

**REACTION PATHWAYS DURING COPROCESSING.  
THE REACTION OF ILLINOIS NO. 6 COAL WITH  
LLOYDMINSTER RESID UNDER MILD CONDITIONS**

Kadim Ceylan and Leon M. Stock\*  
Department of Chemistry  
The University of Chicago  
Chicago, Illinois 60637

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## INTRODUCTION

Over the past few years a number of processes have been developed for the direct liquefaction of coal. Typically, these processes involve thermal degradation of the macromolecular structure of coal, and are followed by hydrogenation to stabilize the degraded material and to increase the hydrogen-to-carbon ratio of the distillable products. In conventional coal liquefaction, a hydrogenated coal derived solvent is used as a vehicle for the transfer of hydrogen to the coal components. Coprocessing of coal with petroleum resid is an alternative technology in which the petroleum resid replaces the donor solvent. Coprocessing of petroleum resid with coal is a bridge between coal liquefaction and hydrocracking that simultaneously upgrades coal and resid. Consequently, coprocessing may offer some special advantages.

It has been observed that a better understanding of the chemistry of coprocessing might yield improvements in the technology (1). Therefore, coprocessing has received recent attention and new effort has been directed to elucidate the reaction pathways (2-6). The coprocessing of Illinois No. 6 and Wyodak coals with Lloydminster and Hondo resid has been thoroughly investigated (7,8), and other studies have discussed the hydrogen atom exchange, hydrogen atom transfer, and carbon-carbon bond cleavage reactions that may occur during coprocessing (9-14).

It seemed appropriate to establish more securely the relationship between the basic work and the reaction pathways that are involved in coprocessing. Accordingly, we have studied the coprocessing reactions of Illinois No. 6 coal with Lloydminster resid under the same reaction conditions that were used to investigate the influence of these fossil materials on hydrogen atom transfer and carbon-carbon cleavage reactions.

## EXPERIMENTAL

Materials and equipment. The coals, resids, and the reference catalyst were supplied by John G. Gatsis of the Allied Research Center.

Illinois No. 6 coal was prepared by the Kentucky Center for Energy Research (KCER) and used as received (Anal. %C, 68.60; %H, 4.51; %N, 1.39; %S, 3.04; %O, 9.65; %H<sub>2</sub>O, 3.15; %Ash, 9.65). Wyodak Coal was obtained from the Pennsylvania State University program and was prepared by KCER, and was dried prior to use (Anal. %C, 63.01; %H, 4.50; %N, 0.90; %S, 1.08; %O, 16.73; %H<sub>2</sub>O, 1.78; %Ash, 12.00). Lloydminster Resid (Anal. %C, 83.6; %H, 11.5; %S, 4.77) and Hondo Resid (Anal. %C, 82.3; %H, 10.3; %S, 6.08; %N, 1.24) were obtained by UOP Research Center and used as is. The catalyst was a UOP proprietary material. The other chemicals were available commercially and they were purified as necessary.

The reactions were carried out in a SBL-2 fluidized sand bath equipped with Techne TC-8D temperature control unit. Three types of reactors were used. The glass capillary reactors were 2.4 mm (i.d.) × 20 cm, the glass tubular reactors were 5 mm (i.d.) × 20 cm, and the stainless steel (SS) reactors had an internal volume of 4.5 ml.

Nuclear magnetic resonance spectroscopy for  $^1\text{H}$  was performed with the University of Chicago 500 MHz system and  $^2\text{H}$  analysis was performed with a Varian XL-400 system. Infrared spectra were recorded with a Nicolet 20 SX spectrometer.

**Procedures.** The procedures for coprocessing were closely parallel to the procedures that were used in the previous study (11). The total quantity of material in the reactors were approximately 75 mg for the glass capillary, 500 mg for the glass tubular reactors, and 1.2 g for the stainless steel reactors. A mixture of the fossil fuel material, in which the resid and coal were combined in a 2:1 ratio (maf basis), was placed into the reactor, and it was carefully sealed under an atmospheric pressure of argon or pressurized with argon or dideuterium. The starting cold argon or dideuterium gas pressure in the stainless steel reactors was approximately 500 psig. The reaction vessels were then immersed into the sand bath which had been preheated at 400 °C. The reactor was vigorously shaken during the reaction. At an appropriate time, the reactor was removed from the sand bath and cooled immediately by immersing it in water. The glass reactors were cut and the stainless steel reactors were carefully vented to the atmosphere and then opened. The reactor contents were extracted into tetrahydrofuran, filtered, and the residue was Soxhlet extracted with tetrahydrofuran. The soluble product was fractionated into asphaltenes (n-heptane insoluble), resins (n-heptane soluble, n-pentane insoluble), and oils (n-pentane soluble) by successive extractions with n-heptane and n-pentane, according to the procedure suggested by Speight and co-workers (15).

## RESULTS AND DISCUSSION

Illinois No. 6 coal was coprocessed with Lloydminster resid. The earlier coprocessing work with these materials was carried out at 420 °C in 2 hrs with a high pressure of dihydrogen, 3000 psi (7,8). Under these conditions, Gatsis and his co-workers achieved very high conversions of the coals into tetrahydrofuran soluble products. We elected to examine the same fossil materials under much milder conditions so that the conversion of the coal would be less complete, and the influences of selected reaction parameters on the product yield and distribution could be investigated. Accordingly, the reaction temperature was decreased to 400 °C, and the reaction time was decreased to 1 hr. Dideuterium was used in some experiments, but at 500 psi. The results are summarized in Table I.

Coal conversion was the principal parameter that we used to evaluate the results. The conversion values were calculated on the basis of the transformation of the insoluble coal into tetrahydrofuran soluble materials. As expected, the conversions that are presented in Table I are considerably less than the conversions that were reported by Gatsis and co-workers (7,8).

The reaction time is an important variable. An increase in the reaction time for the coprocessing of Illinois No. 6 coal and Lloydminster resid from 60 to 90 min in an inert atmosphere increased the conversion from 44 to 54%. Similarly, an increase in the reaction time for the coprocessing of the same substances from 15 to 60 min in a dideuterium atmosphere increased the conversion from 28 to 52%. These findings are in accord with the results and conclusions of Gatsis and his co-workers who also pointed out that the incremental increase diminished after the first 60 min (7,8). The observations for Illinois No. 6 coal and Lloydminster resid indicate that the use of dideuterium increases the conversion from 44 to 52%, the use of a catalyst increases the conversion from 44 to 50% and the incorporation of both a catalyst and dideuterium increases the conversion to 53%. The oil yields are not impacted in the same way. The addition of the catalyst in the absence of dideuterium actually reduces the oil yield from 27 to 22%. Indeed, the highest oil yield was observed when the reaction was carried out with dideuterium but in the absence of the catalyst.

Additional experiments were carried out with Wyodak coal and Hondo resid. It was found that coprocessing of these fossil fuels without the catalyst at 400 °C for 1 hr produced the following reactivity patterns.

### For Coal Conversion and Oil Yield

Wyodak  
Lloydminster > Wyodak  
Hondo > Illinois No. 6  
Lloydminster > Illinois No. 6  
Hondo

The order of reactivity for coprocessing without a catalyst is exactly inverse to the order of reactivity of the same pairs of fossil materials in the exchange of hydrogen atoms with tetralin-d<sub>12</sub> under the same experimental conditions (11).

**For Exchange of Hydrogen with Tetralin-d<sub>12</sub> at 400 °C**

Wyodak                      Wyodak                      Illinois No. 6                      Illinois No. 6  
Lloydminster      <      Hondo                      <      Lloydminster                      <      Hondo

The order of reactivity in the molybdenum-promoted coprocessing reaction is also essentially inverse to the reactivity pattern for exchange with tetralin-d<sub>12</sub>.

Previous work with 1,3-diphenylpropane suggested that Illinois No. 6 coal was the most effective initiator as well as the most effective hydrogen atom donor among the four fossil materials and that Lloydminster resid was the least effective initiator as well as the least effective hydrogen atom donor. Although it is difficult to provide a comprehensive interpretation of the observations for the complex coprocessing system, it is relevant to consider the chemistry of the thermolytic reactions of the coals and resids. Success in coprocessing depends upon facile initiation reactions and the occurrence of uninterrupted chain propagation sequences that redistribute hydrogen atoms, fragment the large coal and resid molecules, and enhance the solubility through adduction. Parallel heteroatom removal reactions are also essential.

Free radical decomposition reactions of the coal macromolecule must proceed in order to initiate the free radical propagation reactions that are necessary to convert it and the resid into lower molecular weight fragments and eventually into n-pentane soluble products. The resids that we have examined are much less effective initiators than the coals. They are also less effective hydrogen atom donors than the coals. Indeed, the observations for the coprocessing of the resid with Illinois No. 6 coal, which is simultaneously the best initiator and best hydrogen donor, suggest that its donor properties interfere with its successful coprocessing because hydrogen donation terminates the essential chain reactions and simultaneously increases the aromatic character of the coal macromolecules. The observations also suggest that blends of coals and resids may offer opportunities for enhanced conversion.

Dihydrogen addition clearly plays a major role in the liquefaction of coals (15,16). Evidence concerning the utilization of dihydrogen in coprocessing is more limited, but Curtis and Cassel have reported that the addition of hydrogen atom donors to the reaction system decreases the dihydrogen gas consumption (5). Their observations also imply that the hydrogen donor capacity of the collection of the fossil materials in the liquid phase can interfere with the desirable addition of dihydrogen to the initially highly aromatic coal molecules. We examined selected spectroscopic properties of the reaction products to gain further perspective on the course of the reaction. Representative nuclear magnetic resonance spectra are shown in Figure 1. Dideuterium was used to probe the role of dihydrogen in the reaction. Although the influence of the gas on the conversion and oil yields was modest, the spectroscopic information clearly establish that deuterium atoms were incorporated into the products. Weak absorptions near 2100 cm<sup>-1</sup> were observed in the infrared spectra of most products. Our preliminary results suggest that more deuterium is incorporated in the oil than in the other fractions, and the representative <sup>2</sup>H NMR spectra indicate that the deuterium is abundantly incorporated into aliphatic structural elements with resonances between 1 and 2 ppm. Lesser amounts of deuterium appear in benzylic and aromatic positions. We estimate that 0.1 to 0.2 mmol of dideuterium is incorporated per gram of the reactants in these reactions at 400 °C and 500 psi dideuterium. These results prompted further study of the distribution of dideuterium among the reactions products. The work is discussed in the next paper.

## CONCLUSION

The experimental results strongly suggest that hydrogen transfer processes occur very rapidly among all the constituents, and that dideuterium is added to the reaction products in the presence and absence of the molybdenum catalyst. The reactivity pattern for the four fossil materials suggest that the

hydrogen atom transfer reactions have a significant influence on the course of the reaction. In particular, the hydrogen donor properties of Illinois No. 6 coal appear to interfere with its conversion.

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Table I. Coprocessing Reactions of Fossil Fuels<sup>a</sup>

Entry	Coal and Resid	Reactor	Gas	Cat, % <sup>b</sup>	conv wt%	soluble product composition		
						asph	resin	oil
1	Illinois No. 6 + Lloydminster	tubular	Ar	-	44.2	28.7	9.7	61.6
2	Illinois No. 6 + Lloydminster	tubular	Ar	-	53.9	21.7	11.2	67.1 <sup>c</sup>
3	Illinois No. 6 + Lloydminster	SS	D <sub>2</sub>	-	27.8	27.6	12.1	60.1 <sup>d</sup>
4	Illinois No. 6 + Lloydminster	SS	D <sub>2</sub>	-	51.5	33.5	3.3	63.2
5	Illinois No. 6 + Lloydminster	SS	Ar	1%	50.0	50.0	7.0	43.1
6	Illinois No. 6 + Lloydminster	SS	D <sub>2</sub>	1%	53.0	33.1	7.1	59.1
7	Illinois No. 6 + Lloydminster	capillary	Ar	-	40.8	22.0	-	78.0 <sup>c</sup>

<sup>a</sup>The reactions were carried out at 400 °C for 1 hr. The coal conversion is based upon the quantity of insoluble residue. <sup>b</sup>The wt% catalyst concentration was calculated from 100 (molybdenum/coal (maf)). <sup>c</sup>This reaction was carried out for 90 min. <sup>d</sup>This reaction was carried out for 15 min. <sup>e</sup>The yield of n-heptane soluble material is reported.

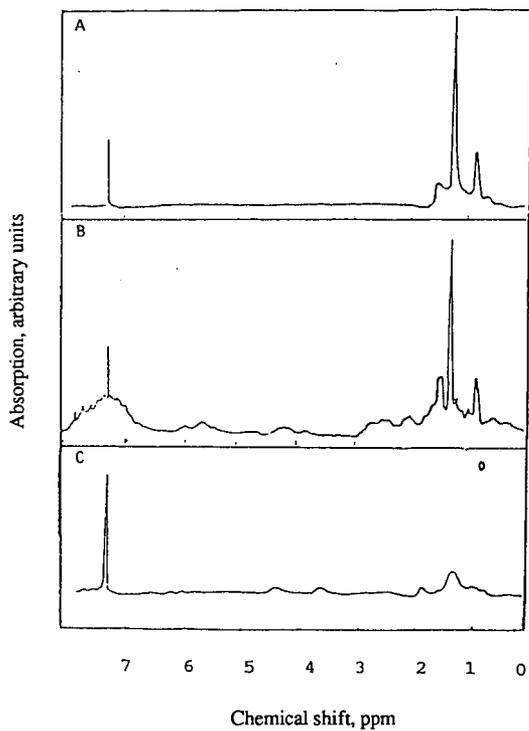


Figure 1. A. The  $^1\text{H}$  NMR spectrum of the oil fraction of Lloydminster resid.  
 B. The  $^1\text{H}$  NMR spectrum of the oil produced in experiment 4.  
 C. The  $^2\text{H}$  NMR spectrum of the asphatene produced in experiment 4.