

DISSIMILAR BEHAVIOR OF CARBON MONOXIDE PLUS WATER
AND OF HYDROGEN IN HYDROGENATION

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Under certain conditions the conversion of lignite, subbituminous and some bituminous coals to benzene-soluble oils proceeds more readily in the presence of carbon monoxide and water than in the presence of hydrogen (1-4).

The purpose of the work described here was to compare the behavior of carbon monoxide plus water with that of hydrogen under mild coal hydrogenation conditions. Pure compounds and materials having structures resembling those that might exist in coal were the objects of the hydrogenations.

The experimental work was conducted in a 500 ml rocking stainless steel autoclave. Analysis of the pure compounds was by gas chromatography and mass spectrometry. Conversions of lignite, lignin, and cellulose were measured by extracting the products with hot benzene and then weighing and analyzing the benzene-insoluble residues. Pressures referred to in the tables are initial pressures. The maximum pressures were about three times the initial pressure. The time at temperature did not include the time required to reach operating temperature or the cooling off period. The reactants were thus exposed to temperatures where a significant amount of reaction was occurring for approximately an additional hour.

RESULTS AND DISCUSSION

The effectiveness of carbon monoxide and water in solubilizing low rank coal may be due to a number of reasons, including (1) hydrogenation with activated hydrogen produced by the water-gas shift reaction, (2) the introduction of alkyl groups, and (3) the unique ability of carbon monoxide to cleave certain types of bonds or to inhibit condensation reactions leading to benzene-insoluble materials.

Mass spectrometric analysis of the benzene-soluble products from a fresh lignite and a less reactive, rapidly aged lignite, revealed that a major difference in composition was an increase in methylated aromatic compounds in the product from the more reactive lignite. This is in agreement with the observation of Sternberg and Delle Donne of our laboratory that coal may be solubilized by the introduction of alkyl groups (5). The relatively high methyl content of the products suggested that the effectiveness of CO and water in lignite solubilization might be due in part to the introduction of methyl groups.

Table 1 lists the relative peak heights of several of the more prevalent compounds in the products. Inasmuch as the solvent used consisted of equal weights of α -naphthol and phenanthrene, the compounds present in largest concentration were the solvent and products derived from the relatively reactive α -naphthol. (In a solvent free system the cresols usually show the highest mass peaks.) Not only are the aromatic compounds from fresh lignite present in higher concentration, but the methylated derivatives of the parent aromatic compound are also consistently and significantly higher. The large content of methyl-naphthol, in both products, indicates that methyl groups are being picked up, either from the lignite, from the carbon oxides, or from traces of formaldehyde. The probable reactions are

carbonylation, carboxylation, and hydroxymethylation, followed by reduction. The presence of relatively large amounts of dinaphthylmethanes suggest that naphthoic acid, hydroxymethylnaphthalene and naphthylmethyl radical may be intermediates in the route from naphthol to methylnaphthalene.

TABLE 1. - Methyl groups in benzene soluble material from hydrogenated lignite
(30 g. lignite, 15 min. at 380°C, 1500 psig CO pressure,
1:1:1 = water:lignite:solvent^a)

Compound	Relative peak heights by M.S. analysis	
	North Dakota lignite (89% conversion)	Aged North Dakota lignite ^b (54% conversion)
Phenol	12	8
Cresols	18	11
Xylenols	14	5
Naphthalene	50	27
Methylnaphthalene	80	24
Naphthol	900	1070
Methylnaphthol	340	240
Phenanthrene	2500	2500
Methylphenanthrene	14	10
Dinaphthylmethane, dinaphthofuran	60	43
Methylnaphthylmethane)	57	26
Methylnaphthonaphthofuran)		

^a Equal parts of α -naphthol and phenanthrene.

^b Heated 24 hr. in air at 105°C, 54% conversion.

Although treatment with hydrogen, with or without water present, gave a smaller total yield of benzene-soluble product, the ratio of methylated to parent aromatic structures were the same, within experimental error, as those obtained in the presence of carbon monoxide and water (4). This result implies that carbon monoxide or dioxide liberated during lignite hydrogenation was reentering the reaction. In the presence of the alkaline lignite ash, carbon dioxide would be expected to add to phenolic materials readily via a Kolbe type carboxylation. One advantage of the reaction with hydrogen is that in the absence of large quantities of water, the carboxylation reaction may proceed rapidly. Reduction of the carboxyl group to a methyl group also occurs more readily with hydrogen than with carbon monoxide and water.

Although methylation may be a factor serving to increase the solubility of lignite, the effect is similar for carbon monoxide plus water and for hydrogen. Methyl group introduction, therefore, does not appear to be a major reason for the greater effectiveness of carbon monoxide and water in lignite solubilization.

The presence of methoxyl groups in lignite prompted several experiments probing the behavior of anisole at mild coal hydrogenation conditions (approximately 4500 psig maximum pressure at 380°C using low activity catalysts). Table 2 shows that in addition to demethylation to phenol, a significant portion of the anisole is converted to benzene and toluene. The highest yield of benzene was obtained with hydrogen. This demonstrates the greater effectiveness of hydrogen in hydrocracking reactions. The absence of dimethylated products suggests that ring methylation proceeds predominantly by an intramolecular shift. It does not appear likely that methoxy or methyl transalkylation occurs to a major extent during coal hydrogenation.

TABLE 2. - Hydrogenolysis of anisole

(20 ml. anisole, 15 ml. water, 1 g. catalyst, 1500 psig, 2 hr. 380°C)

Catalyst	Gas	Wt. pct. of total products			
		Benzene	Toluene	Phenol	Anisole
None	CO	1.9	7.4	6.5	84
Lignite ash	CO	1.5	4.2	18	76
Charcoal	CO	2.0	7.8	6.5	83
Fe	CO	2.6	8.5	10	77
Fe ₃ O ₄	CO	2.9	8.4	8.3	80
Fe ₃ O ₄ ^a	H ₂	6.8	7.7	11	74
Fe ₃ O ₄	H ₂	4.5	8.2	16.5	70

^a No water present.

The possibility that methyl groups could be introduced via CO, CO₂, or methyl alcohol was evaluated by treating phenol under mild coal hydrogenation conditions. Table 3 shows that in the presence of iron oxide, methylation occurs to a significant extent with CO₂ and with methyl alcohol. Although small amounts of the latter might be formed by a Fischer-Tropsch reaction, it appears more likely that either formaldehyde or CO₂ adds to reactive phenolic rings and the compound formed is then reduced by the carbon monoxide or by the hydrogen. Even in the absence of added catalysts, small amounts of cresol, toluene, and xylene were obtained with CO₂ plus either CO or H₂. More reactive phenolic materials can be expected to methylate to a greater extent. The formation of dinaphthylmethanes indicated in table 1 is perhaps a result of carboxylation or hydroxymethylation of the α -naphthol followed by condensation with a molecule of naphthol or methylnaphthol. The condensed product apparently loses phenolic OH groups easily; not more than traces of masses corresponding to oxygen containing dinaphthylmethanes were observed. This mechanism may account for the formation of some high molecular weight materials during coal hydrogenation.

TABLE 3. - Methylation of phenol

(20 g. phenol, 1 g. catalyst, 2 hr. 380°C, 1500 psig)

Catalyst	Gas	Water, g.	Reagent, g.	Wt. pct. of total products
CoCO ₃	CO	15	None	Trace o-cresol
None	CO	15	MeOH, 10	No reaction
Fe ₃ O ₄	CO	15	MeOH, 10	o-Cresol, 6%; anisole, 1.3%; xylenol, trace
None	CO	15	CO ₂ , 15	Traces of o-cresol, toluene, xylene
None	H ₂	None	CO ₂ , 15	o-Cresol, 0.7%; traces of benzene, toluene, xylenol
Fe ₃ O ₄	H ₂	None	CO ₂ , 15	o-Cresol, 6%; benzene, 2.5%; toluene, trace
Lignite ash	H ₂	None	CO ₂ , 15	o-Cresol, 0.4%; benzene, 0.2%

Although not more than traces of formaldehyde can be expected to be present at operating conditions, the high reactivity of formaldehyde with phenols suggests that the small amounts formed are continuously scavenged from the system by reaction with the phenols.

The major high molecular weight oxygen containing compound appeared to be dinaphthofuran. This is probably formed by cyclization of dinaphthyl ether; but oddly, not more than very small amounts of the mass corresponding to this ether was found by mass spectrometry.

A number of compounds were tested for their ease of hydrogenation with carbon monoxide and water and with hydrogen. The hydrogenation of 1-octene proceeded more rapidly with hydrogen than with carbon monoxide and water at the same total pressure (table 4). However, the rate with carbon monoxide and water was four times as fast as expected based on the partial pressure of hydrogen in the autoclave in the absence of a catalyst. In the presence of potassium carbonate, more hydrogen was formed by the water-gas shift reaction but the rate of hydrogenation was only three times that expected. The rate, however, was approaching that obtained with high pressure hydrogen. It thus appears that hydrogen formed by the water-gas shift reaction is activated and has a beneficial effect on the rate of hydrogenation. The lower total extent of hydrogenation, in this system at least, makes it clear that the hydrogen is not activated sufficiently to reach or surpass the hydrogenation rates obtainable with high pressure hydrogen. It may be that, with the proper choice of catalyst, reactants and operating conditions, the hydrogenation rate with carbon monoxide and water could equal or exceed that obtained with hydrogen.

TABLE 4. - Hydrogenation of octene-1
(1 hr. 400°C, 1000 psig, water:hydrocarbon = 1.5:1)

	H ₂	CO ^a	CO-K ₂ CO ₃ ^b	H ₂ ^c
Product (mole pct.)				
Below C ₈	8	9	11	8
n-Octane	61	36	50	26
n-Octene-1	21	41	22	49
n-Octene-2	9	11	13	15
Above C ₈	1	3.5	4	2.5

^a 14.6 Mole pct. H₂ in final gas; 36.5% water-gas shift reaction.

^b 27 Mole pct. H₂ in final gas; 66% water-gas shift reaction.

^c 400 psig initial pressure.

The reduction of p-methylbenzaldehyde to xylene also proceeded at a more rapid rate with hydrogen than carbon monoxide and water (table 5). The yield of condensation products (tolylxylmethanes) was also higher when hydrogen was used.

TABLE 5. - Reduction of p-methylbenzaldehyde
(20 ml. aldehyde, 1 g. Fe₃O₄, 2 hr. at 380°C, 1500 psig)

Gas	Water	Conversion	Products, percent (wt.)			
			Toluene	Xylene	Methylbenzylalcohol	Diaryls
CO	15 ml.	50	25	14	6	4
H ₂	None	94	14	70	3	7

The possibility that carbon monoxide plus water has a unique ability to cleave certain types of bonds in coal was explored by subjecting a variety of compounds to coal hydrogenation conditions (table 6). Very little hydrogenolysis occurred

except with phenyl sulfide; but here again hydrogen was more effective than carbon monoxide and water. The considerable reduction of sulfur in lignite with carbon monoxide and water (4), and the stability of thiophene at these conditions suggests that thiophenic sulfur is not common in lignites.

TABLE 6. - Conversions of miscellaneous compounds
(20 g. compound, 15 ml. water, 1 g. catalyst, 2 hr. 400°C, 1500 psig)

Compound	Catalyst	Gas	Products, percent (wt.)
Phenyl ether	Na ₂ CO ₃	CO	Very little reaction
3-Methylthiophene	Na ₂ CO ₃	CO	Very little reaction
3-Methylthiophene	Charcoal	CO	Very little reaction
Diphenylmethane	Na ₂ CO ₃	CO	Very little reaction
Diphenylmethane	Charcoal	CO	Benzene 1.0, toluene 1.4
Diphenylmethane	Charcoal	H ₂	Benzene 3.1, toluene 3.8
Phenyl sulfide	Charcoal	CO	Benzene 3.6, toluene 2.0
Phenyl Sulfide	Charcoal	H ₂	Benzene 61

Lignin and cellulose, the generally accepted coal precursors, were found to be, like coal, more reactive with CO and water than with hydrogen (table 7). Glucose and presumably certain other carbohydrates share this property. Surprisingly, cellulose is most reactive. This order of reactivity is probably caused by the relatively large number of stable aromatic units in lignin and the ease of pyrolysis of glucose. A carbonyl group appears to be necessary for low temperature charring. Glucose and other carbohydrates that contain a carbonyl group or an incipient carbonyl group form chars on being heated at 250 to 300°C with the liberation of considerable quantities of water. Sorbitol and sorbic acid do not form chars at these conditions.

TABLE 7. - Conversion of lignin and carbohydrates to benzene-soluble material
(1500 psig, 40 ml. water, 2 hr. at temperature)

Material, g.	Gas	Temp., °C	Catalyst, g.	Conversion, % of feed (maf) ^a	Benzene soluble product, wt. % ^a
Lignin, 10	CO	250	None	77	29
Lignin, 10	H ₂	350	None	33	9
Lignin, 10	CO	380	None	80	N.A.
Lignin, 10	CO	380	Na ₂ CO ₃ , 1	92	N.A.
Glucose, 20	CO	350	None	64	6.5
Glucose, 20	H ₂	350	None	60	3
Glucose, 20	CO	350	Na ₂ CO ₃ , 1	93	35
Cellulose ^b , 20	CO	350	None	90	40
Cellulose ^c , 20	CO	350	None	63	17
Cellulose ^b , 20	H ₂	350	None	60	20
Cellulose ^c , 20	CO	350	Na ₂ CO ₃ , 1	94	46
Cellulose ^c , 20	H ₂	350	Na ₂ CO ₃ , 1	90	27

^a Based on charge.

^b Crude cellulose.

^c Ash free cellulose.

The advantage of carbon monoxide and water over hydrogen in liquefying carbohydrates is reflected not only in the higher yields of benzene-soluble product but also in the composition of the residues (table 8). The atomic ratio of

hydrogen to carbon in the residue from hydrogenation with carbon monoxide and water is close to 1:1, whereas the much larger residue obtained in the presence of hydrogen is only 0.73:1.

TABLE 8. - Composition of benzene-soluble products and residues from cellulose
(2 hr. at 350°C, 1500 psig)

	Benzene soluble product (CO + H ₂ O) (40% yield) ^a	Residue (CO + H ₂ O) (10% yield) ^a	Residue (H ₂) (40% yield)
C (%)	83.3	71.4	74.9
H (%)	7.8	5.9	4.6
H/C	1.11	.98	0.73

^a The remaining 50% yield is largely water plus some carbon dioxide.

Sodium carbonate is an effective catalyst for liquefying cellulose, glucose, or lignin in the presence of carbon monoxide and water. Benzene-insoluble residues of less than 5% of the original weight of cellulose and less than 10% of the original weight lignin have been obtained at relatively mild conditions. The product is similar in elemental analysis to that obtained from lignite but is less aromatic.

The ease of conversion of cellulose and glucose to benzene-soluble products with carbon monoxide and water suggests that structural units derived from those found in carbohydrates exist in low rank coals. The reactivity of coals with CO and water may be indicative of the number of carbohydrate-derived structures in the coal. The structure of low rank coals is even less certain than that of high rank coals and it is hoped that this approach will assist in improving our knowledge of low rank coal structure.

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