

CHARACTERIZATION OF NITROGENOUS COMPOUNDS IN DISTILLATES
DERIVED FROM TWO-STAGE COAL LIQUEFACTION

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INTRODUCTION

The nitrogen compounds in coal distillates have not been characterized as fully as the predominant hydrocarbon components, but are of considerable importance due to their adverse effect on fuel stability (1-3) and catalyst lifetime (4) and the potentially adverse health and environmental impact (5-7). A number of different classes of nitrogen compounds are commonly found in coal liquids (e.g. quinolines, indoles, carbazoles (7-10)). These each will affect catalyst deactivation and product stability to different extents.

This report specifically addresses the nature of nitrogen compounds found in Wilsonville streams. In the current study, gas chromatography with a nitrogen-selective detector (GC/N) and gas chromatography/mass spectrometric (GC/MS) techniques were employed to identify and quantitate the major nitrogen-containing components found in concentrates prepared from coal-derived distillates from two series of Wilsonville pilot plant runs. These runs were made with Illinois No. 6 and Wyodak Coals.

While direct GC/N analysis can be done on the whole, untreated distillate, the nitrogen detector is a poor identification tool. Therefore, GC/MS was necessary for compound identification. Consequently, pretreatment of the distillates to obtain N-rich fractions was a necessary step to minimize hydrocarbon interference in GC/MS analyses and allow more detailed examination of the nitrogen components in coal distillates. However, once a typical nitrogen profile has been characterized, GC/N should allow rapid quantitation of the nitrogen compounds in an untreated distillate.

EXPERIMENTAL

Samples

The coal-derived liquids were obtained from the Advanced Coal Liquefaction R & D Facility at Wilsonville, AL. The products from five runs were characterized, three from the liquefaction of Illinois No. 6 bituminous coal (runs 250D, 250H, and 251E) and two from Wyodak subbituminous coal (runs 251-IIB and 251-IIIB). Details of these coals and their processing are given in reference 11.

Samples from the Wilsonville product streams were obtained soon after the runs and stored in a cold room to avoid degradation. Product liquid blends were prepared just before experimentation and their elemental analyses are given in Table I.

Preparation of Nitrogen Concentrates

Nitrogen-containing concentrates were prepared in the following manner. Approximately 80g of coal liquid oil was added to twice that weight of 10% NaOH aqueous solution. The resulting oil and aqueous phases were separated; phenolics were extracted into the aqueous layer. Toluene was added to the oil layer which was added to Amberlyst-15 cation ion exchange resin in a ratio of 4:2:1 of toluene:raffinate:resin, respectively. After three days of gentle mixing, the "OH, N-free" oil was recovered by filtration.

The resin was flushed with pentane and dried in a stream of N₂ at ambient temperature. It was then contacted with methanol saturated with NH₃ to recover the concentrates. About 70% of the methanol was gently stripped from these concentrates by rotary evaporation.

To confirm that essentially no organic nitrogen compounds remained on the resins after NH₃ treatment, resins from the 250D, 250H, and 251E treatments were treated with H₂SO₄. The recovered liquids were neutralized and extracted with CH₂Cl₂. These extracts contained no organic N-containing compounds. The samples of regenerated resin were checked for nitrogen content. The recovered

resins and a sample of fresh resin subjected to NH₃ and H₂SO₄ regeneration all contained nitrogen levels of 4.1 +/- 0.1%.

Chromatographic Separations and Component Identification

Detailed analytical experimental conditions for component separations and identification are given in Table II. Dichloromethane was used as the solvent for GC/MS. Methyl t-butyl ether was the solvent used in GC/N work because of severe peak tailing and detector response problems when dichloromethane was used.

Nitrogen Compound Quantification

The thermionic nitrogen detector (TID) for GC/N quantification work was calibrated using blends of pyridines, anilines, quinolines, indoles, carbazoles, and indoline. Each of these seven types of nitrogen compounds gives a different TID response. Therefore, seven different linear calibration equations were generated. Figure 1 shows a typical GC/N calibration plot and calibration equation of an aniline.

Based on the nitrogen components identified by GC/MS, the nitrogen components in a sample were grouped by types and quantitated using the calibration equations corresponding to the nitrogen types detected. Responses relative to 4-methylpyridine were determined for available model compounds as listed in Table III. As shown, the response factors for a given nitrogen compound type are similar but vary for different types of nitrogen compounds. For the majority of alkylated nitrogen components identified by GC/MS in the samples, we have no standards. Therefore, for a given nitrogen compound class, e.g. C₉-C₁₀ indoles, a single calibration equation based on the parent compound, e.g. indole, was used. There were several nitrogen components boiling above carbazole for which we had no standard whatsoever. In such cases, the peak area of these components were summed and the carbazole calibration equation used to quantitate them.

RESULTS AND DISCUSSION

Ion-Exchange

The A-15 resin adsorbed between 90 and 95% of the nitrogen compounds from the OH-free raffinate generated from the phenolics stripping step. Essentially no organic nitrogen compounds were retained in the A-15 resin after stripping with the ammonia/methanol solution.

Analytical Results

GC/MS was used to identify the nitrogen components in the nitrogen concentrates of the blends and to determine relative amounts of the various nitrogen components. Seven major types of nitrogen-containing compounds were detected in the bituminous coal liquid distillates--pyridines, anilines, quinolines, hydro-quinolines, indoles, indolines, and carbazoles. Four of these types (pyridines, anilines, hydroquinolines, and indoles) were the nitrogen classes in the subbituminous coal liquid distillates. Side-chains on the ring compounds ranged from C₁ through C₁₀ chains. The parent types of nitrogen compounds detected are shown in Figure 2.

The nitrogen compounds identified by GC/MS and quantitated by GC/N are grouped by classes in Table IV. This Table also shows boiling point data for representative nitrogen-containing compounds. Boiling points range from 300°F (C₂ pyridines) up to 700°F (carbazoles). The majority of the nitrogen compounds detected boiled in the 350-700°F range. In addition, the majority of the nitrogen compounds were alkyl substituted (designated herein by the total alkyl carbon number, e.g., C₂ pyridines).

Anilines (C₆-C₈) were the major nitrogen components in all blends, with the catalytic/catalytic run (251E) bituminous product having relatively more anilines and the subbituminous products having relatively fewer anilines than that of the other runs. Run 251E product also had fewer pyridines compared with that of the other runs. The levels of anilines found in the bituminous products are consistent with the fact that the first stage catalyst would increase the extent of hydrogenation and cracking of quinolines and multiple ring species to anilines. However, it was not anticipated that the level of anilines would be so high.

In addition to nitrogen species, GC/MS detected a number of aromatic hydrocarbons, primarily biphenyls, naphthalenes, anthracenes, phenanthrenes, and pyrenes in the nitrogen concentrates of all runs. These occurred because of non-specific adsorption onto the resin. The hydrocarbons accounted for about 30% of the total peak area of the GC/MS data. There was 1-2% phenolic material in the nitrogen concentrates of 250D and 250H (none detected in the 251E nitrogen concentrate).

Table V shows comparative quantitative GC/N and GC/MS data for the bituminous 251E coal liquid distillate. The data compare very well in spite of the semi-quantitative nature of GC/MS.

CONCLUSIONS

For the characterization of coal-derived distillates for nitrogen compound distribution, it is highly beneficial to concentrate a nitrogen-component rich fraction prior to analysis. Extraction of phenolics followed by ion-exchange to concentrate nitrogen compounds appears to work well for pyridines through carbazoles boiling up to about 700°F. Analysis by GC/MS and GC/N selective detection are the preferred techniques to obtain a distribution of the nitrogen components.

Data indicate that the nitrogen concentrates derived from IL No. 6 coal contain seven types of nitrogen ring structures: pyridines, anilines, quinolines, hydroquinolines, indoles, indolines, and carbazoles. Nitrogen concentrates from Wyodak sub-bituminous coal contain mostly pyridines, anilines, hydroquinolines, and indoles. Essentially all of the nitrogen compounds in both types of coal liquids are alkyl substituted. Sidechains on the aromatic rings are C₁ to C₁₀. It was not possible to determine if there was single attachment of longer alkyl chains or multiple attachment of short chains.

High levels of anilines are present, namely about 44% of the total nitrogen components detected in the bituminous coal liquids and 29% in the subbituminous coal liquids. Other investigators have reported anilines in coal-derived liquids (9,10,12). These anilines are presumably the result of the hydrogenation and opening of aromatic nitrogen-containing rings. Anilines should donate hydrogen during coal liquefaction; however, there is a high likelihood that the resulting product forms adducts quickly, thereby resulting in measurable retrogressive reactions. Most retrogressive products have high nitrogen content.

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TABLE I

Elemental Analyses of the Product Blends

Run No.	Carbon	Hydrogen	Nitrogen	Oxygen	Sulfur
250D	86.9	11.4	0.19	1.4	0.09
250H	87.2	11.6	0.13	1.4	0.17
251E	87.5	11.6	0.14	0.8	0.03
251-IIIB	85.7	11.3	0.31	2.60	0.06
251-IIIIB	86.3	12.7	0.15	0.84	0.06

TABLE II

Analytical Operating Conditions

GC/MS		GC/MS	
GC Unit:	Varian 3700 with a Thermionic # detector (TID); 6.70 base current; 17 psig H ₂ ; 4.0V bias; 1.0 ¹⁰ A _{max} atom	GC Unit:	Varian 3500
Column:	60 m fused silica capillary, 0.25 mm i.d.	Column:	60 m fused silica capillary, 0.25 mm i.d.
Coating:	DB-1, 0.25 µm film	Coating:	DB-1, 0.25 µm film
Temperature:	50 to 300°C at 6°/min with a 20 min hold Injector: 300°C; Detector: 350°C	Temperature:	50 to 300°C at 6°/min with a 20 min hold (oven) Injector: 310°C
Carrier:	Helium (37 psig)	Carrier:	Helium (20 psig and 5 ml/min split)
Inlet Split Ratio:	60/1	Sample:	10 µg diluted with 250 µl of CH ₂ Cl ₂
Sampler:	0.2µl of the sample diluted 1:12 with N ₂ B ₆	MS Unit:	PCLAB-2P
		Data System:	Data General Nova 3 with Kratos software
		Mass Resolution:	3000
		Source Temperature:	230°C
		Operational Mode:	Electron Impact
		Sample Rate:	0.5 sec/mass decade

TABLE III

Nitrogen Detector Response Factors

Component	TID Response relative to 4-methyl pyridine = 1.00
pyridine	1.01
2,4,6-trimethylpyridine	1.00
aniline	0.856
2,5-dimethylaniline	0.860
p-methylaniline	0.860
quinoline	0.962
2,4-dimethylquinoline	0.956
tetrahydroquinoline	0.974
indole	1.07
carbazole	0.849
indoline	1.03

TABLE IV
Nitrogen Compounds in Coal Liquids

Component	Boiling Range, °P ^a	WEX Component				
		Bituminous ^b			Subbituminous ^c	
		Run 230D	Run 230E	Run 231E	Run 251-11E	Run 251-11EB
Pyridine	239	0.0	0.0	0.0	0.0	0.0
C ₁ PF	230-300	0.4	1.0	0.0	1.8	1.1
C ₂ PF	303-340	1.4	2.1	0.4	4.2	1.6
C ₃ PF	342-373	1.7	2.0	1.0	3.7	1.6
C ₄ PF	370-393	1.3	1.0	0.4	1.9	4.9
C ₅ PF	400-420	0.0	0.0	0.0	0.6	1.6
Total Pyridines		4.8	6.1	1.8	13.2	10.8
Aniline	363	2.3	3.1	2.9	1.0	1.3
C ₁ An	376-390	7.4	11.0	8.0	2.5	2.7
C ₂ An	400-423	6.8	6.3	11.6	2.3	4.0
C ₃ An	435-470	4.9	4.0	7.4	3.7	4.3
C ₄ An	500-525	5.0	3.9	5.1	1.9	3.6
C ₅ An	529-530	2.0	0.6	0.6	0.6	0.8
C ₆ An	573-590	0.0	0.0	0.0	0.2	0.3
Total Anilines		28.6	29.1	33.6	12.4	17.2
Quinoline	462	0.0	0.0	0.0	0.0	0.0
C ₁ Q	478-498	1.3	1.4	0.1	0.0	0.0
C ₂ Q	513-560	0.3	0.2	0.4	0.0	0.0
C ₃ Q	576-597	0.7	0.7	0.7	0.0	0.0
C ₄ Q	572-593	0.4	0.8	0.1	0.0	0.0
C ₅ Q	607-635	0.0	0.0	0.0	0.0	0.0
C ₆ Q	640-671	0.0	0.0	0.0	0.0	0.0
C ₇ Q	673-690	1.2	0.1	0.1	0.0	0.0
C ₈ Q	685-700	1.2	0.0	0.0	0.0	0.0
Total Quinolines		5.3	3.2	1.4	0.0	0.0
Tetrahydroquinoline (THQ)	480	0.0	1.5	0.0	0.0	0.0
C ₁ THQ	483-489	3.4	3.3	1.9	0.7	1.1
C ₂ THQ	540-580	3.4	1.8	4.7	4.6	4.8
C ₃ THQ	546-585	1.3	0.3	1.6	3.3	4.8
C ₄ THQ	585-600	1.8	0.2	2.7	0.7	1.3
C ₅ THQ	590-613	0.0	0.0	0.0	0.1	0.3
Total THQs		9.9	7.3	10.9	10.4	12.2
Indole	489	0.0	0.0	0.0	0.0	0.0
C ₁ Indole	530-530	0.3	0.0	0.7	0.3	1.1
C ₂ Indole	563-570	0.5	0.6	1.1	1.4	2.1
C ₃ Indole	563-583	0.0	0.0	0.0	1.3	1.6
C ₄ Indole	570-590	0.0	0.0	0.0	0.3	0.3
C ₅ Indole	573-613	2.9	1.7	4.6	2.1	1.3
C ₆ Indole	617-636	6.4	3.9	4.9	2.1	0.8
C ₇ Indole	640-660	3.0	0.7	1.7	1.2	0.3
C ₈ Indole	670-680	0.7	0.0	0.3	0.1	0.0
C ₉ Indole	673-689	0.0	0.0	0.0	0.7	0.0
C ₁₀ Indole	680-693	0.0	0.0	0.0	0.3	0.0
Total Indoles		14.0	8.9	13.3	10.9	7.4
Indoline	466	0.0	0.0	0.0	0.0	0.0
C ₁ Indoline	514-540	0.0	0.3	0.0	0.0	0.0
C ₂ Indoline	540-563	0.0	0.0	0.2	0.0	0.0
C ₃ Indoline	563-580	0.0	1.3	0.0	0.0	0.0
C ₄ Indoline	570-590	0.0	0.1	0.0	0.0	0.0
Total Indoline		0.0	1.9	0.2	0.0	0.0
Carbazole	671	0.4	0.7	0.9	0.1	0.0
C ₁ C	643-670	1.3	1.3	1.0	0.9	0.0
C ₂ C	680-690	0.0	0.0	0.0	0.3	0.0
C ₃ C	673-700	0.0	0.0	0.1	0.4	0.0
Total Carbazoles		1.9	2.2	2.0	1.7	0.0
Tetrahydrocarbazoles	617-690	0.8	0.4	0.4	1.8	0.3
Phenylisoquinoline	520-535	2.0	4.0	2.9	0.0	0.0
Methylisoquinoline	480-530	0.9	0.2	0.3	0.0	0.0
C ₂ diphenylamine	630-630	1.3	0.1	0.3	0.0	0.0
C ₃ diphenylamine	630-670	0.0	0.0	0.2	0.0	0.0
Other H compounds ^d		4.0	3.2	1.6	0.0	0.0
Total Misc. H		9.0	7.9	5.7	1.8	0.3

^a estimated boiling ranges for alkylated compounds
^b CC/N quantitation
^c CC/MS quantitation
^d N.W. 193 and 209

TABLE V
Comparison of GC/N and GC/MS Quantitation

Nitrogen Component	Run 251E, % Components	
	GC/N	GC/MS
C ₁ -C ₄ pyridines	1.8	1.9
C ₀ -C ₅ anilines	35.6	36.5
C ₁ -C ₇ quinolines	1.5	1.6
C ₁ -C ₄ THQs	10.9	11.0
C ₁ -C ₈ indoles	13.3	12.9
C ₂ indolines	0.2	0.4
C ₀ -C ₃ carbazoles	2.0	2.0

Figure 1

A GC/N Calibration Plot

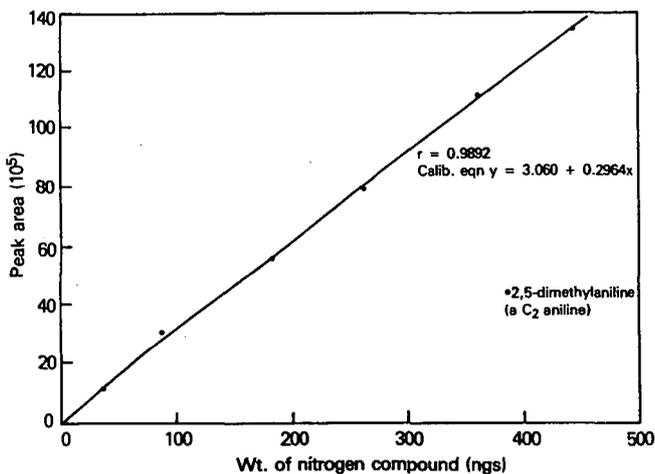


Figure 2

Types of Nitrogen Compounds Detected in Coal Liquids

