

ADDITION OF BASIC NITROGEN PROMOTERS TO ENHANCE LOW SEVERITY TWO-STAGE COAL LIQUEFACTION AND COAL/OIL COPROCESSING

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INTRODUCTION

Conventional coal dissolution theories have held that coal must be heated to temperatures near 400 °-450 °C causing thermal rupture of various labile bonds within the three dimensional cross-linked coal structure and formation of free radical intermediates. Stabilizing the free radicals with hydrogen radicals results in products of lower molecular weight than the parent coal. For many years, however, researchers have hoped to develop methods for dissolving coal at low severity reaction conditions. As early as 1921, Fischer and Schrader (1) reported producing an ether-soluble material by liquefying coal at 350 °C using carbon monoxide and water as reducing agent. More recently, other groups including the Pittsburgh Energy Technology Center (2), the North Dakota Energy Research Center (3), SRI (4), Carbon Resources, Inc. (5), Derbyshire (6), and the Colorado School of Mines (7) have demonstrated the ability to dissolve coal at much milder conditions than previously thought possible. These efforts have been prompted by several scientific and technological incentives associated with low severity coal liquefaction or coal/oil coprocessing:

- reduced hydrocarbon gas make resulting in reduced feed gas consumption, improved distillate selectivity, and enhanced hydrogen utilization efficiency
- suppressed retrogression of primary liquefaction or coprocessing products resulting in enhanced distillate yields and residuum product quality
- production of high boiling residuum which is less refractory and thus more amenable to upgrading in a conventional catalytic hydrocracker
- substitution of cheaper off-the-shelf vessels, piping, and pumps in place of expensive, custom-designed units
- fewer severe slurry handling and materials of construction problems as a result of lower operating temperatures and pressures

Generally, we can conclude from the studies cited above that: 1) if treated carefully, lignites, subbituminous coals, and some bituminous coals are inherently very reactive, and 2) certain bonds in the coal structure can be cleaved or weakened much more efficiently via selective chemical action than by thermolysis. However, kinetic data from low severity liquefaction studies also shows that the rate and extent of coal dissolution at mild conditions is strongly dependent upon intrinsic coal reactivity. Thus, chemical promoters must commonly be used to achieve sufficiently high conversion levels at reasonable reaction times. In searching for effective coal dissolution promoters to be evaluated at low severity conditions, we concluded that, based on results collected at high reaction severity, basic nitrogen compounds warranted extensive study. Atherton and Kulik (8,9) summarized data high severity liquefaction studies using 1,2,3,4-tetrahydroquinoline (THQ) in which THF coal conversion in the range of 85-100 wt% (MAF basis) were obtained using Wyodak subbituminous and Illinois 6 bituminous coals at reaction temperatures of 400 °-450 °C. However, distillate yields from these experiments were much lower than expected, and nitrogen elemental balances indicated nearly complete THQ incorporation into non-distillable products.

Our initial low severity coal liquefaction and coprocessing experiments using THQ as coal dissolution promoter showed that chemical adduction and possibly physical entrapment of the THQ was reduced but that the effectiveness towards promoting coal dissolution remained high (7). The objective of this paper is to describe additional single-stage low severity coal/oil copro-

cessing data using basic nitrogen promoters. Initial results from two-stage (low severity thermal dissolution 1st stage, conventional catalytic upgrading 2nd stage) batch reactor experiments are also presented.

EXPERIMENTAL PROCEDURE

Three coal samples were used in these experiments. Kentucky bituminous coal and Wyodak coal samples from the Wilsonville coal liquefaction pilot plant were used as feed coals in the single-stage batch reactor experiments, while Wyodak coal from the Pennsylvania State Coal Sample Bank (sample PSOC-1405P) was used in the two-stage experiments. Ultimate analysis data for these coals are presented in Table I. Each coal sample was vacuum-dried to less than 0.1 wt% moisture before use.

Cold Lake atmospheric residuum provided by the Alberta Research Council was used as coprocessing solvent. Available characterization data for this feedstock, designated A-8, are shown in Table II. Both 1,2,3,4-tetrahydroquinoline (THQ) ($pK_b = 8.97$) and dipropylamine ($pK_b = 3.00$) were evaluated as coal dissolution promoters. Each was purchased as ACS reagent grade and used without further purification. Reactor runs were completed using commercial grade hydrogen containing 0.5 mole% krypton as an internal tracer for material balance purposes.

Table III lists the single-stage reaction conditions used in this study. Most of the runs were completed at the low severity conditions shown; however, for comparison purposes, several runs were also completed at conventional high severity conditions. Two-stage reaction conditions are summarized in Table IV. Both low and high severity first stage conditions were included in the run matrix, while the second stage reaction conditions were held constant; this allowed us to study the effect of first stage coal dissolution reaction severity on residuum reactivity during second-stage catalytic upgrading.

Coprocessing experiments were performed using a 300 cm³ Autoclave Magedrive II batch reactor interfaced to an Apple IIe personal computer for temperature control. The computer also provides routine temperature and pressure data acquisition during a run. Reactor heatup time to 330 °C-350 °C reaction temperature was approximately 25 minutes. At the end of a run, water was circulated through cooling coils immersed in the reactor contents, allowing cooldown to temperatures below 200 °C in less than 20 minutes. Two-stage runs were performed as follows: at the end of the first stage reaction, the reactor was cooled slightly to facilitate gas removal, and fresh hydrogen was used to inject sulfided 1/16" extrudates of Shell 324 Ni/Mo catalyst into the reactor contents. The reaction temperature and pressure were then adjusted to the prescribed second stage conditions and the run completed.

After cooling the reactor to near room temperature, gaseous products were recovered in evacuated stainless steel vessels and analyzed for light hydrocarbon gases and carbon oxide gases using a Carle Model 111H refinery gas analyzer. The krypton concentration was also measured and used as a tie element for computing product gas yields. Liquid-solid product slurry was removed from the reactor using toluene as a wash solvent and quantitatively centrifuged to separate solids (termed "centrifuge residue") from the liquid product (termed "decant oil"). The toluene was quantitatively removed during vacuum distillation of the decant oil to a 454 °C endpoint in a BR Instrument Corp. spinning band microdistillation apparatus. Portions of the centrifuged residue and 454 °C + decant oil residuum were extracted in a Soxhlet extraction apparatus using cyclohexane, toluene, and tetrahydrofuran (THF). Selected product samples were analyzed for carbon, hydrogen, nitrogen, sulfur, and ash using standard ASTM procedures. Detailed quantitative measurements of THQ or dipropylamine in 454 °C- distillate samples were performed using an HP 5890 capillary gas chromatograph interfaced to an HP 5790B quadrupole mass spectrometer. These data helped provide a measure of nitrogen compound losses by thermal degradation or incorporation. Details of the experimental procedures used in this work have been reported (10,11).

RESULTS AND DISCUSSION

Single Stage Results

Figure 1 summarizes results of single stage coprocessing runs with Kentucky 9 coal in which the effects of nitrogen compound addition (THQ or dipropylamine) and reaction severity (low or high) were studied. Increasing reaction severity resulted in a Kentucky coal conversion increase of approximately 22 wt% in the THQ runs, but only about a 5 wt% increase in the dipropylamine runs. As expected, distillate yield was even more sensitive to reaction severity with yield increases of about 30 wt% and 53 wt% for the THQ and dipropylamine runs, respectively. Much of this increase can be attributed to additional cracking of the Cold Lake residuum at high reaction severity.

Figure 2 presents data for a similar set of experiments using Wyodak rather than Kentucky 9 coal. In this case, however, coal conversion was found to be more sensitive to a change in reaction severity than distillate yield. Increasing reaction severity resulted in a Wyodak coal conversion increase of 40 wt% for the THQ runs and 30 wt% for the dipropylamine runs; distillate yield increases of only 15 wt% and 17 wt% were noted for these runs, respectively.

Taken alone, these conversion and yield data seem to favor high severity coprocessing as the more attractive processing option. However, as shown in Figures 1 and 2, reaction severity also strongly influences the ultimate fate of nitrogen compounds added during coprocessing. In the Kentucky runs, THQ incorporation increased nearly thirteen fold (from 2.9 to 36.9 wt%), while dipropylamine incorporation increased nearly six times (from 2.7 to 15.4 wt%). Incorporation in the Wyodak runs increased by a factor of about 4-5 for both THQ and dipropylamine addition. For the low severity Wyodak runs, nitrogen incorporation was about double that in the low severity Kentucky runs, suggesting the importance of interactions between nitrogen species and acidic oxygen sites in the coal.

In our opinion, these data suggest the following two-stage process option: stage 1 - dissolve the coal to THF soluble products at low reaction severity using a nitrogen promoter such as THQ or dipropylamine (or a process-derived nitrogen-rich stream) where incorporation and degradation losses are minimized, and stage 2 - catalytically upgrade the coal-derived residuum (and petroleum residuum if present) from the first stage to distillate products using conventional hydrocracking reaction conditions and technology. Based on previous studies in our laboratory (12), residuum from the first stage produced in this manner is very reactive and more easily converted to distillate products.

Two-Stage Studies

Based on the single stage results described in the previous section, a series of two-stage batch reactor runs was completed. Figure 3 shows the effect of THQ addition on coal conversion and distillate yield during two-stage processing using a low reaction severity first stage. Nearly three-fourths of the total coal conversion obtained was achieved in the first stage when THQ was present; however, in the "blank" run without THQ only about one third of the conversion was achieved in the first stage. In each run, the proportion of distillate produced in each stage was similar to the coal conversion ratios. This result was somewhat unexpected, but can probably be attributed to one or both of the following: 1) no attempt was made to optimize second stage reaction conditions and, thus, the distillate yields obtained were not maximized, and 2) the presence of a coal/residuum synergism, such that distillate yield is enhanced when coal conversion increases. The net effect of THQ addition in these runs was to increase coal conversion 30.0 wt% (MAF coal basis) and distillate yield 12.8% (MAF coal basis) without increasing hydrogen consumption or hydrocarbon gas make.

Figure 4 shows the effect of first stage reaction severity on coal conversion and distillate yield. The combination of a low severity first stage followed by catalytic hydrocracking resulted in nearly the same performance as the high severity run. However, only about 2.5 wt% hydrogen (MAF coal basis) was consumed in the low severity run, while over 6.0 wt% hydrogen (MAF coal basis) was used in the high severity run. Most of the additional hydrogen was consumed by hydrocarbon gas formation and not by hydrogenation of the liquid product. Thus, low severity coal dissolution appears to be a promising alternative to conventional high severity processing.

SUMMARY AND CONCLUSIONS

Results from single-stage low severity coprocessing runs showed that 1,2,3,4-tetrahydroquinoline (THQ) and dipropylamine both act to enhance coal dissolution and distillate yields without significant thermal degradation or incorporation into residual products. Decreased reaction severity significantly lowered the extent of incorporation, presumably by reducing both chemical incorporation and physical entrapment. Two-stage coprocessing studies demonstrated that, in the presence of THQ as a coal dissolution promoter, low severity coal dissolution followed by conventional catalytic hydrocracking gave coal conversions and distillate yields comparable to conventional high severity processing but with much lower hydrogen consumption and hydrocarbon gas make. These data demonstrate the potential for developing a viable direct liquefaction or coal/oil coprocessing scheme in which coal is dissolved at milder conditions than traditionally envisioned.

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Table I
ULTIMATE ANALYSIS OF FEED COALS

<u>Ultimate Analysis, wt% dry basis</u>	<u>Kentucky 9</u>	<u>Wyodak</u>	<u>Penn State Wyodak</u>
Carbon	69.7	61.4	67.8
Hydrogen	4.7	4.0	5.0
Nitrogen	1.4	1.0	1.2
Sulfur	4.2	0.7	1.9
Oxygen (difference)	9.2	18.6	15.2
Ash	<u>10.8</u>	<u>14.3</u>	<u>8.9</u>
Total	100.0	100.0	100.0

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Table II
PROPERTIES OF COLD LAKE ATMOSPHERIC RESIDUUM

<u>Distillate Fraction</u>	<u>Wt%</u>
Water	0.0
177 °C -	0.4
177 ° - 260 °C	4.1
260 ° - 343 °C	4.1
343 ° - 454 °C	10.9
454 °C +	80.5
 <u>Ultimate Analysis, dry basis</u>	
Carbon	84.2
Hydrogen	12.0
Nitrogen	1.0
Sulfur	1.1
Oxygen (difference)	1.7
Ash	0.0
 <u>Solvent Solubility</u>	
Tetrahydrofuran	100.0
Toluene	100.0
Cyclohexane	100.0

Table III
SINGLE STAGE REACTION CONDITIONS

	<u>Low Severity</u>	<u>High Severity</u>
Reaction Temp. (°C)	344	440
Feed Gas	H ₂	H ₂
Initial Pressure (psig)	850	1000
Maximum Pressure (psig)	1500	2000
Time at Temp. (min)	30	30
Coal/A-8/Nitrogen Compound Feed Ratio	1/1.5/0.5	1/1.5/0.5

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Table IV
TWO-STAGE REACTION CONDITIONS

	<u>Low Severity First Stage</u>	<u>High Severity First Stage</u>
Reaction Temp. (°C)	350	440
Feed Gas	H ₂	H ₂
Initial Pressure (psig)	1500	1500
Maximum Pressure (psig)	2000	2500
Time at Temp. (min)	45	45
Coal/A-8/Nitrogen Compound Feed Ratio	1/1.5/0.5	1/1.5/0.5

Second Stage Reaction Conditions (all experiments):

400 °C, 2500 psig H₂, 45 min., Shell 324 sulfided 1/16" extrudates,
oil/catalyst wt. ratio = 50/1 (approximate)

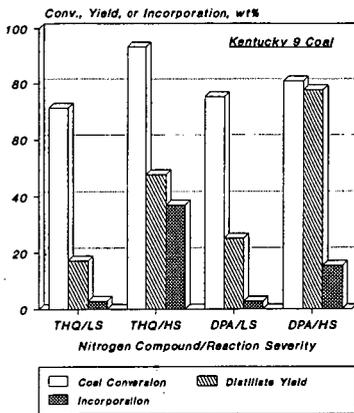


Figure 1. Effect of THQ or Dipropylamine (DPA) Addition and Reaction Severity on Coprocessing of Kentucky 9 Coal (LS = low severity, HS = high severity)

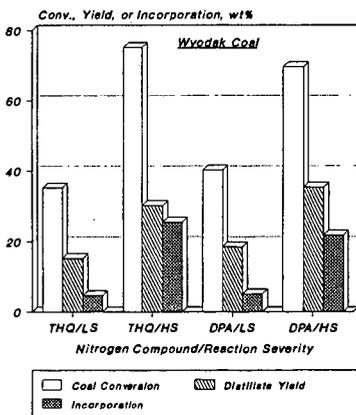


Figure 2. Effect of THQ or Dipropylamine (DPA) Addition and Reaction Severity on Coprocessing of Wyodak Coal (LS = low severity, HS = high severity)

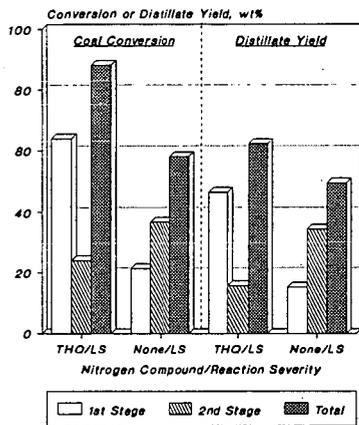


Figure 3. Effect of THQ Addition on Low Severity Two-Stage Coprocessing of Wyodak Coal (LS = low severity)

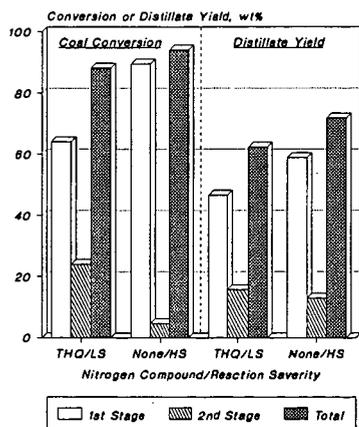


Figure 4. Effect of Reaction Severity on Two-Stage Coprocessing of Wyodak Coal (LS = low severity, HS = high severity)