COMPOSITIONAL DIFFERENCES IN NAPHTHA DERIVED FROM NON-CONVENTIONAL FOSSIL FUELS

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INTRODUCTION

Naphtha derived from non-conventional fossil fuel feedstocks- that is, coal, bitumen, and shale - have the potential to augment the supply of naphtha obtained from petroleum feedstocks. To obtain transportation fuels which meet the current and future environmental regulations, these naphtha will have to be further upgraded. A number of studies suggest that more severe conditions (1-5) are required to obtain suitable heteroatom removal to meet current catalyst requirements both in reforming and hydrotreating.

A number of the studies report on the bulk properties of the naphtha feedstocks and products (elemental analysis, boiling point distributions, etc.). A detailed compositional analysis of the heteroatom and hydrocarbon distribution of the naphtha may offer potential explanations for the severe conditions required and be an important initial step in planning future catalyst formulations for upgrading strategies. These later analyses are not usually reported, at least in significant detail.

EXPERIMENTAL

Samples of naphtha were obtained from the catalytic processing of a western Kentucky tar sand bitumen and for the coprocessing of the bitumen with a Western Kentucky #9 coal in the CAER 1/8 tpd pilot plant. Details of the run and syncrude distillation to obtain the naphtha (IBP-400°F) samples are given elsewhere (6).

Naphtha samples (IBP-380°F) derived from processing an Illinois #6 (bituminous coal) and Black Thunder (subbituminous coal) were obtained from the Wilsonville, Alabama Advanced Integrated Two Stage Liquefaction facility. A light shale oil derived from processing a Cleveland shale (eastern shale) in the CAER Kentort II pilot plant was also included for comparison. Details of the process are given elsewhere (7).

The as-received samples were analyzed by gas chromatography using an HP 5890 series II instrument with a DB-5 column (60m x .32mm; .25μm film thickness). Sulfur compounds were analyzed using a Sievers Model 350B chemiluminescence sulfur detector coupled with an HP 5890 Series II gas chromatograph containing a SPB-1 column (30m x .32mm; 4.0μm film thickness).

Identification of the hydrocarbons was done by GC/MS and injection of standard compounds. Identification of the nitrogen and sulfur compounds was accomplished by injection of standard compounds. However, the lack of commercially available alkyl substituted thiophenes and benzothiophenes prevented a number of peaks in the sulfur chromatogram to be identified using this method. From the retention times obtained from the injection of the available standards and current literature (8), it was possible to separate the sulfur chromatogram into classes of sulfur compounds such as thiophenes and benzothiophenes for comparison.

The elemental analyses of the samples are given in Table 1. Carbon, hydrogen, nitrogen and sulfur were obtained using standard methods. Oxygen was determined for the bitumen, coprocessing and coal-derived naphtha by FNAA. The oxygen content of the shale oil was determined by difference.

RESULTS AND DISCUSSION

A. Hydrocarbon Distribution. The major hydrocarbon classes in the two naphtha samples from Wilsonville are shown in Figure 1. Compounds which are present in greater than .5 wt.% of the total FID chromatogram were identified by GC/MS. The only heteroatom compounds which had a sufficient response in the FID chromatogram are the phenols and these are included in Figure 1 for comparison. Using these guidelines, 65.5 wt.% (Illinois #6 naphtha) and 53.5 wt.% (Black Thunder naphtha) of total areas were identified in the chromatograms.

The major class of hydrocarbons in both coal-derived naphtha samples are cyclohexanes. This class of hydrocarbons includes cyclohexane and one carbon to four carbon substituted cyclohexanes. Methylcyclohexane is the major component in this class for the Illinois #6 derived naphtha. The 2-carbon substituted cyclohexanes are the major components in the Black Thunder derived naphtha. The Illinois #6 naphtha contains higher concentrations of all the cyclohexanes when compared to the Black Thunder naphtha, and this accounts for the overall higher concentration of the cyclohexanes in the Illinois #6 naphtha.

The Illinois #6 naphtha also contains a higher concentration of cyclopentanes than the Black Thunder naphtha. This hydrocarbon class includes cyclopentane and one to three carbon cyclopentanes. The Illinois #6 naphtha contains higher concentrations of all cyclopentanes identified; however, the differences in concentrations of the cyclopentanes in the two naphtha samples are smaller than is observed for the cyclohexanes.

An additional difference in the hydrocarbon distribution is the amount of alkanes, both normal and branched, in these naphtha samples. The Illinois #6 naphtha has significantly more branched and normal alkanes than the Black Thunder naphtha. The normal alkane distributions in both naphtha samples are in the C_4 to C_{12} range.

The hydrocarbon distribution of the naphtha samples derived from catalytically processing a western Kentucky tar sand bitumen and from the catalytic coprocessing the bitumen with a Western Kentucky #9 coal is shown in Figure 2. The major differences in the compositions between the two naphtha samples are in the yields of normal alkanes and aromatics. Coprocessing the bitumen with the coal produced a naphtha with slightly lower amounts of normal alkanes and aromatics when compared to the naphtha produced from processing the bitumen alone using the same process conditions, catalyst, etc. (6). The carbon number distribution of the normal alkanes ranges from C_6 to C_{12} in both naphtha samples. The carbon number distributions in the branched alkanes are the same for both naphtha samples and range from C_7 to C_{13}. The major class of branched alkanes are also the same for both naphtha samples, and are the C_{10} branched alkanes.

A comparison of the naphtha samples from the coal liquefaction process (Figure 1) and the naphtha samples shown in Figure 2 indicate major differences in the hydrocarbon distributions. The bitumen and coprocessing naphtha samples have a significantly higher amount of alkanes, both normal and branched, and aromatics when compared to the coal liquefaction naphtha samples. Another major difference is in the cycloalkane distributions. The naphtha samples derived during the processing of the bitumen and bitumen plus coal have more alkyl substitutions than the naphtha samples derived from the coal liquefaction process. Five carbon substituted cyclopentanes and cyclohexanes were identified in these two naphtha samples. The coal liquefaction derived naphtha samples have a maximum carbon number of 4 as alkyl substituents.

The hydrocarbon distribution of a distillate sample derived from retorting an eastern shale (Cleveland member) in the Kentort II process (7) is shown in Figure 3. In addition to the hydrocarbons, oxygen and sulfur compounds are in sufficient concentrations to have a response in the FID detector and are included for comparison. The hydrocarbon distribution for processing the shale is distinctly different from the distillates described previously. The major class of hydrocarbons were aromatics (24.4 wt.%), normal alkanes (12.4 wt.5) and olefins (0.3 wt.%). Olefins are only detected in the shale-derived distillate and included a small amount of cyclo-olefins. In addition to the presence of olefins, the major composition difference between the shale derived distillate and the previously described naphtha samples is the low yield of cycloalkanes.

B. Nitrogen Compounds. The nitrogen compound class distributions of this sample set are shown in Figure 4. Identification of the nitrogen compound is made using available standard compounds and the thermionic detector (TSD) as described in the experimental section. The concentrations of the nitrogen compound classes are given in area percent of the total area in the TSD chromatogram.

The major nitrogen class in the Illinois #6 and Black Thunder naphtha samples and the bitumen and coprocessing naphtha samples are the anilines. The anilines include aniline and 1 to 4 carbon alkyl substituted anilines. The 1 carbon substituted anilines are the most abundant compounds in this nitrogen class in the Illinois #6 naphtha. The 2 carbon substituted anilines are the most abundant compounds in this class for the other samples in this study.

The pyridines and quinolines are the next most abundant nitrogen classes of compounds identified in the Illinois #6, Black Thunder, bitumen and coprocessing derived samples. The 1 carbon pyridines are the most abundant compounds in this class in the Illinois #6 and Black Thunder naphtha samples. The 2 carbon substituted pyridines are the compounds with the highest concentration in this class for the bitumen derived naphtha and pyridine is the abundant compound found in this class in the coprocessing derived naphtha.

Quinoline and tetrahydroquinoline have the highest concentrations in this compound class in the Illinois #6, Black Thunder, bitumen and coprocessing samples. One and 2 carbon quinolines were identified in the Black Thunder and Illinois #6 naphtha samples. Substituted quinolines were not detected in the bitumen and coprocessing derived samples.

The distribution of nitrogen compounds in the shale derived distillate are significantly different. The number of compounds represented in the TSD chromatogram are larger than those of the other samples and only 26% of the compounds are identified at this time. The data indicate that the amounts of the pyridine, anilines and quinolines in this distillate are similar. The number of alkyl substitutions are similar to those discussed above.

C. Sulfur Compounds. The sulfur classes of the naphtha samples are shown in Figure 5. The major components identified using the Sievers CSD detector are thiophenes and benzothiophenes. Small concentrations of thiols and sulfides were also identified. The thiophene and benzothiophene classes are characterized by 1 to 3 carbon substitutions and their concentrations depend on their source.

SUMMARY

The hydrocarbon and heteroatom compositions of naphtha samples from non-conventional fossil fuels are reported. This on-going project should provide a well characterized set of samples for future research in hydrotreating and reforming of non-conventional fossil fuels.

ACKNOWLEDGMENT

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Table 1

Elemental Analysis of Samples

	Wilsonville Samples		CAER PIPU Samples		Kentort II Eastern Shale Liquid
	Bituminous	Subbituminous	Bitumen	Coprocessing	
C (Wt.%)	86.19	85.34	85.20	84.81	84.58
H (Wt.%)	13.34	12.25	13.66	13.54	11.84
N (Wt.%)	.07	.35	.48	.41	.40
S (Wt.%)	.05	.05	.37	.29	1.79
O (Wt.%)[1]	.35	2.01	.29	.95	1.39

[1] Oxygen determined by FNAA for all samples except the shale liquid. This oxygen content was determined by difference.

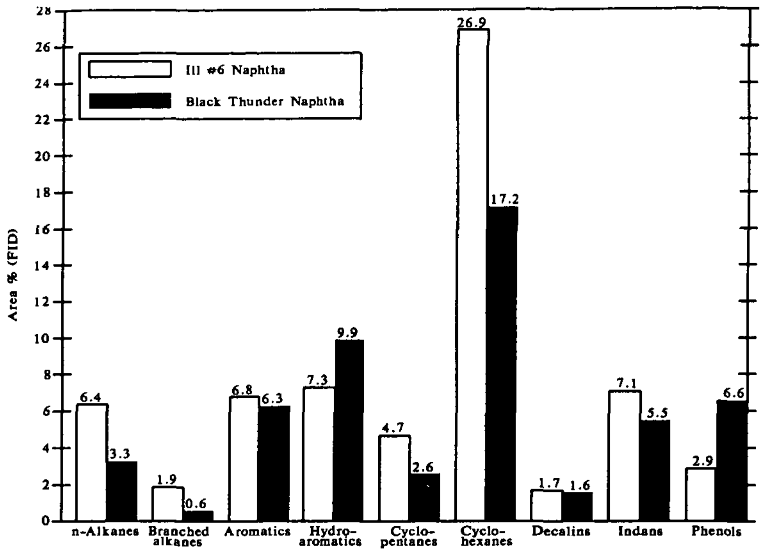

Figure 1. Analysis of Wilsonville naphtha derived from a bituminous and subbituminous coal.

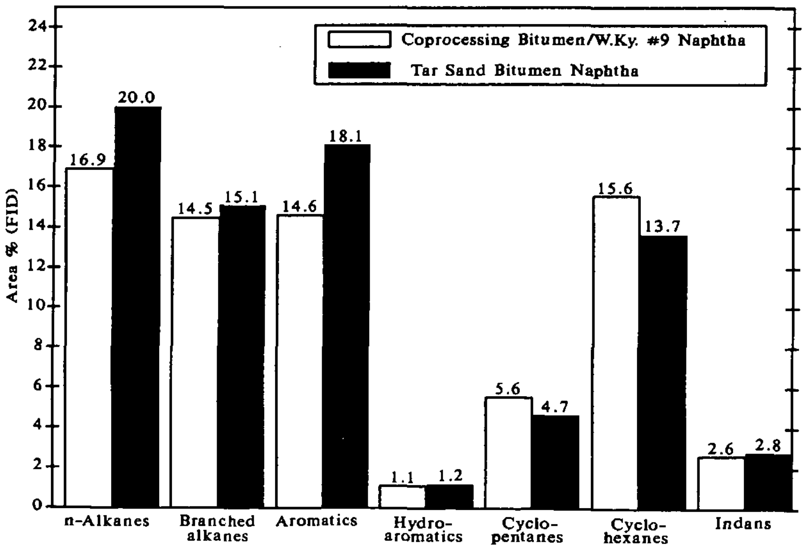

Figure 2. Analysis of naphtha derived from catalytic processing of tar sand bitumen and coprocessing bitumen and a W.Ky. #9 coal.

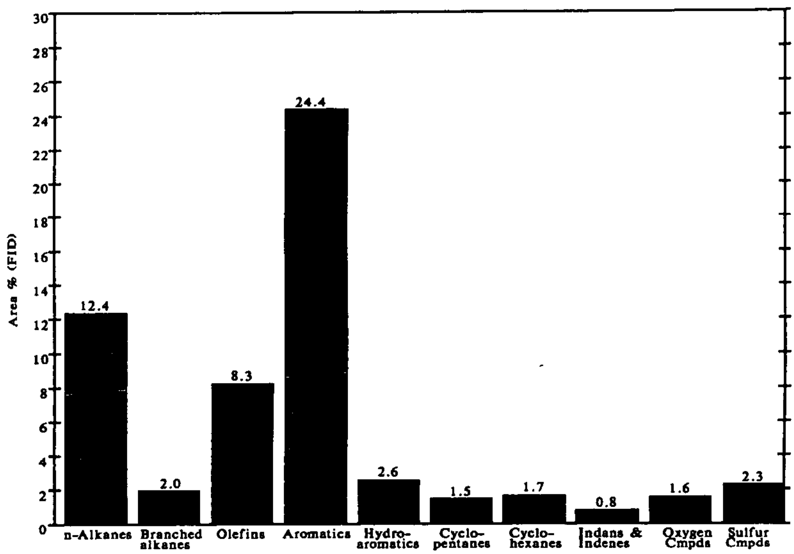

Figure 3. Analysis of a shale derived distillate sample from the Kentort II process.

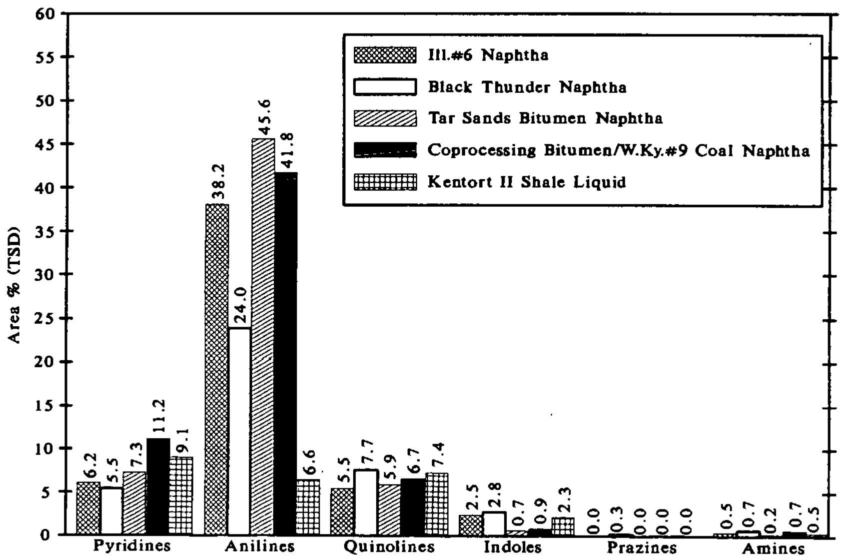

Figure 4. Nitrogen compound class distribution in the sample set.

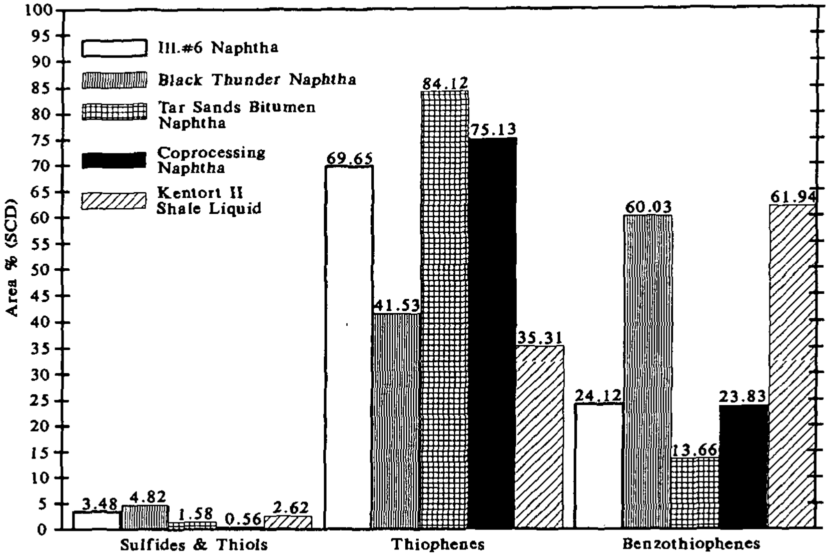

Figure 5. Sulfur compound class distribution in sample set.