

LIQUEFACTION OF WYODAK COAL IN INDOLINE*

Thomas D. Padrick and Steven J. Lockwood

Sandia National Laboratories, Albuquerque, NM 87185

INTRODUCTION

Several investigators have observed an enhancement of Wyodak coal liquefaction when 1,2,3,4-tetrahydroquinoline (THQ) is used as the solvent (1,2). A difficulty in evaluating the cause of this observed enhancement was that THQ possesses both hydrogen-donor and polar (basic nitrogen) characteristics. We examined the liquefaction behavior of Wyodak coal in a variety of heterocyclic solvents to learn the role of the nitrogen functionality in coal liquefaction (3). We observed high conversion for Wyodak coal in indole, a non-hydrogen-donor, nitrogen-heterocyclic solvent. We found that a large fraction of the Wyodak coal was held together by hydrogen bonds which were disrupted by interaction with the N-H functionality of indole to form associatively bound coal-indole complexes. These coal-indole complexes were THF soluble and accounted for the high conversion observed for Wyodak liquefaction in indole under mild liquefaction conditions. We feel this mechanism would also explain the role of the basic nitrogen functionality in other solvents with the N-H structure, such as THQ.

Having an understanding of the role of the basic nitrogen characteristic of the solvent, we began a study of a solvent possessing both basic-nitrogen and hydrogen-donor characteristics. We chose to investigate indoline (2,3-dihydroindole) because it has both solvent characteristics, has a single dehydrogenated species (indole), which along with the hydrogenated form is readily monitored, and knowledge of the liquefaction behavior of its dehydrogenated form had already been obtained. We have now conducted experiments in indoline to learn if there is a possible further enhancement of the liquefaction reaction in this type of solvent due to an actual complexing of the hydrogen donor molecule to the coal molecule. We have determined that liquefaction in indoline, which can first complex to the coal and then donate its hydrogen, is much more effective than liquefaction in either a pure hydrogen donor (tetralin) or a combination of hydrogen donor + nitrogen heterocyclic (tetralin + indole).

EXPERIMENTAL

The data reported below were obtained from batch microreactor runs using Wyodak coal (South Pit Mine) and selected model solvents. The 25 cm microreactors were loaded with an 8 gram sample of a 2/1 solvent to coal mixture. They were then pressurized to 1000 psig with nitrogen. The microreactors were heated (13 minutes to reach reaction temperature) in a fluidized sand bath and held at temperature for the specified time. The microreactors were then cooled (30 seconds for a 200°C quench) in a second fluidized sand bath held at room temperature. Conversion to THF soluble products was obtained by subsampling the whole liquid product from the microreactor, sonicating the sample in THF and then pressure filtering through a 0.2 micron Millipore filter. The filter was then analyzed by gel permeation high performance liquid

* This work supported by the U. S. Department of Energy at Sandia National Laboratories under contract DE-AC04-76DP00789.

chromatography (HPLC) to observe differences in product distribution (4). This technique separates the filtrate into high, intermediate and low molecular weight fractions. These fractions are comparable to the classical preasphaltene (mw \sim 1000), asphaltene (mw \sim 450) and oil (mw \sim 250) fractions obtained by Soxhlet analysis.

RESULTS AND DISCUSSION

We began our study of the effects of indoline on Wyodak coal conversion by liquefying Wyodak coal at various times and temperatures in indoline, indole and tetralin and measuring the conversion to THF soluble products. Figures 1 and 2 show these results.

We can see from Figure 1 that at 375°C the conversion of Wyodak coal to THF solubles is very high for liquefaction in indoline, even at short reaction times. Comparison of the conversions in tetralin and indoline at 20 minutes shows that in indoline the conversion is more than double that obtained with tetralin (82% to 40%). The conversion in both of these solvents continues to increase with time, suggesting continued reaction between the coal and these hydrogen donors. We also observe in Figure 1 that as a function of time at 375°C, conversion of Wyodak coal in indole levels off. This is attributed to the fact that at a fixed temperature a certain level of coal hydrogen bond disruption will take place after the time necessary for complete interaction of the solvent with the coal structure. Beyond this time, no additional indole-coal reactions can occur in this system.

Figure 2 likewise shows that for all temperatures and a 20-minute reaction time, conversion in indoline is greater than conversion in tetralin. However, we do observe that at high temperatures the two hydrogen donor solvents appear to be approaching the same conversion level. This suggests that at high temperature the hydrogen transfer reactions begin to dominate the reaction mechanism and therefore indoline and tetralin begin to behave similarly.

Further evidence that at high temperatures a hydrogen transfer mechanism begins to dominate the liquefaction chemistry can be seen in Figure 3. In Figure 3, we have plotted the ratio of the indole to indoline concentrations measured in the product material formed in an experiment with Wyodak coal and indoline. These concentrations were measured by HPLC analysis. This ratio is a measure of the degree of indoline dehydrogenation. We can see from Figure 3 that between 375°C and 400°C, a significant increase in the hydrogen transfer rate occurs.

The data in both Figure 1 and Figure 2 confirm that when indoline is used as the solvent for Wyodak liquefaction, there is enhancement of the conversion above that obtained in a good hydrogen donor. We believe that this is due to the interaction of the N-H functionality of indoline with the coal structure. This results in coal-indoline complexes, similar to those observed in our study of Wyodak liquefaction in indole. Figure 4a is the HPLC spectrum that we obtained for products of Wyodak liquefaction in indole. Here we see a large peak in the molecular weight distribution due to the indole-coal complex. Figure 4b is the HPLC spectrum for products obtained from liquefaction of Wyodak coal with indoline as the solvent. We see a peak for indoline and indole (dehydrogenated indoline) and a peak for the coal-indole complex and the coal-indoline complex. The peak for the coal-indoline complex never becomes as large as the complex peak in Figure 4a because the complex undergoes hydrogen transfer resulting in an indole molecule and a non-associative coal molecule. Thus in the indoline system, the complex is an intermediate species as compared to the indole system where the complex is a stable product.

The mechanism discussed above is illustrated in Figure 5. In this proposed liquefaction mechanism, the structure for the hydrogen bonded

coal fragment has not been determined in our work but is merely intended to be representative of possible structures. The heat is apparently needed to fluidize the coal sufficiently for solvent access. This fluidization is actually a weakening of the coal-coal hydrogen bonds.

We have proposed that the hydrogen transfer occurs from the indoline molecule involved in the associatively bound complex rather than from neighboring molecules. Thus, the hydrogen transfer and the disruption of the coal hydrogen-bonded structure do not occur independently. To test our hypothesis, we have performed experiments with Wyodak coal in a mixture of indole and tetralin to simulate the total solvent characteristics of indoline, but with separation of these characteristics into individual molecules. Figure 6 is a comparison of the THF conversions for Wyodak coal in these solvents. The conversion using indole + tetralin is much lower than the conversion in indoline (45% vs 82%). This is consistent with our hypothesis, i.e., that liquefaction of Wyodak coal in indoline, where the solvent first complexes to coal molecule and then transfers its hydrogen, is much more effective than hydrogen transfer from a non-interactive solvent.

The results in Figure 6 were somewhat surprising in that we expected the conversion level in the mixture of indole plus tetralin to be at least as high as the conversion found in indole. In order for the conversion in the mixed solvent system to be lower than the indole conversion, we must have interaction between the solvents or one solvent must interface with the mechanism of the other solvent. If we had had interaction between the tetralin and the indole, we would observe a difference in conversion if we increased the overall solvent to coal ratio. We doubled the solvent to coal ratio, but only increased the conversion by a few percent. Tetralin must interfere with the indole liquefaction mechanism to result in the observed conversion level.

We collected the THF solubles from a liquefaction run of Wyodak coal and indole (mostly coal-indole complex). We then reacted this material with tetralin at 375°C for 20 minutes to determine if there was any degradation of the complex and/or production of insoluble material (insols). There was no production of insols or change in the complex concentration. As far as we were able to determine, the tetralin did nothing to the soluble products from the liquefaction of Wyodak in indole. Therefore, tetralin is unable to interfere in the indole liquefaction mechanism after the coal and indole have reacted.

Although the measured conversion for Wyodak coal in tetralin is only 40% at 375°C, the tetralin may interact with a significantly larger fraction of the coal; just not producing THF soluble products. In addition, the coal itself could undergo condensation reactions at sites which are otherwise stabilized through associative bonding with indole, i.e., two hydrogen bonded hydroxyls may eliminate H₂O and form an ether linkage. To determine if either of these situations might be occurring, we reacted the THF insols from the liquefaction of Wyodak in tetralin with indole at 375°C for 20 minutes. If these insols were unaltered coal, then we might expect ~33% conversion of the insols during reaction with indole to bring the overall coal conversion to 60%. However, we measured ~10% conversion. This indicates that either condensation reactions are occurring in the coal or that a step in the tetralin liquefaction mechanism results in retrogressive reactions at 375°C. The former seems more probable and would have occurred in our mixed solvent experiment if tetralin blocked indole access to a portion of the coal hydrogen-bonding sites. Additional experiments are being performed to determine if condensation reactions at coal hydrogen bonding sites are the cause of the low conversion observed during liquefaction of Wyodak in indole + tetralin.

CONCLUSIONS

We have found that indoline is an excellent liquefaction solvent for Wyodak coal, liquefying over 80% of the coal in 20 minutes at 375°C. The indoline system is a good solvent medium for kinetic studies of hydrogen transfer because it has only one, easily monitored, dehydrogenated form. Liquefaction with indoline is much more effective than liquefaction in either a pure hydrogen donor (tetralin) or a combination of hydrogen donor plus nitrogen heterocyclic (tetralin plus indole).

We believe that the effectiveness of indoline is the result of a liquefaction mechanism in which the indoline first functions as a basic nitrogen solvent to disrupt the coal-coal hydrogen bonds and form coal-indoline complexes. The indoline then functions as a hydrogen donor solvent and transfers its hydrogen within the complex to the coal molecule. This mechanism would apply to other similar solvents such as THQ and is much more effective than hydrogen transfer from non-interactive solvents.

We have also determined that if the coal structure is not first interacted with an associative solvent (N-H functionality) to disrupt coal-coal hydrogen bonds, condensation reactions or other retrogressive reactions which make the coal less reactive may occur.

REFERENCES

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FIGURE 1. WYODAK LIQUEFACTION AT 375 C AS A FUNCTION OF TIME

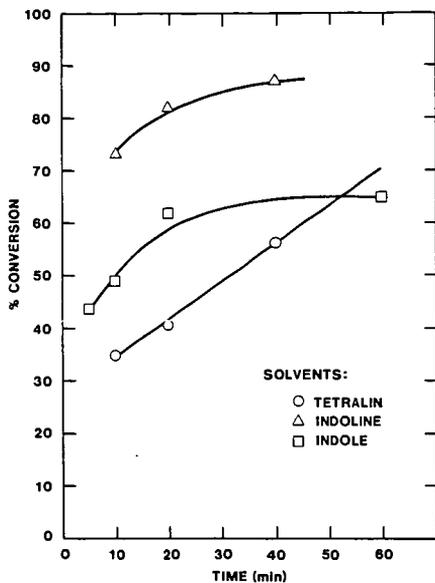


FIGURE 2. WYODAK LIQUEFACTION AS A FUNCTION OF TEMPERATURE

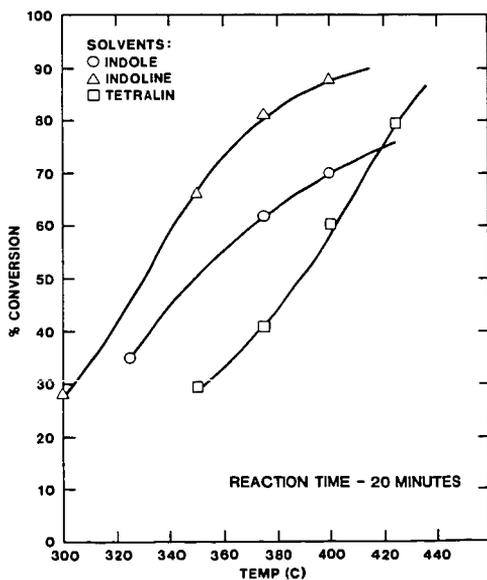


FIGURE 3. PLOT OF INDOLE/INDOLINE RATIO vs TIME FOR WYODAK LIQUEFACTION AT 375 C

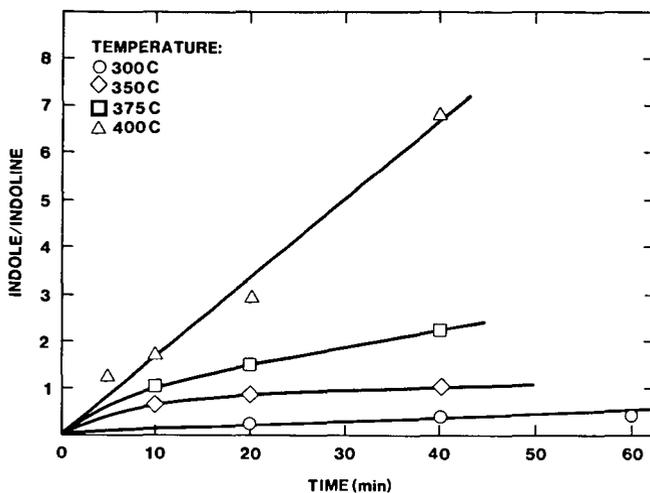
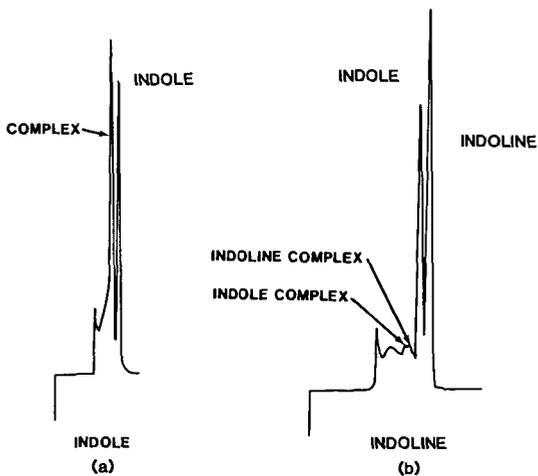


FIGURE 4. HPLC SPECTRA OF WYODAK LIQUEFACTION PRODUCTS



LIQUEFACTION CONDITION: 375C, 20min

FIGURE 5. PROPOSED MODEL FOR THE INDOLINE LIQUEFACTION MECHANISM OF WYODAK COAL

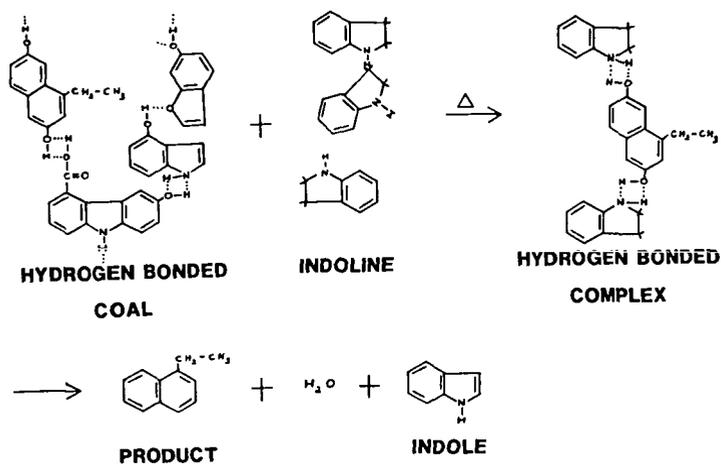


FIGURE 6. THF CONVERSIONS FOR WYODAK COAL IN MODEL SOLVENTS

