

CONVERSION OF BITUMINOUS COAL IN CO/H₂O SYSTEMS
II-pH DEPENDENCE*

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Introduction

We have reported that strongly basic conditions promote the conversion of Illinois No. 6 coal in CO/H₂O systems at 400°C to a product that is fully pyridine-soluble and has 50% benzene solubility and 18% hexane solubility. (1) This work used 4 M aqueous KOH, and CO₂ and H₂ were the product gases. No organic H-donor solvents were used in the conversions; water was the only medium used.

We have since shown in control experiments that (a) with N₂ in place of CO, the strongly basic medium alone only decreases the already small benzene solubility of the coal and (b) CO used with only water provides a product with a benzene solubility of only about 10%. (2) Thus both the base and CO must play an important role in the conversion, and in accord with the suggestion by Appell et al., (3) we have considered that formate was the active reducing agent in the system. (1)

Conversion Chemistry

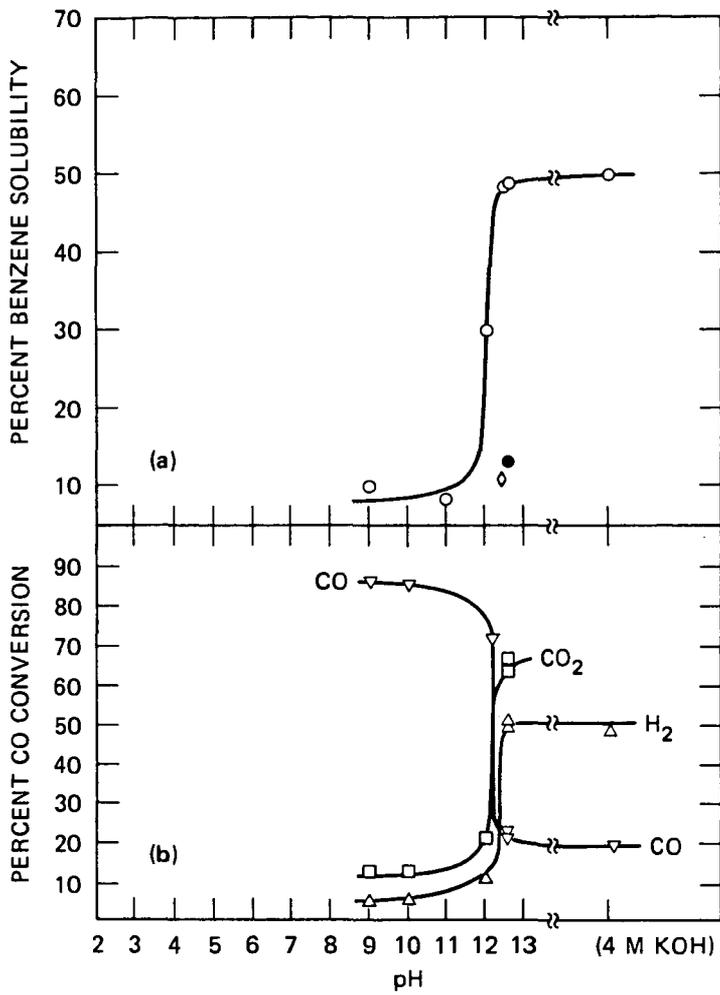
We report here on the study of the conversion at considerably lower basicities and on the question of the intermediacy of formate in the conversion. The data for runs carried out at 400°C for 20 minutes in a stirred autoclave are shown in Figure 1, in which the benzene solubilities of the products are plotted against the pH of the starting aqueous phase determined at 25°C. It is seen that the conversion in a system 4 M in OH⁻ is little different from that in a system with a starting pH of 12.6 (OH⁻ = 0.04 M). The conversion is thus effective down to that basicity level, but then falls suddenly under less basic conditions. This striking loss of conversion effectiveness provides the S-shaped curve shown in the figure.

Also shown in Figure 1 are the product gas analyses. In the effective runs above pH = 12.6, the CO was largely consumed and the product gases were almost equimolar quantities of H₂ and CO₂. The runs below pH 12.6, however, neither yielded substantially converted coal nor consumed CO. There would seem to be a parallel in this system between the conversion of coal and operation of the water gas shift reaction, which provides equal quantities of H₂ and CO₂.



The product analyses for two runs at pH 12.6 are shown in Table 1 along with the composition of the starting coal. Since no organic H-donor solvent is used, the products are uncontaminated and are fully coal-derived. This conditions is in contrast to the common finding from conversions in tetralin or other organic media in which there is incorporation of portions of the organic medium into the products. The contaminant commonly cannot be fully removed, even under high temperature and full vacuum. (4) It is thus possible to calculate a detailed mass balance with our data, using both the elemental analyses of the product fractions and the gas analyses. Such a procedure is presented in Table 2, which compares the quantities of C and H (in mmoles) in both the starting and final systems.

* Paper I in this series is cited as reference 1.



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FIGURE 1 (a) CONVERSION OF COAL TO BENZENE-SOLUBLE FRACTIONS VERSUS pH OF INITIAL MEDIUM (○ = CO; ◇ = H₂; ● = formate/N₂); (b) CO CONVERSION (▽ = CO; △ = H₂; □ = CO₂)

Table 1

COAL CONVERSION AT 400 °C FOR 20 MIN IN
CO/H₂O SYSTEMS AT pH 12.6

Run No.	Benzene-Soluble Product					Benzene-Insoluble Product				
	% Soluble	%H	%C	%N	%S	% Insoluble	%H	%C	%N	%S
Starting Coal	--	--	--	--	--	1	4.66	75.05	1.1	2.1 (org)
26	48	7.26	85.12	1.4	-- ^a	41	5.01	79.53	2.0	-- ^a
28	48	8.25	83.55	0.6	-- ^a	39	4.92	80.75	1.8	-- ^a

NOTE: The coal used in this work is from Pennsylvania State University, number PSOC 26. It has been beneficiated by PSU through its flotation procedure. The runs are conducted on 10 g coal, using 36 g H₂O.

^apending.

The recovery in coal-carbon in this case is 95%, which is a typical value for our studies in these systems. The product gases contain only traces of methane, and we have found only trace quantities of phenolic materials in the final aqueous phase.

Table 2

DETAILED MASS BALANCE FOR RUN 26
(Quantities in mmoles)

<u>Starting Coal</u> (10.0 g)			<u>Product Coal</u> [*] (8.7 g)		<u>Remarks</u>
C	625	→	C	594	95% C recovery
H	460		H	585	125 H gain
<u>Starting Gas</u>			<u>Product Gas</u>		
CO	478	→	CO	103	} 84% C recovery } 120 H lost
			CO ₂	297	
			H ₂	237	

* Composite values for both benzene-soluble and benzene-insoluble product fractions.

The CO₂ and H₂ quantities in the product gases are not the same, although on the basis of the water gas shift reaction we would expect equal quantities of these two gases. The deficit in hydrogen (120 mmole H) is that taken up by the coal. The match in this case may be better than we might expect, but for most runs the agreement is good.

The C-recovery in the gas product CO_x here is typical, and it is likely that the missing C is in the aqueous phase in the form of formate and bicarbonate. We have made no attempt to quantify the inorganic, water-soluble carbon.

This type of mass balancing is readily performed with the products of these conversions. Because the system is "clean," the close balances obtainable provide us with the opportunity to work with coal almost as a "pure" organic compound.*

Figure 1 shows further that at pH = 12.6 the replacement of CO with H₂ was ineffective; the use of potassium formate with N₂ was equally unproductive. A closer look at these results is presented in Table 3, which includes the product gas composition.

Clearly, hydrogen present at the beginning of a run in place of CO does not provide effective conversion of the coal. The considerable contrast to the results obtained in systems containing CO shows that the hydrogen produced in the latter systems is formed concurrently with the coal conversion and does not play a role in the conversion itself.

For the formate case, the quantity of added formate salt was equivalent on a molar basis to twice the hydrogen added to the coal in the high conversion pH 12.6 runs with CO. Thus there was enough hydrogen present for the conversion; however, the system was

* Further study with these "clean" systems is planned. In some preliminary work along these lines with the focus on oxygen balance, it has been observed that the ratio of the hydrogen gained in the coal produce (ΔH_g) to oxygen lost (ΔO_g) was close to 2.0 for several runs. This finding is similar to that discussed by Whitehurst for work with conventional conversion systems. (5)

Table 3

TEST OF THE ROLE OF HYDROGEN AND FORMATE AT pH = 12.6 IN CO-H₂O CONVERSION SYSTEMS AT 400°C/20 MIN

Run No.	Conditions	Benzene-Soluble %	Gas Composition (%)		
			CO	H ₂	CO ₂
26	CO-H ₂ O	48	14	35	47
27	H ₂ /H ₂ O	11	8	86	2
66	N ₂ -H ₂ O-HCOOK ^a	13	1 ^b	90 ^b	9 ^b

^a167 mmoles potassium formate.

^bRelative quantities, ignoring the N₂.

Table 4

COMPARISON OF CO/H₂O AND TETRALIN CONVERSION SYSTEMS

Conversion Medium	Benzene Solubility (%)	H/C ^a		H _{ali} /H _{arom} ^d (BS)
		BS ^b	BI ^c	
Tetralin	37	1.01	0.72	~ 2.7
CO/H ₂ O	48	1.01	0.65	~ 3.0

^aMolar.

^bBenzene-soluble fraction.

^cBenzene-insoluble fraction.

^dBy ¹H nmr.

completely nonconverting. In addition, except for the starting N_2 , the product gas composition was primarily H_2 , with virtually no CO_2 formed. In this case the formate was probably converted to oxalate, a well-known reaction. (6)

Products

A conventional conversion run was performed with tetralin at $400^\circ C/20$ min to provide product material for comparison with the products for the CO/H_2O systems. Both products were fully pyridine-soluble. A detailed comparison is provided in Table 4.

The products are thus very similar in terms of their H/C ratios and H_{ali}/H_{arom} ratios. Other comparisons were made using hplc, 1H nmr, and field ionization mass spectrometry (FIMS) as shown in Figures 2, 3, and 4. The hplc profiles for the benzene-soluble fractions are very similar, with virtually identical retention volumes.

The 1H nmr spectra in Figure 3 are of the benzene-soluble fraction for both the tetralin and CO/H_2O systems and include a spectrum of the benzene-soluble fractions of an SRC sample of Illinois No. 6 coal from the Wilsonville, Alabama plant. The tetralin-derived material clearly contains incorporated tetralin; however, except for that factor the spectra are qualitatively very similar. The H_{ali}/H_{arom} for the SRC is ~ 1.1 , considerably smaller than that value for the other two samples. This difference is most likely due to the higher temperature at which the SRC is produced.

Field ionization mass spectrometry is a mass spectral procedure using low energy ionization, and most molecules are observed with the technique as molecular ions. (7) The procedure is particularly useful applied to coal liquefaction studies, since it can provide a true molecular weight profile for any given fraction.

In Figure 4, which represents the FIMS spectra of the same three benzene-soluble fractions, some differences emerge between the three conversion products. The SRC fraction has the most narrow distribution, followed by the tetralin and CO/H_2O fractions, respectively. The last in particular displays a rather broad distribution, and the detailed differences are expected to be the subject of future study.

Discussion

Our observations can be summarized as follows:

- CO/H_2O systems at initial pH values above 12.6 successfully convert Illinois No. 6 coal to a product that is fully pyridine-soluble and has benzene and hexane solubilities of 50% and 18%, respectively.
- The product gases are H_2 and CO_2 . However, the expected H_2/CO_2 ratio of 1.0 based on the water gas shift reaction is not observed, with the deficit in hydrogen being found in the increased hydrogen content of the coal product.
- These clean systems provide good elemental balances, with typically 95% coal carbon recovery and a good hydrogen balance. The $\Delta H_g/\Delta O_x$ ratio is close to 2 in preliminary work.
- The system with H_2 in place of CO is not effective, and potassium formate under an N_2 atmosphere is equally ineffective.
- The products are very similar to those obtained in conventional tetralin conversions.

These results can be considered from two points of view. First, it is of interest to consider the advantages this chemistry might provide in a large-scale coal conversion process. The conversion is catalytic in base, with the turnover number for OH^- (the molar ratio of H added to the coal to the quantity of base present) calculated from the values in Tables 1 and 2 to be 80-90.* It is thus an efficient process, and while catalyzed, its homogeneous nature would avoid the common problem of catalyst fouling due to carbon deposition. The system thus has good recycle potential and small catalyst/coal loading requirements. Hydrogen is a product gas and useful for subsequent upgrading of the coal product.

* For run 26, 125 mmole H is gained by the coal in a system 0.04 M in OH^- of volume 36 ml. Thus the turnover number = $125/(36 \times 0.04)$.

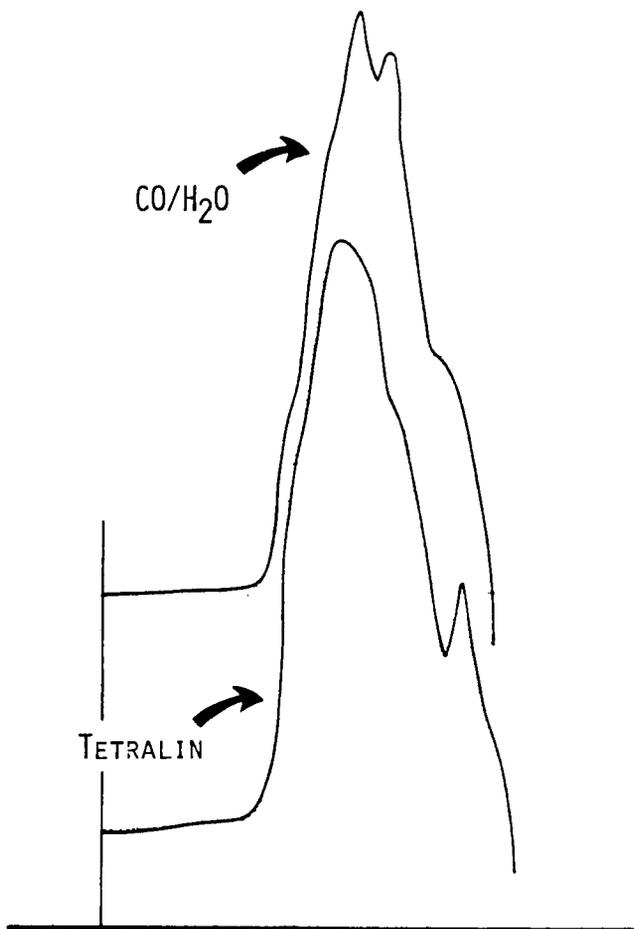


Figure 2. High pressure liquid chromatographs of the benzene-soluble fractions from conversions with Tetralin and CO/H₂O.

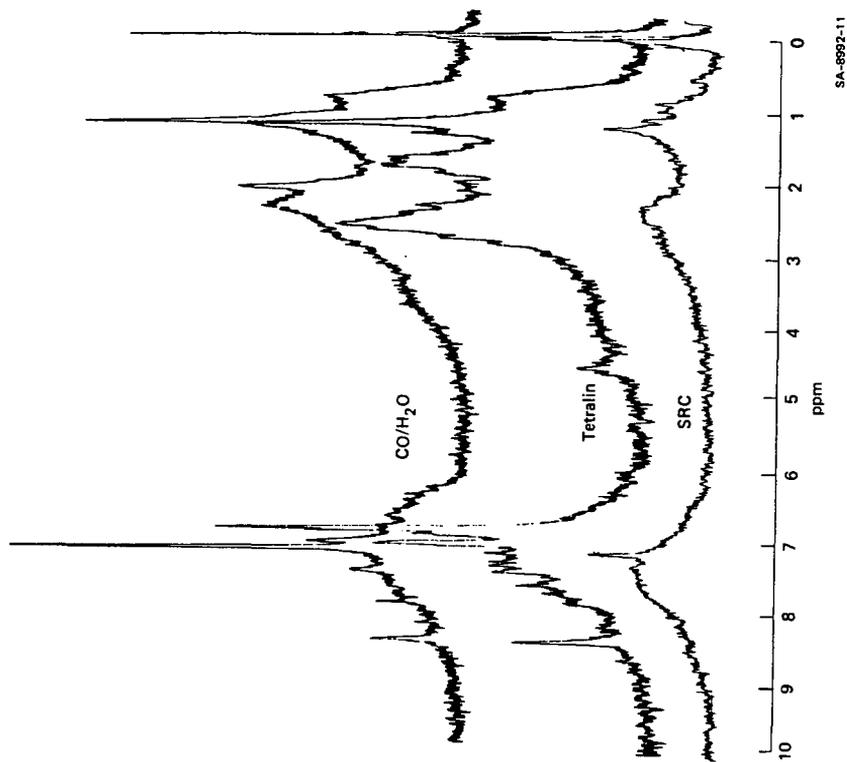


Figure 3. $^1\text{H-NMR}$ spectra of the benzene-soluble fractions of SRC, tetralin, and CO/H₂O conversions.

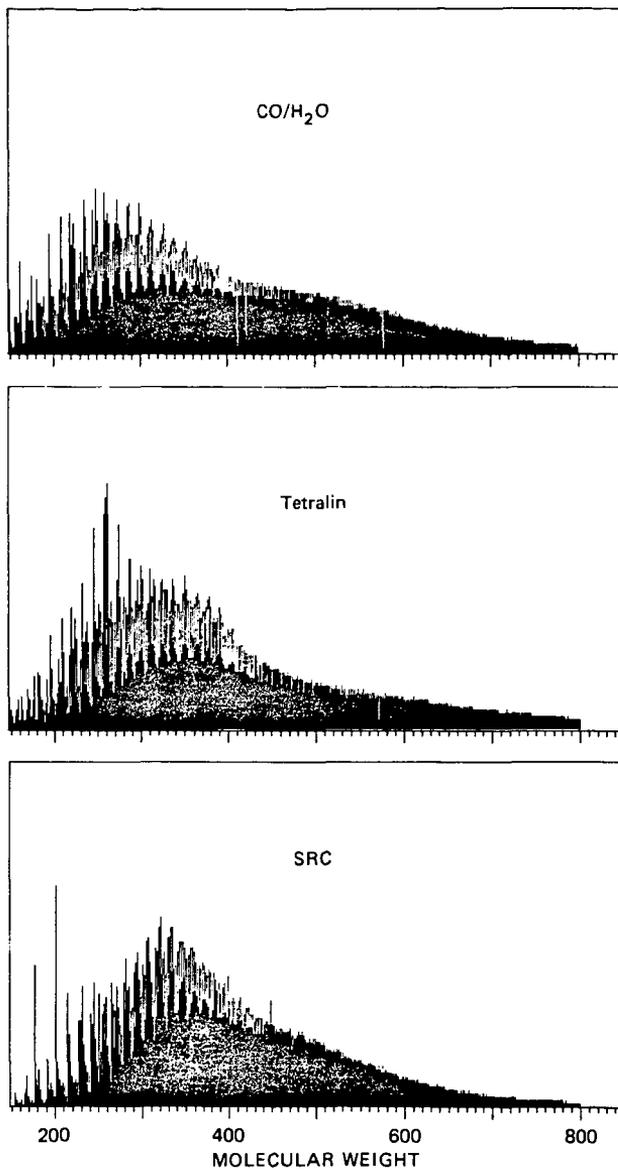


Figure 4. FIMS spectra of the benzene-soluble fractions of SRC, Tetralin, and CO/H₂O conversion.

The second view to be taken of these results concerns the clean nature of the conversions. We suggest that the system would be useful for studies in coal structure and conversion mechanisms since the recoveries are very high, and there is no organic medium to deal with. Both nmr and mass spectrometry studies could be applied to the products from these conversions, and we expect this work to continue along those lines.

Acknowledgment

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