

COAL LIQUEFACTION WITH ^{13}C LABELLED CARBON MONOXIDE

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Low-rank coals may be successfully liquefied under pressure using CO or mixtures of CO and H_2O or CO and H_2 . Following a suggestion in the literature in 1921 (1), Appel and Wender in 1968 reported conversions of both bituminous coal and lignite with $\text{CO}/\text{H}_2\text{O}$ (2). The reaction with lignite was found to be rapid, converting 1:1 lignite/ H_2O to benzene-soluble tar plus gases in 87% yield (maf) coal at 2,000 psi initial CO pressure and 380°C. Successful continuous liquefaction of lignite in a Process Development Unit for 28 day runs was demonstrated by Severson and co-workers at the University of North Dakota Chemical Engineering Department's Project Lignite (3, 4). During these runs the wet, as-received coal was processed with 50/50 CO/H_2 (syngas) at about 440°C and 2,500 psig. The heavy product prepared was called "Solvent-Refined Lignite", SRL. Batchelder and Fu evaluated some of the syngas technology in 1979 with respect to process commercialization (5).

The University of North Dakota Energy Research Center has continued to investigate low-rank coal liquefaction using mixtures containing CO. The use of H_2S along with syngas has resulted in much improved processing (6). Recently, low temperature reactions (below 400°C) using CO as the reductant have shown exceptional promise (7).

Several mechanisms for reduction reactions with CO have been proposed. Previous studies at UNDERC have shown that CO apparently reacts more rapidly with coal than does H_2 , and that the amount of CO that reacts increases as more as-received lignite is added (8). Whether the CO reacts directly with the coal organic structure or with the water in the coal to produce H_2 *in situ*, is unknown. The catalytic effect of coal ash on the shift reaction ($\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$) may also be a significant factor. Finally, it has been suggested that hydrogen formed from closely bound coal water may be especially active "nascent hydrogen" (2, 9).

We carried out a high temperature study of the reaction of isotopically labelled syngas ($^{13}\text{CO}/\text{H}_2$) with a Texas lignite at 450°C and 3400-3700 psi in coal-derived solvent (10). This study was designed to determine the amount of CO incorporation into the distilled products and hydrocarbon gases. No incorporation of the ^{13}C was seen, thus eliminating Fischer-Tropsch type reactions, and direct incorporation reactions, such as carbonylation reactions. The only labelled product found was $^{13}\text{CO}_2$. At that time we did not examine the insoluble products for ^{13}C incorporation.

The present study was designed to investigate low temperature reactions of three coals of differing rank, Big Brown Texas lignite, Wyodak subbituminous, and Powhatan bituminous coal, with pure CO. The conditions chosen also provide baseline data simulating the first stage in a two-stage liquefaction process. Additional development of analytical methods insured that each part of the product could be examined for ^{13}C incorporation and the gases were more carefully analyzed for $^{13}\text{C}/^{12}\text{C}$ ratios in each gaseous carbon-containing product by GC/MS.

Experimental

Reactions were carried out in a multiple minireactor assembly designed for simultaneous use of up to twelve 22 mL tubes. The stainless steel tubes each contained a stainless steel stirring bar which mixed slurry and gases when the assembly was agitated in a fluidized sand bath. Five grams of a 40% as-received coal slurry in a coal-derived recycle solvent distillate was charged. Labelled gas, 50/50

$^{13}\text{CO}/\text{CO}$, or unlabelled CO gas was introduced, via a manifold system, to a pressure of 1,000 psig cold. The assembly was lowered into the bath preheated to the selected temperature, 300°, 340°, or 380°C for 1 hour, rapidly quenched to room temperature, and allowed to equilibrate. Gas weight was obtained by collecting the gas in a preweighed evacuated bomb of known volume relative to the reaction vessel.

The analysis scheme used is outlined in Figure 1. Gas analyses were performed using an automated refinery gas analyzer and $^{13}\text{C}/^{12}\text{C}$ ratios for the gaseous products were obtained using capillary GC/MS.

A portion of the recovered product was extracted with tetrahydrofuran (THF) and a second portion was microdistilled. A third portion of the recovered product was extracted with CH_2Cl_2 and the solvent was removed with a rotary evaporator at room temperature. A 50 MHz ^{13}C NMR spectrum was obtained for the CH_2Cl_2 soluble fraction using a gated pulse sequence with the decoupler on only during data acquisition. Samples in CD_2Cl_2 with TMS and $\text{Cr}(\text{AcAc})_3$ present were pulsed about two hours until the signal to noise ratio was adequate. These spectra were compared with those of samples from reactions performed in the same manner with unlabelled CO. The CH_2Cl_2 insoluble products were examined by 50 MHz Cross Polarization/Magic Angle Spinning (CP/MAS) solid ^{13}C NMR employing total sideband suppression using TOSS dephasing and foldback pulsing before acquisition (11). These spectra were also compared with those of products from reactions run at the same time with unlabelled CO.

Results and Discussion

The weights of product gas, THF insolubles, distillation residue, water, and ash were used to calculate conversions for these reactions. For the purpose of this experiment ^{13}CO and CO were assumed to react at the same rate so that labelled and unlabelled runs could be averaged to obtain yield structures (Table I). The low-rank coals gave better conversion at 300°C but the Powhatan bituminous coal gave better conversions at 340° and 380°C.

Tracer reactions with ^{13}CO are expected to give easily recognizable labelled products because the natural abundance of ^{13}C is only 1.1%. An incorporation of 1% ^{13}C should double the signal. When identical samples for runs with unlabelled CO are compared, an incorporation of only 0.5% should be recognized without difficulty.

The ^{13}C spectra of the soluble and the insoluble products of labelled reactions were carefully compared with those run without labelled CO. No differences were seen for any of the three coal products at 300°, 340°, or 380°C. A comparison of the CH_2Cl_2 insoluble solid spectra from runs using labelled and unlabelled CO are shown in Figure 2.

Gas analyses for selected runs analyzed by capillary GC/MS and GC were used to determine the ratios of ^{13}CO to ^{12}CO and $^{13}\text{CO}_2$ to $^{12}\text{CO}_2$ and the number of moles of each isotopic compound in the product. The number of moles of CO_2 that was produced from CO was easily calculated since a 50% labelled ^{13}CO was used. The remaining CO_2 produced was assumed to arise from the coal, the only other carbon source present. The number of moles of H_2 found in the product was less than 1/5 the moles of CO_2 formed from CO during the reaction of the two low-rank coals at 300°C. However, during reaction of the bituminous coal, Powhatan (POW1), less CO_2 was formed from the CO added (Figure 3), possibly because the number of moles of water present in the charged coal, POW1, was much smaller, which could limit the shift reactions during the POW1 liquefaction at 300°C. The absence of coal moisture does not, however, limit the conversion of POW1 by CO at higher temperatures, since water may be released by coal thermolysis at 340° and 380°C which could react readily with CO (12).

Table I. Multiple Minireactor Reactions of CO With 40% Coal Slurries for 60 Minutes

No. Runs Averaged	Coal	Temperature, °C	Average Yield (wt % of maf coal)				Average Closure
			Conversion	Gas	Distillate	Soluble Residuum	
5	BB1*	300	20	13.5	3.6	8	92
3	WY01**	300	24	18	3.7	16	95
3	POW1***	300	16	4.3	6.4	14	96
2	BB1	340	62	24	11.8	27	95
1	WY01	340	51	30.5	2.0	17.5	94
2	POW1	340	83	29	6.2	46	88
2	BB1	380	77	2	9.3	40	92
2	WY01	380	72	39	-3.0	35	95
2	POW1	380	87	26	1.9	59	101

Solvent was UNDERC CPU Run 66 D1160 Distillate.

*BB1 - Big Brown Texas lignite, 8.12% ash, 24.40% water.

**WY01 - Wyodak, Wyoming subbituminous coal, 8.37% ash, 24.03% water.

***POW1 - Powhatan, Ohio bituminous coal, 10.78% ash, 2.02% water.

Summary

No ^{13}C incorporation into products other than CO_2 was detected after reactions of Big Brown Texas lignite, Wyodak subbituminous coal, or Powhatan bituminous coal with 50/50 $^{13}\text{CO}/\text{CO}$ at 300°, 340° or 380°C in recycle solvent for 1 hour. No evidence for a Fischer-Tropsch type mechanism, CO insertion, or carbonylation reactions was found.

These data are consistent with a mechanism involving CO entering into the shift reaction with in situ water. The differing response of the coals can be explained by invoking coal ash liquefaction and shift catalysis and the amount of water intimately connected with each coal (13, 14). The change in response by Powhatan at higher temperatures may be due to a shift mechanism initiated by water released from thermal reactions (12). The success of low temperature CO liquefaction would not be unexpected if a shift reaction mechanism were in operation since the equilibrium constant for the shift reaction favors H_2 and CO_2 at lower temperatures.

Acknowledgment

UNDERC carried out this work for the U.S. Department of Energy under Cooperative Agreement No. DE-FC21-83FE60181.

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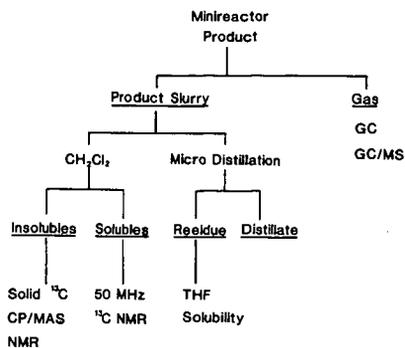


Figure 1. Analysis scheme for minireactor products.

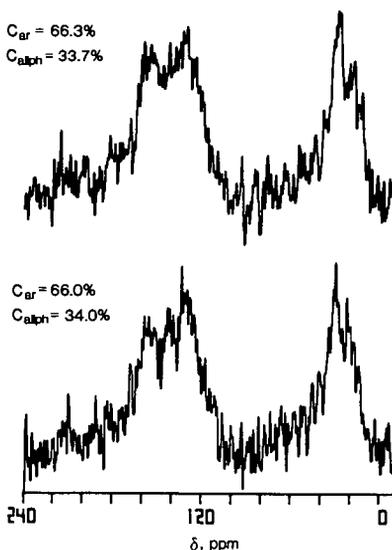


Figure 2. 50 MHz CP/MAS ^{13}C NMR Spectra of insoluble heavy ends from CO reaction with Big Brown lignite (top) and 50/50 $^{13}\text{CO}/\text{CO}$ reaction with Big Brown lignite (bottom).

Relative Product Distribution Gases

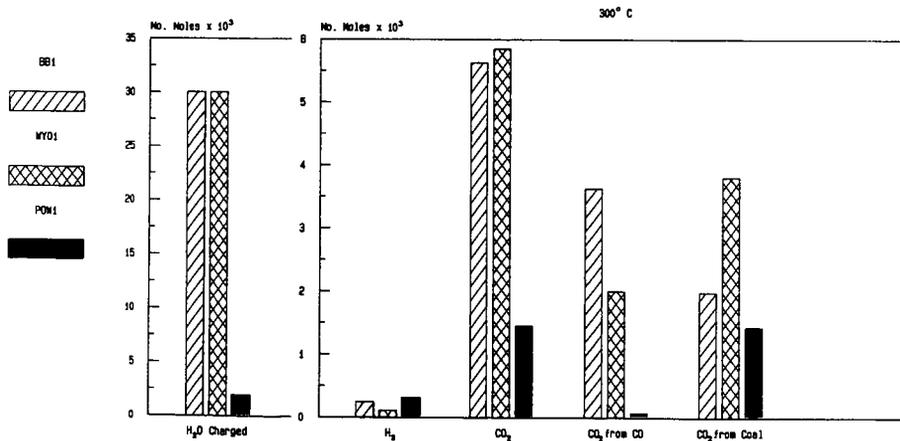


Figure 3. Gaseous product distribution at 300°C from reactions with 50/50 $^{13}\text{CO}/\text{O}$.