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## RATE ENHANCEMENT FOR CATALYTIC UPGRADING COAL NAPHTHAS

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## CATALYTIC HYDROTREATMENT OF COAL-DERIVED NAPHTHA: THE REMOVAL OF INDIVIDUAL NITROGEN AND SULFUR COMPOUND FROM THE ILL. #6 NAPHTHA USING COMMERCIAL CATALYSTS

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### ABSTRACT

The amount of individual nitrogen and sulfur presented in the feed and hydrotreated Illinois #6 naphtha were determined. The major nitrogen class in the naphtha are anilines. The major sulfur components identified are thiophenes and benzothiophenes.

The aniline and quinoline is harder to remove than pyridine. The aniline and pyridine, without any carbon substituted, is the easiest one to remove in their class. The quinoline, without any carbon substituted, is approximately as hard as one carbon substituted quinoline to remove. Both Co-Mo and Ni-W catalysts follow the similar pattern of the nitrogen removal at different temperatures.

The sulfur compounds of the III. #6 naphtha was separated to three classes, i.e. sulfides and thiols, thiophenes and benzothiophenes, for comparisons. The thiophenes was the major component of the hydrotreated naphtha at most temperatures; however, the sulfides and thiols class becomes the major component at temperatures greater than 300°C.

### INTRODUCTION

Gasoline, derived from naphthas, accounts for about 50% of today's usage of transportation fuels in the U.S. Any successful coal liquefaction program must produce environmentally acceptable gasoline feedstocks. A number of the studies suggest that current naphtha hydrotreating catalysts do not have sufficient for today's refinery activity (1-5). To meet the requirements for today's hydrotreating, at least a

10-fold increase in catalytic activity is needed to upgrade coal-derived naphtha at a commercially acceptable rate.

Since sulfur is the major heteroatom in most petroleum (6) and because sulfur removal was required for the  $Pt-Al_2O_3$  naphtha reforming catalyst introduced in 1950, the hydrodesulfurization of petroleum-derived naphtha is commonly practiced. In recent years the need to more effectively utilize heavier resids has led to hydrotreating processes for heavier feedstocks. Typically nitrogen is the most abundant heteroatom in coal-derived naphtha (7-9). Therefore, several studies have focused on the hydrodenitrogenation of nitrogen-containing compounds (10-16). Although the hydrotreatment of nitrogen- and sulfur-containing compunds are well studied, few of these report on the relative rate for heteroatom removal; most of them are concerned with hydrodesulfurization of sulfur-containing compounds (17,18).

This study was designed to define whether heteroatom removal is at an uniform rate for all compounds in each heteroatom class or whether some heteroatom compounds are especially difficult to convert. To characterize a catalyst in terms of its selectivity for individual heteroatom removal reactions for individual compounds, methods to determine the amount of each sulfur and nitrogen compounds present in the feed and hydrotreated naphtha is needed. Recently instrumentation with the potential to sample directly from a flame ionization detector to determine the amount of sulfur present in the effluent from a capillary gas chromatograph has become available. Likewise, a nitrogen sensitive GC detector can be utilized for a quantitative

determination of individual nitrogen compounds. Thus, the naphtha can be analyzed for composition using a high resolution capillary column gas chromatography.

### EXPERIMENTAL

Hydrotreatment of the Illinois *#* 6 naphtha sample was carried out using two commercial catalysts (Co-Mo-Alumina, American Cyanamid HDS-1442A and Ni-W-Alumina Harshaw Catalyst, Ni-4301, E 1/12, Lot 16, Drum 29) over a range of temperature (200-400°C) and weight hourly space velocities (1-6 g/g/hr). Details of the experimental conditions are given elsewhere (19).

Individual nitrogen compounds in the feed and hydrotreated III. #6 naphtha were analyzed using a Thermionic Specific Detector (TSD) coupled with an Varian 3700 gas chromatograph using a KOH treated Carbowax column (30 m x a 32 mm). Identification of the heteroatom compounds was accomplished by comparison of retention time and doping with standard compounds.

One micro-liter samples with various concentrations of aniline in octane were injected to test the linearity and sensitivity of the TSD. A linear relation between nitrogen concentration and GC area was observed over a 0-50 ppm N range (Figure 1). This figure also shows that The TSD is very sensitivity; that is, a large GC area is obtained for a ppm of nitrogen.

Sulfur compounds were analyzed using a Sievers Model 350B Sulfur Chemiluminescence Detector (SCD) coupled with a HP 5890 Series II gas chromatograph containing a SPB-1 column (30m x 0.32mm). The SCD is based on

the chemiluminescent reaction between  $O_3$  and the combustion products of sulfur containing compounds formed in the hydrogen/air flame of the FID:

$$SO + O_3 - SO_2 + O_2 + energy$$

The SCD is extremely sensitive (ca. 20 picogram) and linear over 5 orders of magnitude. The SCD is equimolar (per S atom) for all sulfur containing compounds. An additional advantage is that both an FID signal for hydrocarbons and the S signal can be attained from a single injection.

The elemental analyses of the naphthas are shown in Table 1. Carbon and hydrogen analyses were performed using a Leco CHN analyzer. Oxygen analyses were obtained using the Fast Neutron Activation Analysis (FNAA) method and were performed by the University of Kentucky Radioanalytical Service. Trace level total nitrogen was analyzed using a Xertex DN-10 total nitrogen analyzer equipped with a chemiluminescence detector. Table 2 shows the heteroatom content of hydrotreating naphtha.

### RESULTS

### Nitrogen Compounds

Characterization of the III. #6 naphtha using the TSD couple with the capillary GC shows these materials to contain extremely complex mixtures of nitrogen compounds. It contains about 300-400 individual compounds as shown in Figure 2. Specific identification has been made for about 53% of the compounds and these are given in Table 3. The nitrogen compound class distribution is shown in Figure 3. The concentrations of the nitrogen compound classes are given in area percent of the total area in the TSD chromatograph.

The major nitrogen class in the naphtha samples are the anilines comprised of aniline and 1 to 4 carbon substituted anilines. The 1 carbon substituted anilines are the most abundant compounds in this nitrogen class for the III. #6 naphtha.

Pyridines and quinolines are the next most abundant nitrogen of compounds among these identified. The 1 carbon pyridines are the most abundant compounds in its class. Quinoline and tetrahydroquinoline have the highest concentrations in the quinolines compound class. One and 2 carbon quinolines were also identified in these naphtha samples.

### Nitrogen Compound Conversion at Different Temperatures

The reaction temperatures for the hydrotreatment of III. #6 naphtha was varied from 220 -400°C. The weight hourly space velocity was 1 g/g/hr. The hydrogen and naphtha g-mole ration was 2.6.

### **Pyridines**

Figures 4 and 5 show the results of the conversion of compounds in the pyridine class at different temperatures using Co-Mo-Alumina and Ni-W-Alumina catalysts. At temperatures higher than 300°C, almost all of the pyridines were removed using either catalysts.

In this class, pyridine is the easiest compound to convert for both catalysts. On the other hand, 3-ethyl-pyridine is the most difficult compound to convert in this class. The removal of nitrogen depends on the position of the alkyl substituent on the aromatic ring. The conversions of pyridine substituted by a methyl or ethyl group decreases according to 4 > 2 > 3 for both catalysts.

### <u>Anilines</u>

The temperature dependence for the removal of the aniline nitrogen class for the Co-Mo (Figures 6 and 7) and for the Ni-W (Figures 8 and 9) catalysts show that anilines are harder to remove than pyridines. Even at a temperature of 400°C, a few anilines remain in the samples, especially for the Ni-W catalyst.

Aniline, without carbon substituent, is the easiest compound to convert in this class for both catalysts; pyridine is likewise the easiest of the pyridines class to convert. For both catalysts the substituted anilines with 2 to 4 carbon are harder to convert than aniline with one carbon substituent. 2,5-DiMethyl-Aniline is the most difficult compound to convert in the class for both catalysts. These data also show that the removal of nitrogen depends on the position the group(s) substituted anilines is: unsubstituted > 4 > 3 > 2. This is the case for both catalysts, and differs from the results for the pyridines. This difference is more apparent at the high temperatures, i.e., temperatures greater than  $300^{\circ}$ C.

### <u>Quinolines</u>

The conversion of compounds in the quinoline nitrogen class with the Co-Mo catalyst or the Ni-W catalyst at different temperatures are shown in Figures 10 and 11. The data show that quinoline is also harder to convert than the pyridines, is converted at about the same rate as the anilines.

Quinoline, without substitution, is converted at about the same rate as the one carbon alkyl substituted quinoline with either catalysts. The substitution of alkyl groups on the quinoline ring, at least for those compounds present in the naphtha feed, does not significantly impact the rate of conversion. For example, the conversion of 4-methyl-quinoline is only slight easier than that of the 3-methyl-quinoline.

### Indole and Indoline

Indoline is easier to remove than 1,2-dimethylindole for both catalysts (Figures 1,2 and 13). Both indoline and 1,2-dimethylindol were completely converted at temperatures above 350°C.

### Nitrogen Compound Conversion Versus Space Velocity

The space velocity of the III. #6 feed was varied while keeping the reactor temperature at 300°C and pressure at 660 psi. The fractional conversion for each of the nitrogen compounds that have been identified was determined for the various space velocities.

The results of the pyridine class of compounds for the Co-Mo catalyst (Figures 14 and 15) and for the Ni-W catalyst (Figures 16 and 17) show that the pyridines follow 1st-order kinetics for both catalysts.

The results for conversion of compounds of the aniline class for the Co-Mo catalyst (Figures 18-21) show that anilines also follow the 1st-order kinetics at the higher space velocities used in these studies but deviation from 1st order occurs at lower space velocities for the Co-Mo catalyst. However, when an ethyl group is present in the 2, 3 or 4 position of aniline 1st-order kinetics applies for all space

velocities tested. In addition, the 2 to 4 carbon alkyl group substituted anilines follow 1st order kinetics over the range of space velocities tested. Note that the aniline class compounds which follow the 1st-order reaction over all of the space velocities tested are those the compounds that are the most difficult to convert.

The results for the Ni-W catalyst show that most of the compounds of the aniline class follow the 1st-order reaction well. The only exceptions were the methyl substituted anilines at the higher space velocities.

For the quinoline and indoline classes, all compounds follow the 1st-order reaction for both catalyst (Figures 26-29).

### Sulfur Compounds

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The availability of only a few alkyl substituted thiophenes and benzothiophenes limits the number of peaks in the sulfur chromatograph that can be identified by injection of standard compounds. However, from the retention times obtained from the injection of the available standards and retention times reported in the literature (20) allows for a grouping of the sulfur chromatogram peaks into classes of sulfur compounds such as thiophenes and benzothiophenes.

The sulfur classes of the naphtha samples are illustrated in Figure 30. The major components identified using the Sievers CSD detector are thiophenes and benzothiophenes with small amounts of thiols and sulfides were also identified. The thiophene and benzothiophene classes are comprised mainly of 1 to 3 carbon alkyl substituted compounds.

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The conversion of sulfur compounds that have been identified at different temperatures show that most of the sulfur is removed at 250°C using the Co-Mo catalyst and 300°C using Ni-W catalyst (Figures 31 and 32, respectively). Since only a few of the sulfur compounds have been identified, most of the conclusions cannot be based upon specific compounds. However, it is apparent that the conversion of the sulfur compounds do not show significant dependence upon alkyl substitution. For both catalysts, 2-ethylthiophene is the hardest one to convert among the identified compounds.

The amount of sulfides and thiols in the naphtha reaches a minimum value at  $225^{\circ}$ C, then increases with temperature to a maximum value at about  $300^{\circ}$ C, and then remains essentially constant with further increases in temperature (Figures 33 and 34). This was observed for both catalysts. The increase of sulfides and thiols may be due to the recombination of H<sub>2</sub>S with olefins (21).

### DISCUSSION

Alkyl-substituted heterocyclic compounds were major compounds found in the Illinois #6 naphtha. The effect of substituents on the converted of heteroatoms from the naphtha were found in different ways. The HDN reactivities of pyridine, aniline and quinoline according to the position of substituent added is as follows:

> pyridine > 4-R-pyridine > 2-R-pyridine > 3-R-pyridine, aniline > 4-R-aniline > 3-R-aniline > 2-R-aniline, and quiniline  $\approx$  3-methyl-quinoline  $\approx$  4-methyl-quinoline.

where R = methyl or ethyl group.

These differences of the effect of alkyl-substituted on HDN may be due to steric and/or electronic effects. Many publications had shown that the steric and electronic effects play an important role on the HDS of a number of sulfur heterocycles (17,18,22,23). From the point of view of steric hindrance, the reactivities of HDN should be 4 > 3 > 2. However, from the point of view of electronic effect, since alkyl groups are electron-donating and the catalysts used in the test are acidic in nature, the reactivities of HDN should be  $4 \approx 2 > 3$ . Since the magnitude order of HDN of alkyl-substituted aniline follows the case of steric effect, the HDN of alkyl-substituted aniline is dominated by steric effect. In addition to the steric effect, the results for the HDN of alkyl-substituted pyridine shows that electronic effect becomes more important. The electronic effect for HDN of pyridine is more significant than aniline is reasonable since the nitrogen atom of pyridine is in the aromatic ring and nitrogen atom of aniline is in amino group attached to aromatic ring. The effect of alkyl substituents on the reactivity of quinoline becomes relatively insignificant. Gates et al. (23) reported that HDN reactivities of 2,6-, 2,7-, and 2,8-dimethylquinoline is approximately the same as that of guinoline.

In general, hydrotreatment of the heavy fractions of coal derived materials is complicated by the molecular weight, and the corresponding large size, of the molecules converted. The large size introduces severe diffusional problems during processing. However, this is not a problem in the hydrotreatment of coal derived naphtha, since the dominant fraction of the material contains only one ring of five or six carbons; two ring components are the largest molecules that will be encountered

and these represent only approximately 10% of the nitrogen compounds (Table 3) and approximately 24% of the sulfur compounds (Figure 30). Thus, diffusion limitations due to size exclusion should not be a problem in the study.

The conversion of pyridines and quinolines at different space velocities follow a 1st-order reaction for both catalysts. The conversion of anilines follow a 1st-order reaction only at the higher space velocities for Co-Mo catalyst; however, for the Ni-W catalyst, most of the anilines class compounds follow a 1st-order reaction at all space velocities used in this work. The 1st-order reaction of HDN implied that the effect of competition of chemisorption between heteroatoms on nitrogen compounds is insignificant. This can be explained by expressing the rates in terms of Langmuir-Hinshelwood kinetics:

$$\gamma_{n,i} = \frac{k_{i}K_{n,i}P_{N,i}}{1 + \sum_{i} (K_{N,i}P_{N,i}) + \sum_{i} (K_{o,i}P_{o,i}) + \sum_{i} (K_{s,i}P_{s,i})}$$
[1]

where k is a reaction constant, K is a equilibrium constant for adsorption, P<sub>i</sub> is partial pressure of component i, and N, S, and O represent nitrogen, sulfur and oxygen heteroatoms respectively. In this expression, hydrogen partial pressure was ignored since the hydrogen was presented essentially excess. The assumption was also made that rate limiting step is the chamical reaction rate on the surface, an equilibrium is established with respect to adsorption of all species. A first order reaction of HDN reaction means that the denominator term of equation [1] should be close to unity and equation [1] becomes:

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$$\gamma_{N,l} = k_l K_{N,l} P_{N,l} \qquad [2]$$

Thus, the presence of sulfur and oxygen heteroatoms do not affect the HDN reaction. This is acceptable since nitrogen heteroatoms have higher adsorptivity than sulfur and oxygen heteroatoms for acidic catalyst.

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### Table 1

### Elemental Analysis of Naphtha

	<u>Illinois #6</u>
С	85.67%
н	13.24%
N	166 ppm
S	1100 ppm
0	1.26%

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### Table 2

## Nitrogen, Sulfur and Oxygen Content of Products from the Hydrotreatment of Illinois #6 Naphtha

Temp.	N	S	N	S	WHSV		
<u> </u>	<u>Wt. ppm</u>	Wt. ppm	<u>% HDN</u>	<u>% HDS</u>	g/g/hr.	<u>Catalyst</u>	Feed
220	1163	153	30.0	86.1	1	Co-Mo	Ⅲ. #6
250	780	70	53.1	93.6	1	Co-Mo	Ⅲ. #6
300	325	4	80.5	99.6	1	Co-Mo	Ⅲ. #6
300	616.6	9.3	62.9	99.2	2	Co-Mo	Ⅲ. #6
350	19	4	98.9	99.7	1	Co-Mo	Ⅲ. #6
400	18	3	98.9	99.8	1	Co-Mo	Ⅲ. #6
220	1240	341	25.4	68.9	1	Ni-W	Ⅲ. #6
250	899	177	45.9	83.9	1	Ni-W	Ⅲ. #6
300	387	21	76.7	98.1	1	Ni-W	Ⅲ. #6
300	747.9	43.7	55.0	96.1	2	Ni-W	Ⅲ. #6
300	882.5	46.1	46.9	95.8	3	Ni-W	Ⅲ. #6
350	30	11	98.2	99.0	1	Ni-W	Ⅲ. #6
400	20	11	98.8	99.0	1	Ni-W	Ⅲ. #6

### Table 3

### Illinois #6 Naphtha Total TSD Detector Area = 1492076

<u>R.T.</u>	Area	_Area %
4.771	22078	1.48 unknown
5.22	27811	1.86 unknown
6.954	24747	1.66 unknown
9.224	5496	0.37 pyridine
9.771	22852	1.53 unknown
10.254	21219	1.42 2-methylpyridine
11.307	12335	0.83 unknown
12.453	5706	0.38 2-ethylpyridine
12.771	7589	0.51 3-methylpyridine
12.987	3581	0.24 4-methylpyridine
13.146	16480	1.10 unknown
13.805	13557	0.91 unknown
14.14	19432	1.30 unknown
14.947	12790	0.86 2,4,6-trimethylpyridine
15.27	15072	1.01 unknown
15.629	3036	0.20 e-ethylpyridine
15.787	11003	0.74 unknown
15.93	1972	0.13 4-ethylpyridine
16.675	11691	0.78 3,5-dimethylpyridine
18.62	2660	0.18 3,4-dimethylpyridine
18.781	15020	1.01 unknown
19.738	16271	1.09 unknown
21.258	5592	0.37 N,N-dimethylaniline
22.328	10909	0.73 unknown
23.3	11243	0.75 2,3-cyclopentenopyridine
<b>23.92</b> 3	2212	0.15 N,N-diethylaniline
26.97	7843	0.53 N-methylaniline
27.115	17100	1.15 N-ethylaniline
27.3	6499	0.44 unknown
27.722	14584	0.98 unknown
27.975	87086	5.84 aniline
29.362	77360	5.18 2-methylaniline
29.874	53223	3.57 4-methylaniline
30.529	8050	0.54 3,5-dimethylaniline
30.608	91912	6.16 3-methylaniline
31.022	24212	1.62 2-ethylaniline

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<u>R.T.</u>	Area	Area %
31.375	33592	2.25 2,4-dimethylaniline
31.798	27533	1.85 4-n-butylaniline
32.093	5986	0.40 1,2,3,4-tetrahydroisoquiniline
32.447	22011	1.48 4-ethylaniline
32.675	6687	0.45 indoline
32.79	32582	2.18 quinoline
33.054	35592	2.39 3-ethylaniline
33.161	18006	1.21 3,5-dimethylaniline
33.435	15944	1.07 2,3-dimethylaniline
33.736	16568	1.11 p-isopropylaniline
33.846	14219	0.95 isoquiniline
34.243	12207	0.82 unknown
34.808	17591	1.18 4-propylaniline
35.227	21533	1.44 2-ethyl-6-sec-butylaniline
35.354	17138	1.15 unknown
36.56	14940	1.00 1,2,3,4-tetrahydroquiniline
37.289	6641	0.45 4-methylquiniline
37.654	3727	C.25 3-methylquiniline
39.059	10075	0.68 unknown
45.669	24344	1.63 1,2-dimethylindole
47.051	10228	0.69 unknown

Total = 73.31%

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Figure 1.



## Calibration of N Detector Using Aniline

N , ppm

Figure 2.





# Nitrogen Compound Class Distribution in the Naphthas







Figure 5.

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Figure 8.













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2-E-P -×- 3-E-P -\*- 4-E-P

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Figure 16.



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Figure 22.



































Figure 30.

# Figure . Sulfur Compound Class Distribution in the Naphthas











# Sulfides and Thiols at various T. Co-Mo, III.#6 Naphtha



# Sulfide & Thiols at Various T. Ni-W, III.#6 Naphtha









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