

THE HYDROGENATION OF COAL WITH CARBON MONOXIDE AND WATER

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In 1921 Fischer¹ reported the use of carbon monoxide and water in coal dehydrogenation. The yields of ether-soluble material recovered (13 to 35%) were actually higher than those obtained with hydrogen at the same temperatures and pressures. Other investigators following this lead confirmed the results with coal,²⁻⁴ but did not succeed in hydrogenating asphalt with carbon monoxide and water.⁵ Although the early results looked promising, the relatively low conversions, the emphasis on a one step process for converting coal to gasoline, and the impact of the Fischer-Tropsch reaction caused the carbon monoxide plus water approach to coal hydrogenation to be ignored after 1925. This method of hydrogenation has been classified under hydrogenation with nascent hydrogen⁶ because of the belief that activated hydrogen was being formed by the water-gas shift reaction.

The hydrogenation of coal with carbon monoxide and water was reinvestigated with the objective of preparing an oil which could then be converted to more volatile fuels by known hydrocracking techniques. Bituminous coal (Bruceton, hvab), a North Dakota lignite, and a Texas lignite, all -100 mesh, were used in this work. The bituminous coal and the North Dakota lignite were ball milled and stored under nitrogen. The Texas lignite powder had been stored in loosely capped cans for two years prior to use. The hydrogenations were conducted in a 500 ml stainless steel rocking autoclave. The extent of reaction was determined by extracting the product with benzene and weighing the dry residue. The percent conversion is 100 less the percent of benzene-insoluble residue (maf basis).

An equal weight of phenanthrene was used as a solvent in the runs with bituminous coal. Most of the work with lignite was conducted with an equal weight of 1:1 α -naphthol-phenanthrene as solvent. For purposes of comparison, several runs were made without a solvent.

RESULTS

The effects of temperature, pressure and time on the conversion of coal to benzene-soluble and volatile materials using carbon monoxide and water are shown in figures 1 to 4. The conversion increases with temperature, in the range investigated, for bituminous coal (figure 1). Conversions of bituminous coal are increased considerably by the phenanthrene solvent. About 10% of the solvent is hydrogenated, mainly to dihydrophenanthrene.

In the case of lignite (figure 2), the amount of conversion goes through a maximum between 375° and 400°C. The decrease in yield above 400°C is believed to be a result of conversion of some of the soluble product to insoluble high molecular weight material. Conversions of lignite are improved by a solvent but the effect is smaller than that observed with bituminous coal. In addition to hydrogenation of the phenanthrene, some of the α -naphthol is converted to naphthalene and tetrahydronaphthalene during the reaction.

The conversions of bituminous coal and lignite increase sharply with pressure up to about 1,000 psig initial pressure (figure 3). Above 1,000 psig the increases in conversion with increases in pressure are smaller.

A striking feature of the solubilization of lignite with carbon monoxide and water is the rapidity of the reaction (figure 4); conversion to benzene-solubles at the optimum conditions seems to be essentially complete in about 10 minutes. After the initial rapid reaction, the small amount of remaining solubilization may be masked by carbonization of some of the soluble product. Mass spectrometric analysis of the benzene soluble product taken at different times indicates that the rapid solubilization reaction is accompanied by a slow cracking reaction which leads to an increase in the lower molecular weight components of the product.

The reaction of lignite with hydrogen is slower. After 10 minutes of reaction, the solubilization is less than half that obtained with carbon monoxide and water. At longer residence times the extent of solubilization approaches, but does not reach, the value obtained with carbon monoxide and water.

The ultimate analysis and physical appearance of the benzene-soluble oil is very similar with either method of hydrogenation. The carbon monoxide and water undergo the water-gas shift reaction so that hydrogen is present during the reaction. At the completion of the lignite runs using carbon monoxide and water, the composition of the gas is usually within the limits: CO, 25-45%; CO₂, 35-50%; H₂, 15-25%; CH₄, 0.6-1.5%; and traces of higher paraffins and olefins.

The increase in hydrogen and the reduction in sulfur and oxygen contents during solubilization is shown in table 1. There is little, if any, reduction in the nitrogen. This run was conducted with more water and a higher carbon monoxide pressure than usual in order to obtain a high conversion without a solvent. The brown-black product was a pourable oil. In testing a number of lignites, the sulfur content of the benzene-soluble product averaged near 0.2%.

TABLE 1. Analysis of lignite and products
(1:1 Lignite-water, 2,000 psig
initial CO pressure, 2 hr. 380°C)

	Lignite ¹	Benzene-soluble tar ²	Residue
C	64.6	84.8	51.4
H	4.8	7.9	3.1
N	1.0	1.0	0.9
S	0.7	0.2	1.1
Ash	7.2	0.5	36.2
O	21.7	5.6	8.2
H/C mole ratio	0.89	1.1	0.7

¹ Burke County, North Dakota, -100 mesh, analysis water-free basis.

² Obtained in 87% conversion, maf basis.

Aged lignites were less reactive than freshly ball-milled lignite (table 2). An irreversible change occurs in the lignite on aging in air. The large decrease in reactivity obtained by heating powdered lignite at 105°C and the minor decrease obtained on drying under vacuum suggest that the deactivation is largely a result of oxidation of the lignite. A small increase in the conversion of a deactivated lignite can be obtained by increasing the amount of water used in the reaction. This procedure is generally applicable when a modest increase in the conversion of a low reactivity coal is desired.

TABLE 2. Solubilization of aged lignites
(10 minutes at 380°C, 1,500 psig
CO pressure).

<u>Aging conditions</u>	<u>Water content,⁴ percent</u>	<u>Conversion, percent</u>
Fresh ¹	19	89
4 weeks in air ¹	13	77
105°C, 24 hr., ¹ in air	< 1	54
100°C, 0.5 hr., vacuum ¹	< 1	86
2 years in storage ²	6	77
2 years in storage ^{2,3}	6	83

¹ North Dakota lignite.

² Texas lignite.

³ 1:1 = water:lignite used in place of the standard.
0.5:1 = water:lignite ratio.

⁴ Determined in a stream of N₂ at 110°C. for 1 hour.

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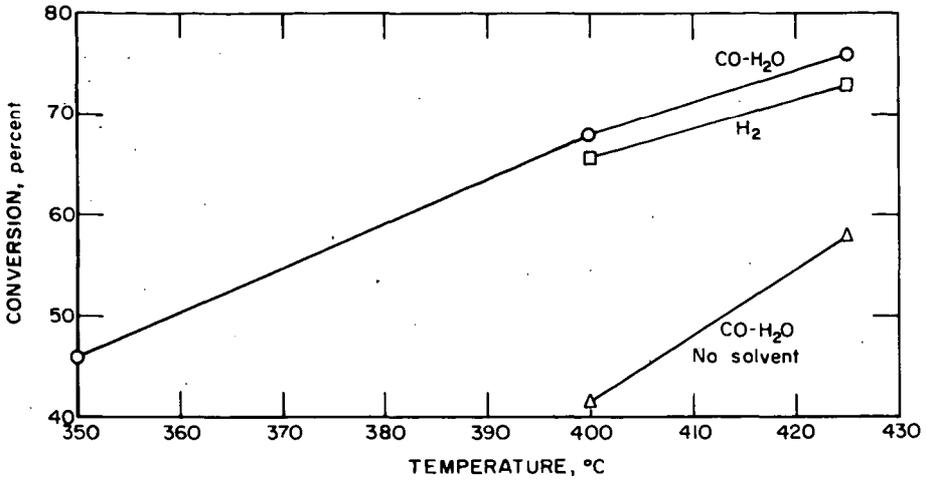


Figure 1.—Effect of temperature on bituminous coal conversion (2 hrs, 2,000 psig initial pressure, 1:1:0.5 = coal : phenanthrene : water).

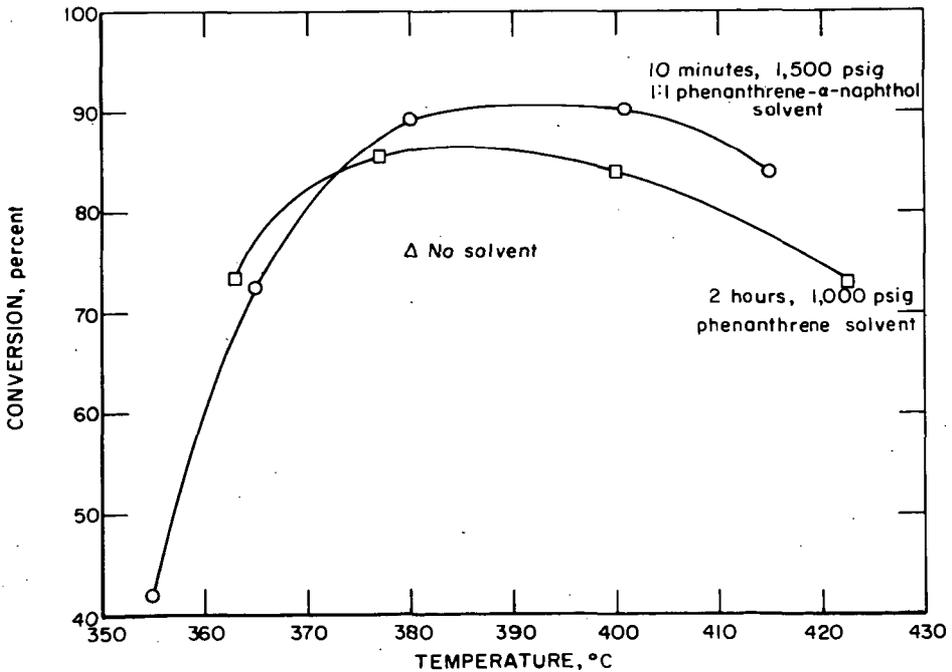


Figure 2.—Effect of temperature on lignite conversion (1:1:0.5 = coal : solvent : water).

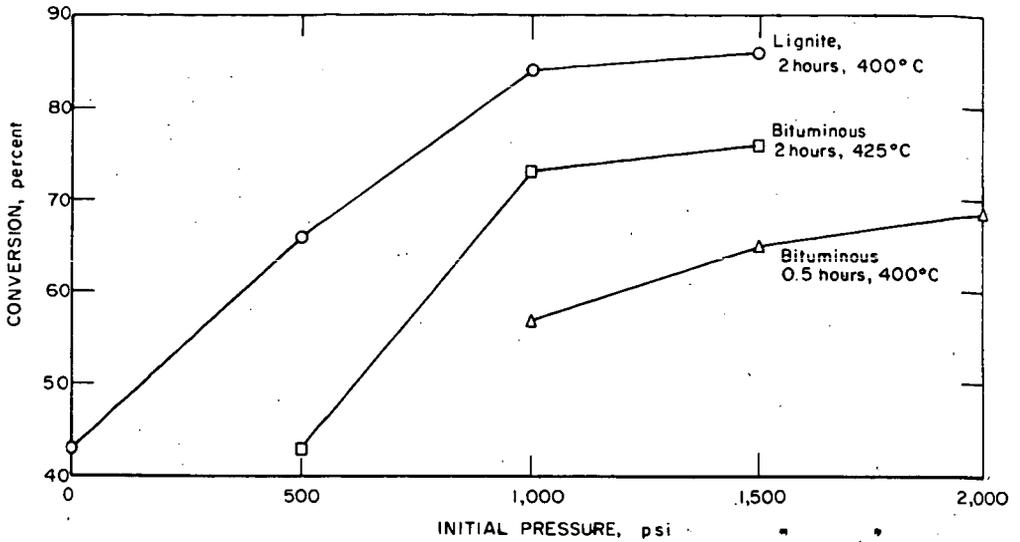


Figure 3.—Effect of pressure on coal conversion (1:1:0.5=coal:phenanthrene:water)

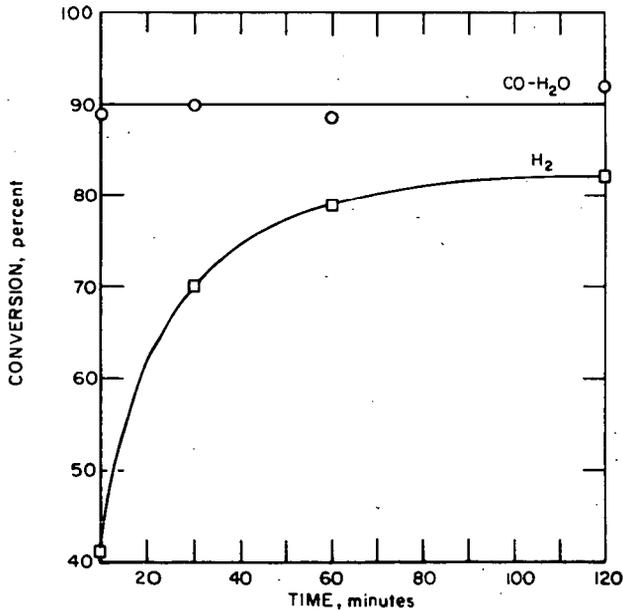


Figure 4—Effect of time on lignite conversion (1,500 psig initial pressure, 380°C).