

LOW SEVERITY CO-PROCESSING USING
HOMOGENEOUS BASIC NITROGEN PROMOTORS

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INTRODUCTION

The possibility of dissolving coal at low severity reaction conditions has intrigued researchers for many years. As early as 1921, Fischer and Schrader (1) reported production of 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 (2-5), the North Dakota Energy Research Center (6-10), Stanford Research Institute (11-14), Carbon Resources, Inc. (15,16), and the Colorado School of Mines (17-19) have investigated various methods of low severity dissolution. Their efforts have been prompted by the fact that many incentives exist for converting coal at milder conditions than utilized in present day technology. Several of these incentives are listed below:

- * Reduced hydrocarbon gas make resulting in reduced feed gas consumption and enhanced hydrogen utilization efficiency
- * Suppressed retrogression of primary coal dissolution products resulting in enhanced distillate and residuum product quality
- * Production of high boiling residuum which is less refractory and thus amenable to upgrading in a conventional second-stage hydrocracker
- * Substitution of less expensive off-the-shelf vessels, piping, and pumps in place of expensive, custom-designed units
- * Less severe slurry handling and materials of construction problems as a result of lower operating temperatures and pressures.

In searching for effective coal dissolution promoters to be evaluated at low severity co-processing conditions, we concluded that, based on results from high severity studies, basic nitrogen compounds warranted extensive study. Atherton and Kulik (20,21) summarized data from several high severity liquefaction studies using 1,2,3,4-tetrahydroquinoline (THQ) in which THF coal conversions in the range of 85-100 wt% (MAF basis) were obtained with Wyodak subbituminous coal and Illinois 6 bituminous coal at reaction temperatures of 400°-450°C. However, distillate yields from these experiments were much lower than expected, and nitrogen material balance measurements indicated significant adduction of the THQ into non-distillable products.

Thus, while basic nitrogen compounds appear attractive as coal dissolution promoters, the adduction problem limits their usefulness in high severity co-processing. We hypothesized that utilizing basic nitrogen compounds at lower severity would reduce adduction sharply, but that effectiveness towards promoting coal dissolution would remain high.

Our first low severity co-processing experiments to test this hypothesis were conducted using Wyodak subbituminous coal and either unhydrotreated or mildly hydrotreated shale oil each containing approximately 1.0 wt% heterocyclic basic nitrogen (19). Mild hydrotreatment of the shale oil prior to co-processing greatly improved both liquid yield and THF soluble coal conversion. Yield and nitrogen balance results suggested that significantly less adduction of nitrogen compounds in the shale oil occurred at low severity reaction conditions compared with earlier high severity coal/shale oil co-processing experiments.

The success of these preliminary runs provided the incentive to begin a more fundamental study on the use of basic nitrogen compounds to promote coal dissolution and increase distillate yields at low severity reaction conditions. Initial results from model compound studies are reported in this paper.

EXPERIMENTAL PROCEDURE

Kentucky 9 bituminous coal and Wyodak subbituminous coal were used as feed coals in the low severity co-processing experiments. Ultimate analysis data for these coals is presented in Table I. Coal samples were vacuum-dried to less than 1.0 wt% moisture content before use.

Cold Lake atmospheric residuum was used as co-processing heavy oil. Available characterization data for this feedstock, designated A-8, are shown in Table II. Sample A-8 has been extensively studied as a co-processing feed and performs well at low severity reaction conditions (19). The seven model nitrogen compounds listed in Table III were evaluated as coal dissolution promoters. Each compound was ACS reagent grade and was used without further purification. These compounds were chosen to provide a wide range of base strength as measured by aqueous pK_b values. For convenience, the coding system shown in Table III will be used to reference each of the seven model nitrogen compounds.

Runs were completed using either commercial grade hydrogen or carbon monoxide. Each feed gas contained 1.0 mole% krypton used as an inert tracer. Distilled water in an amount equal to 50 wt% of the MAF feed coal was added to runs using carbon monoxide feed gas.

Table IV lists the reaction conditions used in this study. A majority 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.

Co-processing experiments were performed using a 300 cm³ Autoclave MagneDrive II batch reactor interfaced to an Apple IIe personal computer for temperature control. The computer was also routinely used for temperature and pressure data acquisition during a run. Reactor heatup time to 330°-350°C reaction temperature was approximately 30 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.

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 tracer concentration was also measured and used as a tie element for determining product gas yields.

The liquid-solid product slurry was removed from the reactor using toluene as a wash solvent and quantitatively centrifuged to separate solids from the liquid product (termed "decant oil"). The residue (termed "centrifuge residue") contained unconverted coal and mineral matter coated with liquid product. Toluene added during slurry recovery and centrifugation was quantitatively removed during distillation. Decant oil samples were distilled to a 454°C endpoint using an ASTM-type microdistillation apparatus. Portions of the centrifuge residue and decant oil 454°C+ residuum were extracted in a Soxhlet extraction apparatus using cyclohexane, toluene, and tetrahydrofuran. Standard elemental analyses for carbon, hydrogen, nitrogen, sulfur and ash content were performed on all liquid and solid product samples. Oxygen content was determined by difference.

Detailed quantitative measurements of individual model nitrogen compounds in 454°C- distillate samples were performed using an HP 5890 capillary gas chromatograph interfaced with an HP 5790B quadrupole mass spectrometer. These data helped provide a measure of nitrogen compound losses by thermal degradation or adduction.

RESULTS AND DISCUSSION

Effect of Model Nitrogen Compound Addition

Low severity co-processing experiments were completed to evaluate the seven model nitrogen compounds listed in Table III as coal dissolution promoters. THF soluble coal conversion results from these runs are shown in Figure 1. The greatest improvement in coal conversion was noted using 1,2,3,4-tetrahydroquinoline (THQ) (N1) and dipropylamine (N2). Addition of piperidine (N4), 4-piperidinopyridine (N5), or diphenylamine (N7) had little effect on the extent of coal dissolution. Similar results were observed using hydrogen gas at low severity reaction conditions.

As shown in Figure 2, addition of each model nitrogen compound significantly influenced the yield of C₄-454°C liquids obtained at low severity liquefaction conditions. Once again, 1,2,3,4-tetrahydroquinoline (N1) and dipropylamine (N2) strongly enhanced process performance, while addition of each of the remaining five nitrogen compounds (N3-N7) reduced the liquid yield obtained. These results are entirely consistent with preliminary nitrogen adduction data showing that neither THQ nor dipropylamine adducted at low severity reaction conditions while approximately 10-15 wt% 4-piperidinopyridine was adducted into the insoluble organic matter fraction.

A comparison of the data presented in Figures 1 and 2 also shows that no direct one-to-one correlation between the levels of coal conversion and liquid yield can be developed. This result has commonly been observed when using nitrogen compounds as conversion promoters, and points out the fact that conversion data alone cannot be used to infer information about liquid yields. Rather, distillations must be performed and used in material balance calculations to provide a direct measure of recoverable liquids.

Effect of Reaction Severity

Figure 3 summarizes coal conversion and liquid yield results from a series of THQ (N1) and dipropylamine (N2) addition experiments using Kentucky 9 coal and hydrogen gas at both low and high severity reaction conditions. Increased reaction severity resulted in a THF soluble coal conversion increase of approximately 22 wt% for the THQ runs, but only about 5 wt% increase for the dipropylamine runs. As

shown, the liquid yield was much more sensitive to an increase in reaction severity, with yield increases of about 30 wt% and 53 wt% for the THQ and dipropylamine addition runs, respectively. Much of the increase noted can be attributed to increased cracking of the A-8 heavy oil at high severity conditions.

Preliminary nitrogen balance data for the high severity runs suggested that about half the THQ was adducted into the IOM fraction, and that over 90 wt% of the dipropylamine was cracked to ammonia and propane. In the absence of these losses, liquid yield results for the high severity runs would be higher than shown in Figure 3. Nevertheless, these data substantiate our hypothesis that compounds such as THQ and dipropylamine can be identified which remain effective coal dissolution promoters at low severity co-processing conditions. Improving low severity liquid yields will apparently require a second stage catalytic hydrocracker to process the high boiling residual material produced in the low severity co-processing first stage. Based on previous studies from our laboratory, this residuum should be very reactive and easily converted to distillable liquids.

Effect of Coal Rank and Feed Gas Composition

Additional low severity co-processing runs were completed to study the effects of coal rank (subbituminous vs. bituminous) and feed gas (H_2 vs. CO/H_2O) on the performance of THQ (N1) and dipropylamine (N2) as coal dissolution promoters. Results from these experiments are summarized in Figures 4 and 5. For the Kentucky 9 bituminous coal runs, use of hydrogen and either THQ or dipropylamine slightly improved both coal conversion and liquid yield. Conversely, significantly better wyodak coal conversion and liquid yield were achieved using CO/H_2O , a result which would be expected based upon aqueous water-gas shift chemistry. Additional coal samples, including several Argonne premium coals will be studied to expand the coal rank relationships shown in Figures 4 and 5.

SUMMARY AND CONCLUSIONS

Results of low severity co-processing experiments completed to date clearly demonstrate the potential for using homogeneous basic nitrogen compounds to promote coal dissolution and increase liquid yields without significant nitrogen losses via adduction or thermal degradation. Both 1,2,3,4-tetrahydroquinoline and dipropylamine significantly improved coal conversion and distillable liquid yields, although, in general, no direct relationship between improvements in conversion and yield structure can be inferred. A comparison of liquid yields from low severity and high severity experiments suggests that a two-stage process consisting of a low severity coal dissolution first stage followed by a second stage catalytic hydrocracker would improve coal conversion and liquid yield while, at the same time, minimizing nitrogen losses via adduction or thermal degradation. Work to evaluate this co-processing concept is currently underway.

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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>
Carbon	69.7	61.4
Hydrogen	4.7	4.0
Nitrogen	1.4	1.0
Sulfur	4.2	0.7
Oxygen (difference)	9.2	18.6
Ash	<u>10.8</u>	<u>14.3</u>
Total	100.0	100.0

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, wt% 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, wt%</u>	
Tetrahydrofuran	100.0
Toluene	100.0
Cyclohexane	100.0

Table III
 MODEL NITROGEN COMPOUNDS STUDIED

<u>Compound</u>	<u>Aqueous pK_b</u>	<u>Code Symbol</u>
1,2,3,4-tetrahydroquinoline	8.97	N1
dipropylamine	3.00	N2
7,8-benzoquinoline	9.20	N3
piperidine	2.88	N4
4-piperidinopyridine	8.04	N5
5,6-benzoquinoline	10.05	N6
diphenylamine	13.23	N7

Table IV
CO-PROCESSING REACTION CONDITIONS

	<u>Low Severity</u>	<u>High Severity</u>
Reaction Temp. (°C)	344	440
Feed Gas	CO/H ₂ O, 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

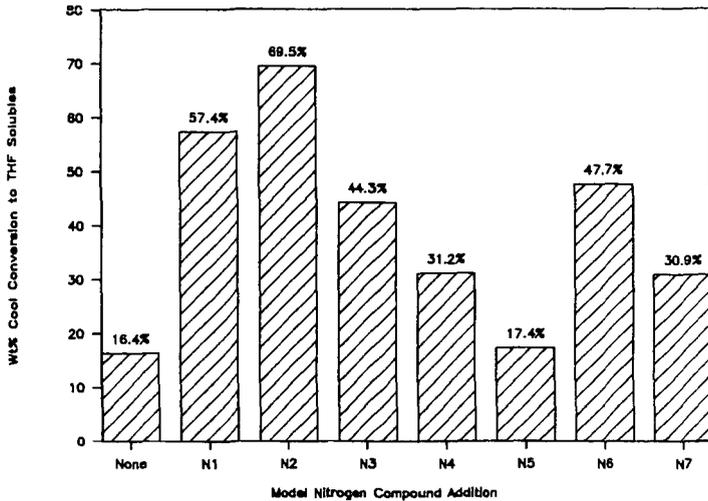


Figure 1. Effect of Model Nitrogen Compound Addition on Low Severity Conversion of Kentucky 9 Coal With Carbon Monoxide Feed Gas

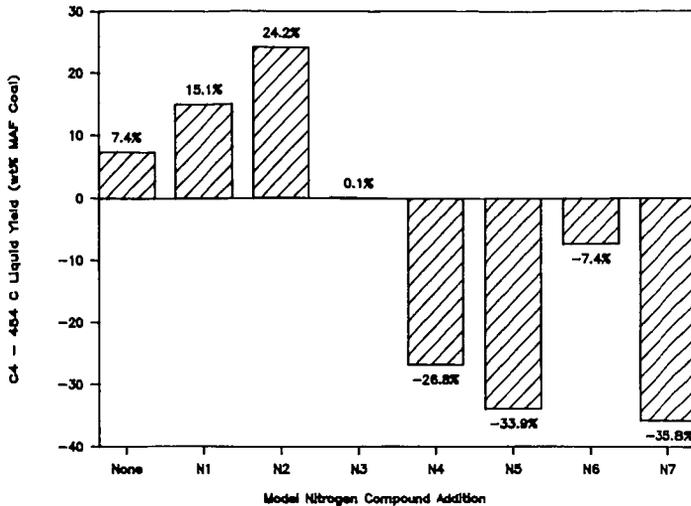


Figure 2. Effect of Model Nitrogen Compound Addition on Distillate Liquid Yield from Low Severity Co-Processing of Kentucky 9 Coal with Carbon Monoxide Feed Gas

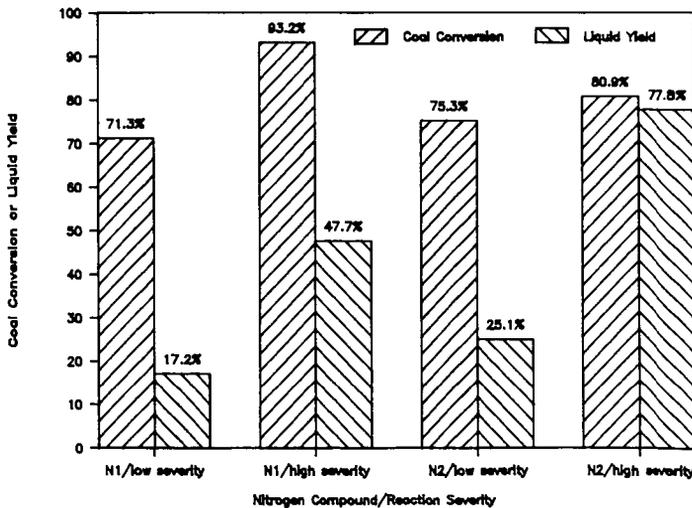


Figure 3. Effect of Model Nitrogen Compound Addition and Reaction Severity on Kentucky 9 Coal Conversion and Distillate Liquid Yield with Hydrogen Feed Gas

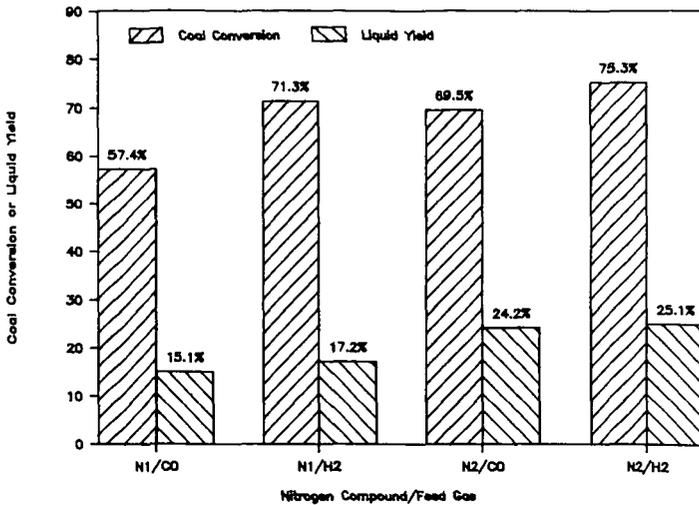


Figure 4. Effect of Model Nitrogen Compound Addition and Feed Gas on Kentucky 9 Coal Conversion and Distillate Liquid Yield at Low Severity Co-Processing Conditions

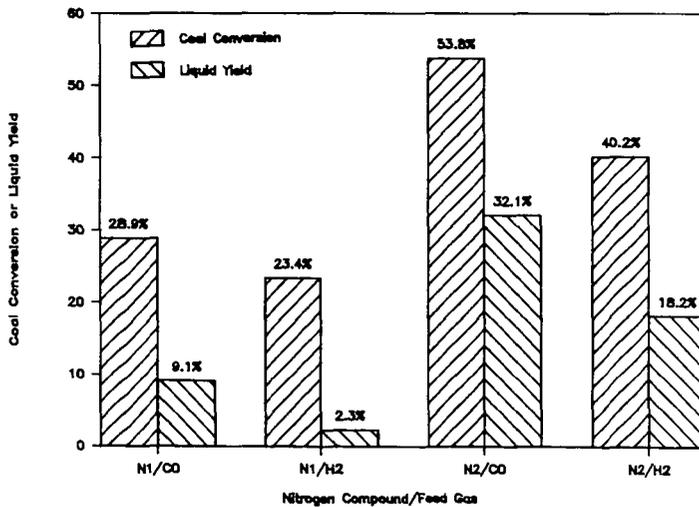


Figure 5. Effect of Model Nitrogen Compound Addition and Feed Gas on Wyodak Coal Conversion and Distillate Liquid Yield at Low Severity Co-Processing Conditions