

## INDUSTRIAL CATALYSTS FOR AROMATICS REDUCTION IN GAS OIL

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### ABSTRACT

Six commercially available Ni-Mo/Al<sub>2</sub>O<sub>3</sub> catalysts were tested for HDN, aromatics reduction and HDS on a hydrocracked gas oil (249 - 524°C) in a fixed bed reactor operating in the upflow mode. Acceptable HDN, HDS, and aromatics reduction were obtained for three of the six catalysts. Total aromatics concentrations were determined using four different methods, two of which were also used to determine PNA concentrations. Each method gave a different aromatics concentration, however, linear correlations were established between the results obtained by each method. Contrary to expectations, superior HDN and HDS performance and comparable PNA reductions were observed in a heavier fraction (343+°C) than in the total liquid product.

### INTRODUCTION

The expected depletion of the lightest conventional feedstocks has placed a greater emphasis on upgrading technologies. These technologies generally involve hydrocracking the "bottom of the barrel" and hydrotreating the resulting distillates to reduce the amounts of sulphur and nitrogen<sup>1,3</sup>. The substitution of conventional petroleum with synthetic crudes is on the rise. This trend is expected to shift the hydrocarbon distribution toward the aromatic at the expense of the saturates in the blended feedstocks<sup>4</sup>. Studies have shown that, due to their high content of aromatic components, combustion of synthetic fuels generates higher particulate concentrations than combustion of conventional fuels in both diesel engines and heating appliances. Because of the varied health hazards associated with particulate emissions<sup>5,6</sup>, refiners are confronted with stricter regulations aimed at controlling particulate emissions and unburned hydrocarbons in diesel exhaust through reduced aromatics levels.

Thus, aromatics reduction has become a key upgrading parameter in light of stringent environmental regulations and industry trends toward low-quality component blends derived from conventional crudes and synthetic crude distillates. The optimization of product quality and product performance becomes critical both from an environmental and a marketing perspective. While regulations have focussed on aromatics determined by fluorescent indicator adsorption (FIA) in diesel fuels, the guidelines for aromatics determination in the gas oil fraction are much more ambiguous. Consequently, it is essential to have a reliable method for aromatics determination in these heavy cuts.

The work reported herein is part of a much larger study aimed at evaluating the performance of commercial catalysts during the hydrotreating of gas oil. One of the performance indicators in that study was the reduction in the amount of aromatic components. Many conventional hydrotreating catalysts (e.g., sulphided Ni-Mo/Al<sub>2</sub>O<sub>3</sub>), normally designed for hydrodesulphurisation, show excellent hydrodenitrogenation activity and perform aromatics reduction as well.

This paper provides technical information related to product properties upon hydrotreating a hydrocracked gas oil. The data will focus on aromatics determination and aromatics reduction for six commercially available hydrotreating catalysts.

## EXPERIMENTAL

The hydrotreating experiments were performed in a stainless steel tubular fixed-bed reactor operating in the upflow mode. The key process parameters were T = 375°C, P = 1750 psig and LHSV = 0.5 h<sup>-1</sup>. The feedstock was the fraction boiling between 249°C and 524°C obtained from hydrocracking a 50/50 volumetric blend of Cold Lake/ Lloydminster resid.

Specific gravities were determined at 15.5°C on a Paar DMA 48 Instrument while dynamic viscosities were determined at 25°C on a Brookfield DV II instrument. Sulphur was determined on a Leco SC-132 sulphur analyzer while carbon and hydrogen as well as trace nitrogen were determined commercially. Both simulated distillations (ASTM D-2887) and vacuum distillations (ASTM D-1160) were performed in-house.

Carbon-13 NMR analyses were obtained on a Bruker ACE-200 instrument. Solutions were prepared by diluting 2.0 cm<sup>3</sup> of the sample with 2.0 cm<sup>3</sup> of a 0.10 mole dm<sup>-3</sup> solution of tris(2,4-pentanedionato)chromium(III) in CDCl<sub>3</sub>. The instrument was operated in the inverse gated decoupled mode for NOE suppression using a 6.5 us pulse (90°C) and a repetition time of 10 s. In a typical experiment 5000 transients were collected as 8K data points which were zero filled to 16K. A Lorentzian line broadening of 5 Hz was applied to the free induction decay prior to processing. Integration for paraffins, naphthenes and aromatics was as described by Young and Galya<sup>7</sup>.

Low resolution mass spectrometric analyses for aromatic types were obtained commercially. The method of Robinson and Cook<sup>8</sup>, which has been adopted as ASTM D-3239, was used with minor modifications. As well, the weight per cent of total aromatics was determined by a column chromatographic technique as described by Watson<sup>9</sup>. The method of Fitzgerald *et al*<sup>10</sup>, for the determination of aromatic components by UV/Vis spectroscopy, was adapted in-house to account for expected differences in the sample composition.

## RESULTS AND DISCUSSIONS

The project from which these data were derived concerned the selection of hydrotreating catalysts for the Bi-Provincial Upgrader facility<sup>11</sup> currently under construction. The design specifications for hydrotreated product quality included, among others, nitrogen at 500

wppm, sulphur at 400 wppm and total aromatics by Watson's method<sup>9</sup> at 45 wt.%. The properties of the feedstock and of the products obtained from hydrotreating this material using six different catalysts have been recorded in Table 1. The data indicate that all of the products exceed the design specifications for nitrogen and total aromatics content and that three of the six products meet the sulphur specifications as well.

The aromatics content of the feedstock and the six hydrotreated products have been measured using four different methods (Table 2). Both <sup>13</sup>C NMR<sup>7</sup> and the Watson method<sup>9</sup> measure total aromatics only. With <sup>13</sup>C NMR the paraffinic and naphthenic carbon content as well as the aromatic carbon content of the sample may be determined while with the Watson method, any moiety which has not been eluted from a silica containing chromatographic column with an aliphatic hydrocarbon is considered aromatic. Consequently, in this latter technique any compound which contains an aromatic unit would be considered as aromatic. The UV/Vis method<sup>10</sup> may be used to determine both total aromatics and polynuclear aromatics (PNA). The technique requires a *a priori* assumption or knowledge of the types of aromatic components in the sample so that the absorption maximo and absorptivities of corresponding model compound types may be used to calculate the concentrations of related components in the sample of interest. The method seems to be highly dependent on the materials chosen to represent the PNA components, the sensitivity has been found to be low, and the method was found to overestimate both PNA content and total aromatics content. However, the UV/Vis method may be useful for determining trends. The last method used for aromatics determination was a modification of Robinson and Cook's mass spectrometric technique<sup>8</sup>. Saturates are separated from aromatics by column chromatography and each fraction is introduced into the mass spectrometer for classification by Z number. Because "aromatics" is loosely and operationally defined, each of the techniques determines a different quantity and consequently results in method dependent values for aromatics content.

Among the various methods, the best agreement for total aromatics content appears to be between the UV/Vis and MS methods. Bearing in mind the limitations of the UV/Vis method, this correspondence may be more fortuitous than real and probably reflects the large number of tetra- and penta-aromatic standards used in the technique and that the mono-aromatics account for the major portion of the total aromatics content of the samples. Also, it may be seen that while the absolute values for total aromatics vary considerably according to method, a relationship exists between the different methods. This relationship has been further explored by plotting the total aromatics content obtained via NMR, chromatographic and UV/Vis analyses in the hydrotreated total liquid product against that obtained from mass spectrometry (Figure 1). Linear regression analysis has resulted in correlation coefficients of 0.971, 0.988 and 0.997 respectively for the following equations:

$$\text{NMR} = 0.31 * \text{MS} + 3.95 \dots\dots\dots(1)$$

$$\text{Watson} = 0.84 * \text{MS} + 10.0 \dots\dots\dots(2)$$

$$\text{UV/Vis} = 1.06 * \text{MS} - 1.44 \dots\dots\dots(3)$$

Again, the fortuitous relationship between aromatics determined by the UV/Vis method and the MS method noted above has resulted in excellent correlations between the methods. However, it is noted that the correlation coefficient drops to 0.75 if the aromatics content of the feedstock is included in the regression analyses. It is possible that the deviation of the data point for the feedstock from the regression line encompassing the hydrotreated products may be due to the sensitivity of the method to the choice of reference standards. The inclusion of the data point for the feedstock in the remaining two methods alters the correlation coefficients only slightly but results in appreciable changes in the slope of the regression line.

One interpretation of equations 1-3 above could be that on average, only 31% of the carbon atoms are in aromatic rings, the remainder being in alkyl side chains and naphthenic substituents. Consistent with this, 16% of the aromatic components in the sample could be considered saturate on the basis of polarity because of long chain alkyl substituents on the aromatic moiety.

Only the UV/Vis method can be compared to the MS method for aromatics content by ring number. Meaningful results have been obtained for only mono-aromatics, di-aromatics and total PNA (Figure II). The insensitivity of the UV/Vis method to higher ring number components precluded further correlations. The data indicate that while the correlation coefficients were acceptable, the UV/Vis technique overestimates mono-aromatics while severely underestimating higher ring number aromatics.

Lee *et al*<sup>12,13</sup> have found similar correlations between aromatics determined by mass spectrometry and NMR, FIA (ASTM D-1319) and SFC for diesel fuels and middle distillates. Since the NMR analyses methodology adopted by these authors differed from our approach, no basis for data comparison existed. However, the fact that such correlations exist for diesel and middle distillate cuts<sup>12,13</sup> and for the gas oil fraction suggests that these correlations may be part of a more general phenomenon.

The heteroatom distribution as well as the PNA (UV/Vis method) and total aromatics (Watson method) content of the 343+°C fractions of the feedstock and hydrotreated products were determined (Table 3). The data indicate that both the heteroatom content and the aromatics content have increased in the feedstock while, for the most part, these values have decreased for the hydrotreated product relative to those in total liquid product. Surprisingly, this has resulted in higher conversions in the heavier gas oil fractions (Table 4) and consequently indicates the superior catalytic activity of these catalysts for the heavier components.

## CONCLUSIONS

Although the Ni-Mo/Al<sub>2</sub>O<sub>3</sub> catalysts used in this work will not perform deep aromatics hydrogenation, they will remove 30 - 60% of the total aromatics in the hydrocracked gas oil while at the same time exhibiting a 90 - 99% conversion of sulphur and nitrogen. The catalysts investigated show superior performance with the heavier gas oil fractions. The

amount of aromatics determined, and consequently the aromatics conversions, are method dependant. This must be considered in potential environmental legislation as well as in fuel oil and catalyst marketing and underscores the requirements for standardization. The trends determined for the very narrow range of compounds reported here may be part of a broader, more general phenomenon.

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TABLE 1  
FEEDSTOCK AND HYDROTREATED PRODUCT PROPERTIES

	FEED-STOCK	PROD. A	PROD. B	PROD. C	PROD. D	PROD. E	PROD. F
Density (kg/dm <sup>3</sup> )	923.3	872.8	890.2	890.2	886.3	889.2	880.4
Viscosity (cP)	38	13	22	21	19	22	16
Carbon (wt%)	87.09	86.60	87.04	87.02	86.91	86.78	86.50
Hydrogen (wt%)	11.61	12.74	12.15	12.26	12.47	12.38	12.65
Sulphur (wppm)	14123	795	984	517	393	391	247
Nitrogen (wppm)	1799	102	276	204	62	129	30
Sim. Dist. (wt%)							
IPB - 177	-	4.1	1.5	1.4	1.8	1.5	2.7
177 - 249	1.6	7.4	4.3	3.8	4.7	4.2	5.9
249 - 343	31.4	39.2	35.7	36.3	36.5	35.8	37.4
343 - 524	65.4	49.3	58.5	58.5	57.0	58.5	54.0
524+	1.6	-	-	-	-	-	-

Note: A, B, C, D, E, F are commercially available catalysts.

TABLE 2  
TOTAL AROMATICS (WT.%) BY METHOD

METHOD	FEED-STOCK	PROD. A	PROD. B	PROD. C	PROD. D	PROD. E	PROD. F
<sup>13</sup> C NMR	27.0	9.8	13.9	13.9	12.2	13.6	11.1
Watson	55.1	25.7	35.2	37.3	33.8	36.3	29.3
UV/Vis	32.4	18.1	30.7	33.8	28.0	30.6	24.0
Mass Spec.	50.45	18.94	29.92	33.72	27.45	30.55	23.73

TABLE 3

## HETEROATOM AND AROMATICS DISTRIBUTION IN THE 343+°C FRACTIONS

	FEED-STOCK	PROD. A	PROD. B	PROD. C	PROD. D	PROD. E	PROD. F
Density (kg/dm <sup>3</sup> )	940.6	888.7	905.4	904.2	900.7	903.4	895.4
Nitrogen (wppm)	2050	37	230	145	60	161	15
Sulphur (wppm)	16400	265	718	488	265	240	60
Aromatics, UV/Vs (wt%)							
Monoaromatics	23.3	16.7	25.1	29.9	25.7	27.0	21.5
Polynuclear Arom.	12.9	4.1	4.7	4.4	4.4	4.5	4.2
Total Aromatics	36.2	20.7	29.8	34.3	30.1	31.5	25.7
Aromatics, Watson (wt%)	57.9	22.1	35.9	38.4	33.8	37.1	28.0

TABLE 4

HETEROATOM AND AROMATICS CONVERSION (%)  
IN THE TOTAL LIQUID PRODUCT AND THE 343+°C FRACTION

TEST	CAT. A	CAT. B	CAT. C	CAT. D	CAT. E	CAT. F
Total Liquid Product						
Sulphur	94.4	84.7	88.7	96.5	92.8	98.3
Nitrogen	94.4	93.0	96.3	97.2	97.2	98.2
Aromatics, Watson (wt%)	53.3	36.1	32.3	38.7	34.1	46.8
343+ Fractions						
Nitrogen	98.2	88.8	92.9	97.1	92.1	99.3
Sulphur	98.4	95.6	97.0	98.4	98.5	99.6
Aromatics, Watson (wt%)	61.8	38.1	33.7	41.7	36.0	51.7

Figure I. Effect of Analysis Method on Aromatics Content in Gas Oil

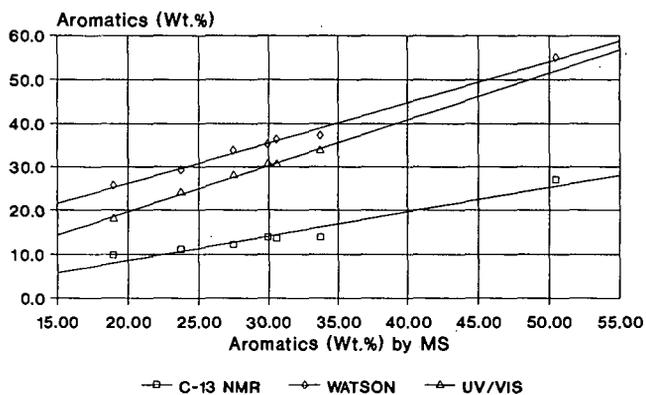


Figure II. Correlation Between UV/Vis and Mass Spectrometric Methods for Aromatics Content by Ring Number

