80.0	20.0

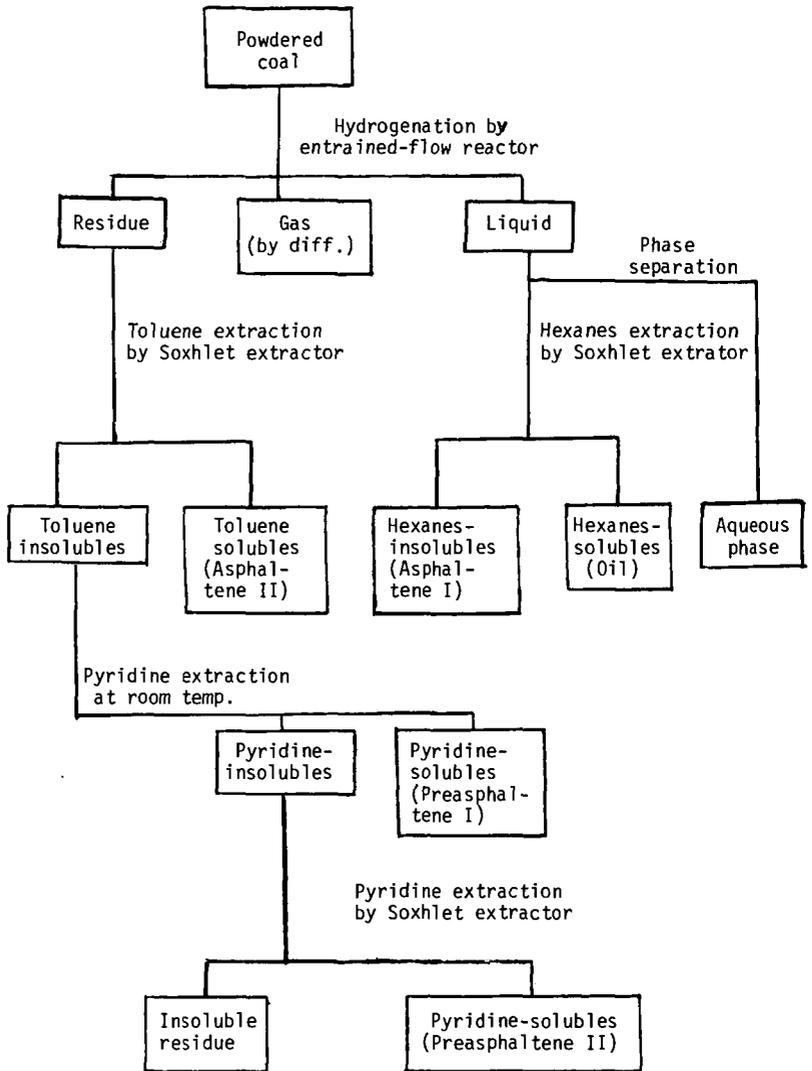


Fig. 1 - Flow diagram of product separation

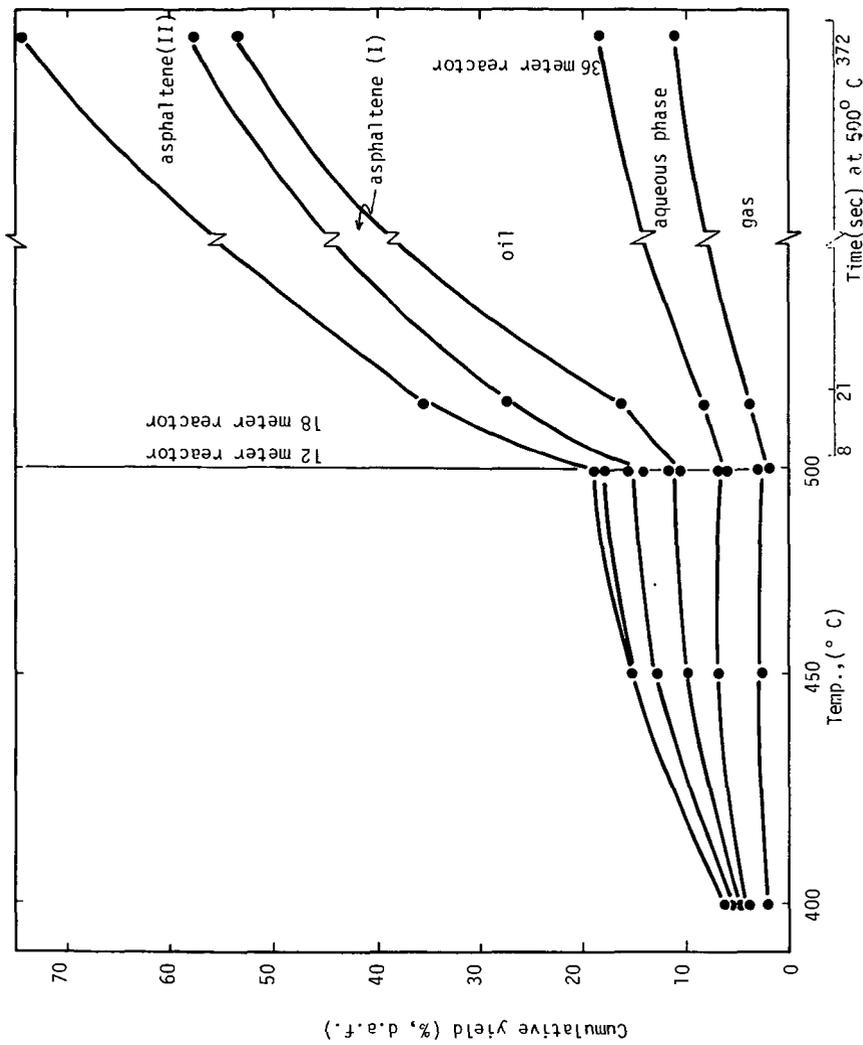


Figure 2. Effects of temperature and time on hydrogenation with ZnCl₂ catalyst.

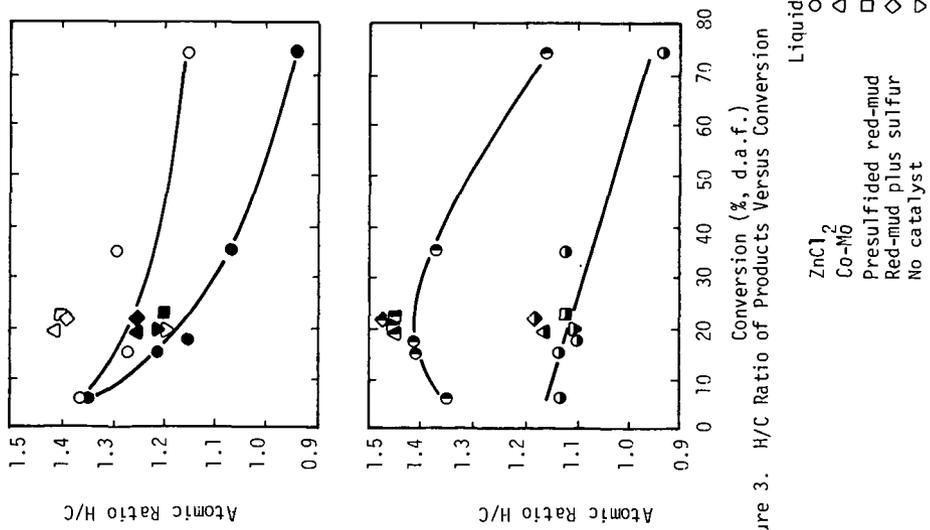


Figure 3. H/C Ratio of Products Versus Conversion

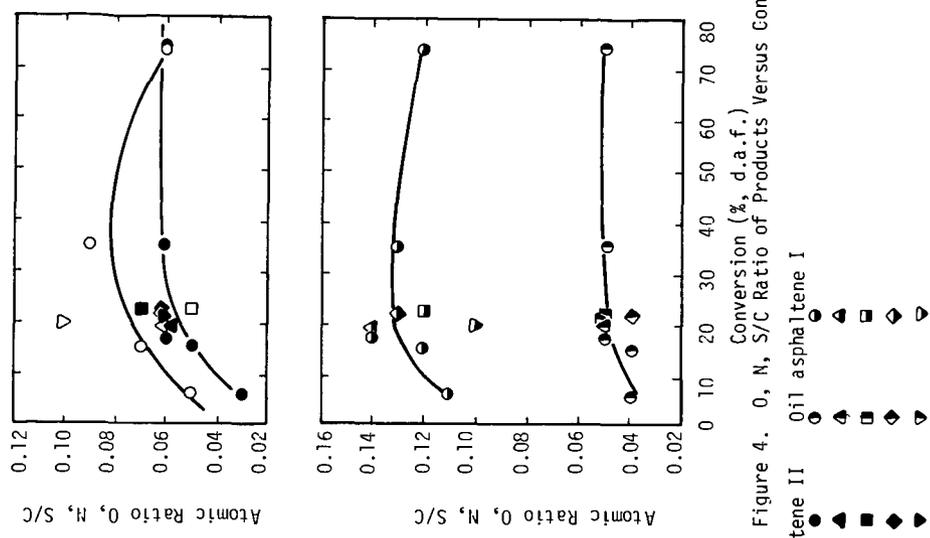


Figure 4. O, N, S/C Ratio of Products Versus Conversion

- ZnCl₂ ○
- Co-Ni △
- Presulfided red-mud □
- Red-mud plus sulfur ◇
- No catalyst ▽
- Liquid asphaltene II ●
- Liquid asphaltene I ▲
- Oil asphaltene II ◐
- Oil asphaltene I ◑

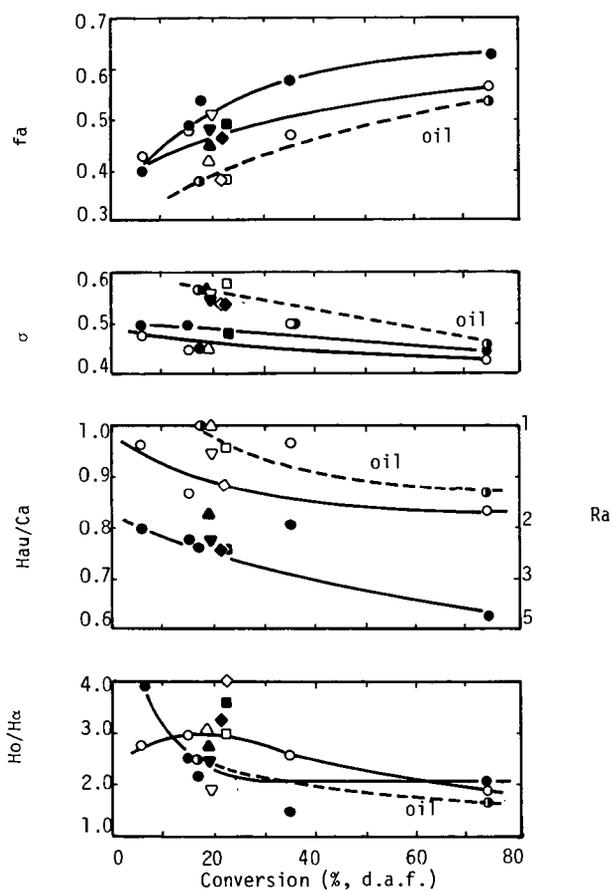


Figure 5. Change of Structural Parameters of Products with Conversion

	Liquid	Asphaltene-II	Oil
ZnCl ₂	○	●	●
Co-Mo	△	▲	
Presulfided red-mud	□	■	
Red-mud plus sulfur	◇	◆	
No catalyst	▽	▼	