

REACTION PATHWAYS IN COPROCESSING

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Keywords: Coprocessing, Catalysis, Hydrogen Utilization

INTRODUCTION

The coprocessing of coal and petroleum resid has been under active study as a method for the simultaneous utilization of two lower-valued fossil resources. Our research has focused on the coprocessing technology that was developed by Gatsis and coworkers^{1,2} in which optimal reaction conditions (3000 psi total pressure, 420°C, 2:1 resid:coal, and 1 wt percent of a molybdenum-based Universal Oil Products catalyst) enabled the conversion of about 90% of the coal to toluene-soluble products and about 80% of the asphaltenes to heptane-soluble products. We have investigated the chemistry by carrying out the reaction in a dideuterium atmosphere at low and high severity³ and by studying the reactions of representative aliphatic and aromatic hydrocarbons and phenols.⁴

EXPERIMENTAL

Materials. Illinois No. 6 coal was prepared by the Kentucky Center for Applied Energy Research and was used as received (Anal. % C, 68.60; % H, 4.51; % N, 1.39; % S, 3.04; % O, 9.65; % H₂O, 3.15; % ash, 9.65). Lloydminster petroleum resid (Anal. % C, 83.6; % H, 10.3; % S, 4.77; % N, 0.59; % O, 0.54) was obtained from the UOP Research Center. The catalyst was a molybdenum-based UOP proprietary material.

Procedure. Lloydminster petroleum resid (280 g) and Illinois No. 6 coal (165.4 g) and the catalyst (0.2 wt % Mo) were added to an 1800-mL rocking autoclave. The autoclave was sealed and pressurized first with hydrogen sulfide and then with dideuterium to give a 10 vol % hydrogen sulfide and 90 vol % dideuterium at the desired total pressure. The autoclave was heated to the desired temperature in about two hours and then cooled or retained at the temperature as appropriate. The work-up procedure, which has been described previously,³ enabled the isolation of gases and insoluble products as well as the solvent separated oil, resin, and asphaltene.

Analysis. Elemental analyses of the starting coals, resids, and solvent separated products were carried out at Universal Oil Products. Gas analyses for deuterated methanes, ethanes, propanes, butanes, butenes, benzenes, and toluenes were carried out at the Institute of Gas Technology.

Deuterium NMR spectra were obtained on a Varian XL 400-MHz spectrometer, and proton NMR spectra were recorded at 500 MHz. The D/(H + D) ratio was evaluated for the aromatic and the alpha, beta, and gamma aliphatic positions. Detailed procedures that describe the magnetic resonance experiments have been published.^{3,5}

RESULTS

The extent of conversion of the coal and resid into gases, oils, resins, asphaltenes, and solids is displayed in Figure 1. Typical results that illustrate the manner in which deuterium is incorporated into the reaction products are shown in Figure 2. The reaction chemistry of 1-pentyl-2-naphthol, which illustrates the complexity of the catalyzed transformations of even rather simple molecules, is summarized in Figure 3.

DISCUSSION

Molybdenum catalysts have been under study for many years. Indeed, more than 25 contributions were presented at a symposium of the Division of Petroleum Chemistry in Washington in August, 1994. While the detailed molecular mechanisms for these catalysts are not yet fully established, they are effective agents for the reduction of aromatic molecules, especially bi- and trinuclear substances, and for hydrodeoxygenation, hydrodesulfurization, and hydrodenitrogenation. Their hydrodeoxygenation activity is illustrated in Figure 3. In high severity coprocessing, the catalyst removes virtually all the oxygen, 74% of the sulfur, and 42% of the nitrogen from the products of Illinois No. 6 coal and Lloydminster resid. The catalyzed transformations of pure hydrocarbons and heterocycles have been studied by many research teams. For example, Curtis and her coworkers showed that the heteroatom removal and reduction reactions lead to monobenzenoid aromatic compounds, thus benzofuran yields ethylbenzene and 2-naphthol provides tetralin.⁶

The catalyst apparently also accelerates electrophilic reactions, and alkylation occurs during the process. Thus, when low concentrations of phenol are incorporated into the coprocessing reaction system, it undergoes alkylation before it is deoxygenated.⁴ Aromatic deuterium exchange also apparently proceeds in an electrophilic order as suggested by the fact that phenols exchange much more rapidly than benzenes.

Hydrogen-deuterium exchange is facile. The selectivity for the incorporation and exchange of aromatic as well as alpha, beta, and gamma [AromaticCH₂(α)CH₂(β)CH₂(γ)] aliphatic hydrogen was measured for the series of coprocessing reactions. The results at high reaction severity indicate that the hydrogen and deuterium content has almost reached the equilibrium value dictated by the relative abundances than substances in the reaction system. At low severity, the deuterium is selectively incorporated at the aromatic and alpha aliphatic positions. Then, as the reaction proceeds, the amount of deuterium in the beta and gamma aliphatic positions increases, and the quantity of this isotope in the aromatic and alpha positions eventually decreases. Deuterium exchange in thermal reactions shows a much different order. The reactivity at activated benzylic (alpha) positions is clearly dominant under these conditions, with much less chemistry at the aromatic and unactivated aliphatic positions. The molybdenum catalyst and the reagents that were used in this study present a novel pattern of reactivity in which both free radical hydrogen transfer and ionic proton transfer occur rapidly. This dualism of parallel radical and electrophilic chemistry importantly contributes to the success of this coprocessing process.

The outcome is strongly influenced by the high initial hydrogen sulfide concentration, which is augmented by the formation of additional amounts of this acid from the resid and coal. Molybdenum sulfide catalysts contain thiol groups with H/Mo ratios from 0.12 to 0.37.^{7,8} Furthermore, it is known that the exchange of H₂ and D₂ is very rapid.⁹ Thus, the rapid equilibration of H₂S with the D₂ atmosphere in this reaction system is assured.



Hydrogen sulfide is certainly effective as a hydrogen atom transfer agent in thermal coal conversion chemistry.¹⁰ Thus, the myriad of different radicals that are formed in the initial thermal decomposition of the coal macromolecules are rapidly converted to stable molecules by very fast hydrogen atom transfer reactions. The catalyst probably does not participate in these initial reactions, other than by insuring the exceedingly rapid conversion of ineffectual dideuterium into effective hydrogen deuterium sulfide. The thermal coal to asphaltene conversion is not the limiting reaction in coprocessing, Figure 1. One important factor in this successful conversion is the fact that the reaction between the initial coal fragment radicals and other coal constituents can be effectively suppressed by rapid hydrogen transfer. A second factor is that the smaller core molecules are efficiently converted by the catalyst into desirable hydrocarbons free of heteroatoms. These suggestions can be coupled with current ideas of coal structure and coal decomposition to provide a reasonably satisfying picture of coal conversion during coprocessing.

It is well known that the slow conversion reactions of the collections of molecules that constitute the asphaltenes limit the success of this coprocessing reaction.¹² Our new results show that this situation prevails in spite of the fact that the hydrogen atoms of the asphaltenes exchange quite readily, Figure 2. The parameters that govern the reactivity of these molecules have not yet been adequately elaborated.

Acknowledgment. We are indebted to the coal sample program at the Kentucky Center for Applied Energy Research for starting material. We also gratefully acknowledge the special efforts of the analytical group at Universal Oil Products and the Institute of Gas Technology. Irene Fox of the Analytical Chemistry Laboratory at Argonne National Laboratory provided insight concerning the interpretation of the H/D analyses that were obtained by LECO equipment. We are also indebted to the United States Department of Energy for the support of this research via AC22-88PC88811.

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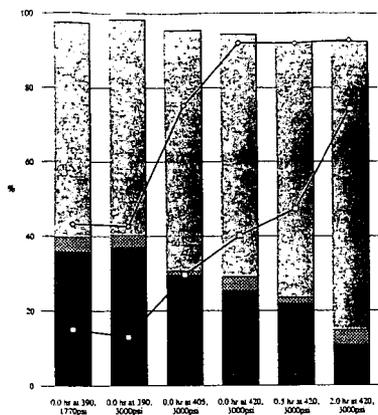


Figure 1. Coal (40 to 90%) and asphaltene (15 to 75%) conversion are portrayed by the lines. The yields of solids, asphaltenes, resins, oils, and gases are displayed from bottom to top in black, gray and white in the bar graph as a function of reaction conditions for the coprocessing reaction of Lloydminster resid and Illinois No. 6 coal.

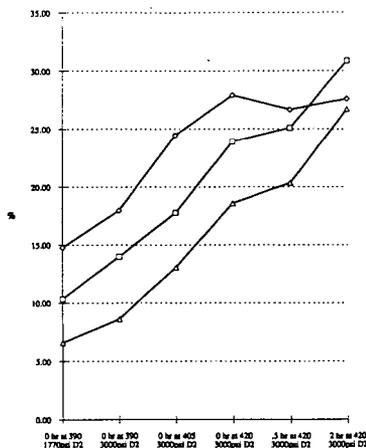


Figure 2. Aromatic % deuterium content, $D/[H + D]$, in the oil (triangle), resin (square), and asphaltene (diamond) fractions as a function of reaction conditions for the coprocessing reaction of Lloydminster resid and Illinois No. 6 coal. Related information is available for alpha, beta, and gamma aliphatic positions.⁵

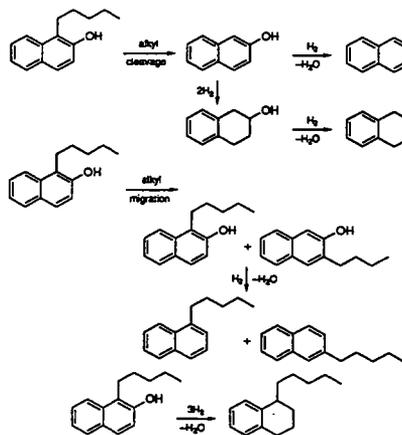


Figure 3. Reaction pathways for 1-pentyl-2-naphthol under the conditions of the catalyzed coprocessing reaction.⁴