

EFFECT OF HYDROTREATING ON THE STABILITY OF SYNTHETIC CRUDE FROM WESTERN CANADA

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ABSTRACT

The storage stability of distillates from the hydrocracking of Western Canadian bitumen atmospheric residue was studied over 60 days. naphtha-jet and gas oil fractions of the hydrocracked distillates were shown to be unstable with respect to the formation of existent gum, total insoluble materials and asphaltene. The storage stability was significantly improved when these two fractions were mildly hydrotreated. The data were used to generate correlations that predict the stability of synthetic crudes.

INTRODUCTION

The refining industry in North America is consistently moving towards the utilization of heavier feedstocks for the production of synthetic crude. Current production of synthetic crude oil from oil sands and heavy oils is achieved by hydrogen addition as well as carbon rejection technologies. The primary products from these heavy feedstocks require different degrees of hydrotreating to obtain transportation fuels that meet current specifications. The hydroprocessing of bituminous materials and residues results in coke deposition on the catalyst as well as sludge formation in the product oil [1]. The products obtained are rather unstable, generally described as storage instability. Storage stability of hydrocarbon fuels therefore refers to their tendency to produce coloured species, soluble gums, and insoluble sediment during storage [2]. The storage and thermal stability of liquid stocks, especially diesel and jet fuel, have been topics of intense study especially by the military [3, 4]. To our knowledge, there has been very little study on the stability of hydrocracked products from the residues of Canadian heavy oils or the synthetic crude so blended after hydrotreating the hydrocracked distillate fractions.

The objective of the study was to quantify the rate of deterioration of the hydrocracked material and the hydrotreated distillates in terms of colour change and formation of soluble gums and insoluble materials, as well as to establish the presence or absence of the precursors to instability in the liquid fractions.

EXPERIMENTAL

The feedstock for this study was 50/50 Cold Lake/Llyodminster atmospheric residue (399°C +). The hydrocracking of the residue to distillate fractions was performed on a commercial NiMo/Al₂O₃ catalyst using a continuous bench scale stirred tank reactor. The experiments were carried out using the following conditions: Pressure < 20,685 kPa, temperature < 450°C and LHSV < 1 h⁻¹. The catalyst was presulphided and conditioned for 120 hours. To obtain the required amount of distillate products the experiment was continued for another 16 hours. The product samples had to be analyzed as soon as they were generated and distilled to give the fractions required for further processing (hydrotreating) or analysis. Distillation of the hydrocracked materials was carried out in order to obtain fractions which were tested for storage and colour stability and further characterized to identify materials causing instability. The hydrocracked materials were distilled into naphtha, jet-fuel, diesel, gas oil and Residue. The naphtha and jet-fuel fractions were analyzed for both colour and storage stability and then combined as feedstock for hydrotreating. Similarly, diesel and gas oil fractions were analyzed for colour and storage stability and then combined as feedstock for hydrotreating. The catalysts used for naphtha-jet and diesel-gas oil hydrotreating experiments were C-411 and C-424 catalysts respectively. Detailed experimental procedures and equipment are described elsewhere [5].

Analytical Methods and Analyses of Samples

Specific gravities were determined in triplicate at 15.5°C on a Paar DMA 48 instrument. Dynamic viscosities were determined in triplicate at 40°C using a Brookfield DV II instrument. Heptane insoluble asphaltenes were determined using the method of Pearson et.al. [6]. Existent gum was determined by the jet evaporation technique according to ASTM D 381-86. Hydrocarbon-types were determined in low boiling (IBP-249°C) distillates by the fluorescent indicator adsorption

method according to ASTM D 1319-77 and gave the volume percent of saturates, olefins and aromatics. The aniline point of the various distillate fractions was determined according to ASTM D 611-82. Bromine Numbers were determined according to procedures in ASTM D 1159-82. Carbon, hydrogen and nitrogen were determined using a CHN Analyzer. Trace nitrogen was determined on an Antek 771 pyroanalyzer coupled to an Antek chemiluminescent nitrogen detector. Basic nitrogen was determined according to procedures outlined in UOP Method 269-70T. Sulfur was determined on a Leco SC-132 sulfur analyzer. The colour of the petroleum products was determined by the Lovibond Tintometer method as described in IP 17/52. The oxidation stability of middle distillate fractions was determined according to ASTM D 2274-88 and these procedures have been found useful for estimating the storage stability of distillate fuels boiling between 175 and 370°C. The procedures in ASTM D 4625-87 were followed for the prediction of storage stability. Hydrocarbon-type analyses on the liquid samples were performed using a modified ASTM D 2007-75 and ASTM D 2579-78 procedures. The saturates and the aromatic fractions were analyzed by low resolution mass spectrometry by modifications to procedures in ASTM D 3239 and ASTM D 2786-71. The polars fraction, which contained mostly nitrogen heterocycles, was similarly analyzed via high resolution mass spectrometry.

RESULTS AND DISCUSSION

Effect of Hydrocracking:

The hydrocracking of the feedstock resulted in a 66.7% conversion of material boiling above 524°C (Table 1). The asphaltene content which is more or less a measure of the hydrogen deficiency of an oil was reduced to one third of its original value after hydrocracking and mainly remained in the 524°C+ fraction. The increase in the hydrogen to carbon ratio after hydrocracking was synonymous with the decrease in the asphaltene content. The viscosity and density of the hydrocracked materials decreased as expected. Of particular interest is the ratio of non-basic nitrogen to basic nitrogen in the hydrocracked sample. Some nitrogen compounds have been known to contribute to fuel instability, while others are inert. As shown in Table 1 hydrocracking reduced the total nitrogen in the feed, but the basic nitrogen increased.

Effect of Hydrotreating :

The hydrotreating was carried out on the naphtha-jet fuel fraction as well as on the diesel-gas oil fraction. For simplicity, these hydrotreated fractions are referred to as hydrotreated naphtha-jet and hydrotreated Gas Oil respectively. The hydrotreating step not only removed the heteroatoms (S, N, O), but also refined and stabilized the products. Sulfur was released in the form of H₂S, nitrogen in the form of NH₃, and oxygen in the form of H₂O. The following tests were performed to determine the effect of hydrotreating on the stability of different distillate fractions.

Stability Tests:

Total Insolubles: The oxidation stability results performed on naphtha-jet fraction are shown in Table 1. The data indicate that the total insolubles were much higher in the unhydrotreated material than in the hydrotreated samples. This data confirmed that hydrotreating stabilized the reactive hydrocarbons thereby rendering them less reactive than they otherwise would have been. The effects of hydrotreating on the long term storage stability of different fractions are shown in Table 2 and Table 3. In the unhydrotreated naphtha jet fraction, after 60 days of storage time, the total insolubles increased from 0.03 to 19.2 mg/100ml whereas in the hydrotreated sample, the total insolubles were at 0.25 mg/100 ml after storage for 60 days. In the unhydrotreated gas oil fraction, the total insolubles were 15.9 mg/100 ml after 60 days of storage, while for the hydrotreated sample, the total insolubles were only at 3.6 mg/100 ml after 60 days of storage.

Existent Gum: It is generally believed that the products of initial oxidation, probably peroxides, catalyze the oxidation of normally less reactive hydrocarbons to increase the rate of gum formation. Most of the oxidation products are said to be soluble in naphtha but decompose during evaporation to give gum that is largely composed of acidic material. Some of the studies show a correlation between gum content and total nitrogen content, while in other studies the gum content is said to increase with boiling range. The results in Tables 2 show that the existent gum in the naphtha-jet fraction decreased from 8.8 mg/100 ml before hydrotreating to zero after hydrotreating. After storage of the unhydrotreated fraction for 60 days, the existent gum was 142 mg/100 ml as opposed to a hydrotreated sample stored for the same 60 days which had 0.80 mg/100 ml. Undoubtedly, hydrotreating affects the existent gum content of naphtha-jet fractions.

Colour : The results of the colour test are shown in Table 1. Colour is one of the most distinguishing characteristics of untreated hydrocracked distillates. On distillation after hydrocracking, the naphtha-jet fraction is from clear to pale yellow. However, when exposed to

ordinary room conditions, this hydrocracked fraction will start to darken and also to deposit gum. Colour change is therefore indicative of the aging of the sample. The naphtha-jet fraction before hydrotreating had a colour number of 0.5 to 1.0 and after hydrotreating the colour number was reduced to zero. The gas oil fraction had a colour number of 3.5 to 4.5 before hydrotreating and after hydrotreating the colour number was reduced to 1.5 to 2.

Viscosity : The viscosity of the fractions (Table 2 and 3) is influenced more by storage time than by hydrotreating. Both the naphtha-jet and the gas oil fractions showed an increase in viscosity with storage time.

Aniline Point : There is an inverse relationship between aniline point and aromatic content. Aniline Point is usually increased slightly with the molecular weight and boiling point of a sample, and rapidly with the paraffinicity of oil samples. The higher aniline point value denotes a lower aromatic content and a higher paraffin content. Tables 2 and 3 show a higher aniline content after hydrotreating for both the naphtha-jet and the gas oil fractions. In Table 4, the analyses for paraffins and aromatics confirm the above conclusions. Overall, the monocycloparaffins are being converted to dicycloparaffins, leaving a decrease in the paraffinic content after aging. Both the mono- and di-aromatic constituents of the distillates increased at the expense of the paraffinic components, which suggests that saturated paraffinic components undergo some form of condensation with aromatic constituents.

SUMMARY:

The work presented here was undertaken to address the issue of the storage stability of middle distillates obtained from Western Canadian heavy oil/bitumen. Fuel stability is the general resistance of a fuel to change. Two types of stability were investigated. The first was storage stability, which reckons the ability of the fuel to stay in storage for a long period of time with little deterioration. The second was thermal stability which is the ability of the fuel to resist with little deterioration high temperature stress for a short period. The study results show that the deterioration of the fuel through storage manifested itself in colour change, development of soluble and insoluble gum, and changes in the physical and chemical properties of the fuel, like viscosity, density, nitrogen, sulfur, aromatics and asphaltene content. The results obtained also suggest that hydrocracked or thermally cracked materials should be hydrotreated/processed as quickly as possible. The detail hydrocarbon-type analyses of different fractions before and after hydrotreating showed that hydrotreating reduced refractory materials, including polar compounds, that cause storage instability.

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TABLE 1: COLOUR AND STORAGE STABILITY OF SAMPLES

	FSTK ⁽¹⁾	HC ⁽²⁾	IBP-249	249-524	After Hydrotreating	
					IBP-249	249-524
Asphaltene Content (wt%)	15.86	5.31	0.02	0.06	0.02	0.05
Viscosity @ 40 deg C (cP)	8.75E+05	22.4	0.69	24.1	0.88	11.4
Density @ 15.5 deg C (g/cc)	1.0266	0.9292	0.7934	0.9295	0.7822	0.889
API Gravity (API)	6.33	20.78	46.85	20.73	49.40	27.67
Sludge (wt%)	-	0.74	-	0	-	0
Bromine No. (mg Br/100 g)	-	17.3	-	10.7	-	1.2
Hydrocarbon Types by FIA						
Aromatics (Vol.%)	-	-	21.1	-	3.4	-
Saturates (Vol.%)	-	-	75.5	-	95.4	-
Olefin (Vol.%)	-	-	3.4	-	1.2	-
Aromatics by Mass Spec.	-	-	-	-	-	-
Colour						
IBP - 177 C	-	-	0-0.5		0	
177 - 249 C	-	-	0.5-1.0		[IBP 249]	
249 - 343 C	-	-	-	3-3.5		1.5-2.0
343 - 524 C	-	-	-	4.5-5		[249-524]
Aniline Point (deg C)	-	-	46.7	61.8	63.4	74.5
Elemental Analysis						
Total Nitrogen (wt%)	0.546	0.410	0.104	0.291	<1 ppm	146ppm
Basic Nitrogen (wt%)	0.117	0.129	0.088	0.125	<1 ppm	25ppm
Non-Basic Nitrogen (wt%)	0.429	0.281	0.016	0.166	<1 ppm	121ppm
C (wt%)	83.15	86.66	85.00	87.14	85.17	87.07
H (wt%)	10.36	12.33	13.03	11.08	13.84	12.50
S (wt%)	5.231	1.043	0.488	1.402	144 ppm	800ppm
H/C Ratio (Atomic)	1.49	1.70	1.83	1.52	1.94	1.71
Oxidation Stability						
Filterable Insolubles (mg/100ml)	-	-	3.23	-	0.11	-
Adherent Insolubles (mg/100ml)	-	-	6.00	-	0.03	-
Total Insolubles (mg/100ml)	-	-	9.23	-	0.14	-
Existent Gum (mg/100ml)	-	-	8.8	-	0	-
Simulated Distillation (wt%)						
IBP - 177 C	0	7.60	40.00	0	44.00	2.50
177 - 249 C	0	8.80	52.50	0.80	48.50	4.30
249 - 343 C	0.50	17.00	6.80	27.50	6.00	34.50
343 - 524 C	32.00	44.10	0.70	69.30	1.30	58.70
524 C+	67.50	22.50	0.00	2.40	0.20	0

(1) Feedstock

(2) Hydrocracked product

TABLE 2 - NAPHTHA-JET FUEL FRACTION - EFFECT OF HYDROTREATING ON STORAGE STABILITY

PROPERTIES	IBP - 249 °C Unhydrotreated		IBP - 249°C Hydrotreated	
	At Time 0	After 60 days storage	At Time 0	After 60 days storage
Aniline Point [°C]	46.7	47	63.4	64.2
Viscosity [CP @ 40°C]	0.69	1.22	0.88	1.03
Asphaltene Content [wt%]	0.02	0.20	0.02	0.14
Existent Gum [mg/100ml]	8.8	142	0	0.80
Storage Stability [mg/100ml]				
Filterable Insolubles	0.03	0.90	0	0.14
Adherent Insolubles	0	18.30	0	0.11
Total Insolubles	0.03	19.20	0	0.25

TABLE 3 - DIESEL - GAS OIL FRACTION - EFFECT OF HYDROTREATING ON STORAGE STABILITY

PROPERTIES	249 - 524°C Unhydrotreated		249 - 524°C Hydrotreated	
	At Time 0	After 60 days storage	At Time 0	After 60 days storage
Aniline Point [°C]	61.8	61.7	74.5	74.6
Viscosity [CP @ 40°C]	24.1	28.3	11.4	14.5
Asphaltene Content [wt%]	0.06	0.25	0.05	0.23
Storage Stability [mg/100ml]				
Filterable Insolubles	0.20	15.33	0.11	3.31
Adherent Insolubles	0	0.63	0	0.29
Total Insolubles	0.20	15.96	0.11	3.60

TABLE 4 - MASS SPECTROMETRY ANALYSIS RESULTS OF THE HYDROCRACKED SAMPLES

HYDROCARBON	NAP-JET Before Storage (wt%)	NAP-JET After Storage (wt%)	GAS-OIL Before Storage (wt%)	GAS-OIL After Storage (wt%)	HT* GAS-OIL Before Storage (wt%)	HT* GAS-OIL After Storage (wt%)
Paraffins	36.40	32.52	17.15	17.17	22.23	19.02
Cycloparaffins	39.93	39.97	29.10	29.18	46.36	47.45
Monoaromatics	22.46	24.78	29.22	27.23	25.72	25.80
Diaromatics	0.73	1.14	14.92	15.14	3.74	4.82
Triaromatics	0	0	2.29	2.52	0.36	0.55
Tetraaromatics	0	0	0	0	0	0
Pentaaromatics	0	0	0.43	0.32	0.24	0.25
Unidentified	0	0	0.03	0.01	0	0
Aromatic Sulfur	0.03	0.43	2.97	3.35	0.97	1.56
Polar Compounds	0.45	1.16	3.89	5.08	0.38	0.55

* Hydrotreated