INFLUENCE OF THE CATALYST ACIDITY ON THE HYDROCRACKING OF MINAS VACUUM DISTILLATE INTO MIDDLE DISTILLATE *

by

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ABSTRACT

Hydrocracking process is probably the most versatile of modern petroleum process. This versatility has been achieved by the development of specific families of catalysts, of processing schemes designed to allow these catalysts to function efficiently and optimal refining relationships between hydrocracking and other refinery processes. A study was conducted to determine the hydrocracking of Minas vacuum distillate into middle distillate with the operating conditions : temperature : from 390° to 410°C, pressure : 100 kg/cm^2 and H_2/HC ratio = 1000 lt/lt. A catatest unit operated in a continuous system was used in these experiments. The experimental data show that the conversion of the feedstock, the activation energy and the product characteristics of Minas vacuum distillate hydrocracking depended on the operating temperature and the acidity of the catalyst. And low acidity of Ni-Mo/Al_2O_3-SiO_2 catalyst produce a high selectivity of middle distillate.

I. INTRODUCTION

Hydrocracking is probably the most versatile of modern petroleum processes. This versatility has been achieved by the development of specific families of catalysts, of processing schemes designed to allow these catalysts to function efficiently, and optimal refining relationships between hydrocracking and other refining processes. (1)

Hydrocracking is distinguished by its objective of producing products of significantly lower-molecular weight than that of the feed, and involves correspondingly large hydrogen consumption.

Hydrocracking catalysts are bi-functional, containing both hydrogenating and cracking sites. The best choice of catalysts for a specific objective requires a particular balance between these two functions.

The kinetic of hydrocracking process with respect to the variety of feedstock characteristics gives rise to an interesting case to study, i.e. the feasibility of obtaining lube base stock and fuel oil from Minas Waxy Residue (MWR), because the high wax content of the latter represents the point of difficulty when the conventional process is to be used.

A case study for MWR to the production of 100,000 MT/y lubricant base stock and 180,000 MT/y middle distillate has been made. (2)

The economic calculation, based on literature and other realible data, show the advantage of hydrocracking compared to conventional processing. And the influence of the acidity of bi-functional catalyst on the hydroconversion of wax into middle distillate and lube base stock was also carried out. (3)

In order to obtain more data on the hydrocracking catalysts, an experiment has been carried out to study the hydrocracking of Minas vacuum distillate into middle distillate with operating conditions : temperature : from 390° to 410°C; pressure : 100 kg/cm^2

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and H_2/HC ratio : 1000 lt/lt by using two different acidities of Ni-Mo/Al_2O_3-SiO_2 catalyst. A catatest unit operated in a continuous system was used in these experiments.

Research on the hydrocracking of vacuum distillate is practically free of asphaltene, its negative effect upon the catalyst performance does not arise in this case.

II. EXPERIMENTAL

The characteristics of feedstocks is shown in Table 1. The dimethyl-disulfide contained less than 4 per cent of impurity was blended with the Minas vacuum distillate, as much as 2 wt % on feedstock. The hydrogen used contained less than 0.1 per cent volume of impurity (mostly nitrogen). Two types of Ni-Mo/ Al_2O_3-SiO_2 hydrocracking catalysts with two different acidities, were used in these experiments. The hydrodesulfurization catalyst (for obtaining the H_2S and CH_4 from dimethyl-disulfide) was Co-Mo/Al_2O_3 catalyst.

Table 1
Characteristic of feedstock used

Characteristic		
Boiling range	°C	350° - 550°
Yield on crude oil	wt %	34.7
Density at 70°C		0.824
Viscosity at 98,9°C	cSt	4.35
Wax Content	wt %	46
Asphaltene Content	wt %	∠0.05
Conradson Carbon Residue (CCR)	wt %	∠0.03

The hydrocracking experiments were carried out in a micro-catalyst activity test unit (Catatest), without gas recycle, shown diagrammatically in Fig.1. The volume and inside diameter of the reactor are 200 cc and 19 mm respectivelly. The reactor temperature, H_2-injection and liquid product in the high pressure separator were regulated automatically. The liquid products were fractionated to get the following cuts : IBP - 80°C, 80°C - 150°C, 150°C - 250°C, 250°C - 380°C, whereby distillation apparatus, with the 30 theoretically plate, operating by 4/1 reflux ratio, was used.

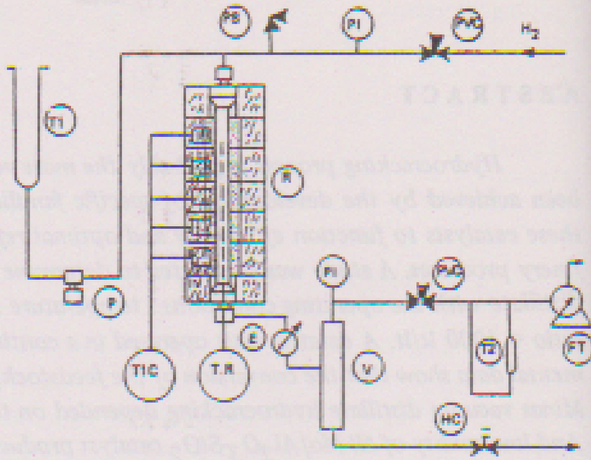

Figure 1
Catatest Unit

E	– Condenser	R	– Contact tube
FT	– Gas meter	T1	– Batch
P	– Pump	T2	– Sample
PVC	– Pressure regulator	T1C	– Temperature regulator
P1	– Pressure gauge	TR	– Temperature recorder
PS	– Pressure safety valve	V	– Separator

The 380°C bottom product was dewaxed by solvent dewaxing. The method of analysis are shown on the Table 2.

Table 2
Types and methods of product analysis

Type of Products		Methods of analysis
Fractionated liquid products •		
. IBP - 80°C		
. 80 - 150°C		
Paraffin content	(vol %)	ASTM D.1019
Naphthene content	(vol %)	ASTM D.86 and
Aromatic content	(vol %)	ASTM D.611
. 150° - 250°C		
Smoke point	(mm)	ASTM D.1319
. 250° - 380°C		
Density at 40°C		IP.190

III. RESULTS AND DISCUSSION

Experimental data of hydrocracking of Minas vacuum distillate at the operating conditions : temperature : from 390° to 410°C, pressure : 100 kg/cm^2 and H_2/HC ratio : 1000 lt/lt with two different acidity of Ni-Mo/Al_2O_3-SiO_2 catalyst are shown on the Table 3 and Fig. 2, 3, 4, 5 and 6. These experimental data will be discussed in two following topics :

- Distribution of hydrocracked products
- Characteristics of hydrocracked products.

A. *Distribution of hydrocracked products*

By increasing the operating temperature from 390° to 410°C the conversion of feedstock and the yield of by-products (IBP-150°C) increase by using two different catalyst acidities, i.e;

42.76 and 22.48 wt % increase in conversion of feedstock and

16.00 and 58.7 wt % increase in yield of by products

for the high and the low catalyst acidity respectively.

Low selectivity of the middle distillate products (kerosene and gas-oil) was observed by increasing of the operating temperature from 390° to 410°C; i.e. 25.3 and 7.5 wt % decrease in selectivity of the middle distillate products by using the high and the low catalyst acidity respectively.

Arrhenius equation of the constant rate can be written as follows :

$$k = A\, e^{-E/RT}$$

$$\text{or } \log k = -\left(\frac{E}{2.303\, R}\right)\left(\frac{1}{T}\right) + 2.303 \log A$$

If the feedstock conversion (X) is proportional with the rate constante (k), the activation energy of hydrocracking of Minas vacuum distillate (E) can be obtained by determination the value of the slope of straight line -log X = f(1/T°K). Based on the

Table 3

Characteristic of hydrocracked products

Type of products		Operating temperature °C					
		390°		400°		410°	
		High Acidity	Low Acidity	High Acidity	Low Acidity	High Acidity	Low Acidity
Feedstock conversion	wt %	40.43	40.53	54.38	50.93	83.19	63.01
Fractionated liquid products							
IBP - 80°C (Light Naphtha)							
Yield	wt %	1.70	-	5.78	0.63	6.50	0.51
80° - 150°C (Heavy Naphtha)							
Yield	wt %	43.53	2.30	8.45	4.53	15.73	7.66
Paraffin content	vol %	48.27	34.84	54.75	48.27	55.24	54.75
Naphthene content	vol %	40.50	51.72	24.45	40.50	26.14	34.45
Aromatic content	vol %	11.23	13.34	11.80	11.23	8.62	11.80
150° - 250°C (Kerosene)							
Yield	wt %	13.23	7.40	15.46	13.51	24.33	20.33
Smoke point	mm	22.5	18.0	24.0	19.0	28.1	20.0
250° - 380°C (Gas-oil)							
Yield	wt %	20.11	30.81	21.59	31.90	23.54	34.34
Diesel Index		73.0	68.7	79.2	74.8	83.2	78.2

experimental data on the Table 3 and Figure 2, the apparent activation energies were observed E = 32.114 and 21.641 kcal/mole for high and low acidity of catalysts respectively.

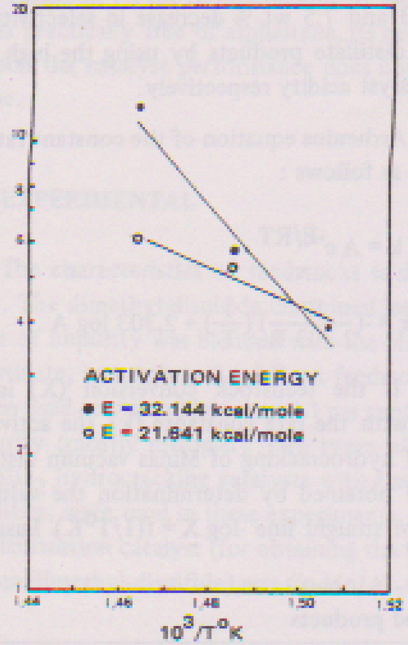

Figure 2

A plot of log X against $1/T^oK$

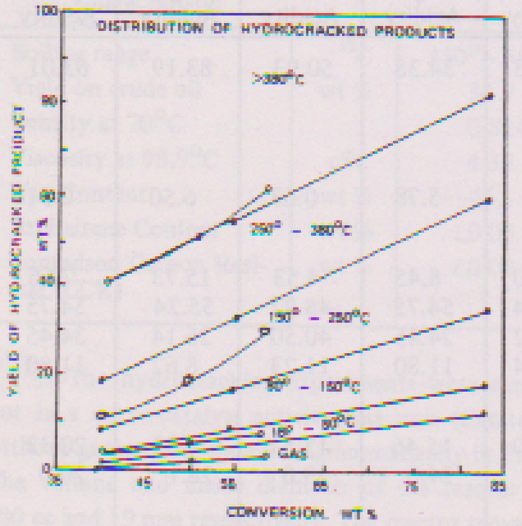

Figure 3

A plot of yield of hydrocracked products against conversion

High conversion of feedstock and high activation energy, obtained by high acidity of Ni-Mo/Al_2O_3 -SiO_2 catalyst, suggest, that formation of intermediate

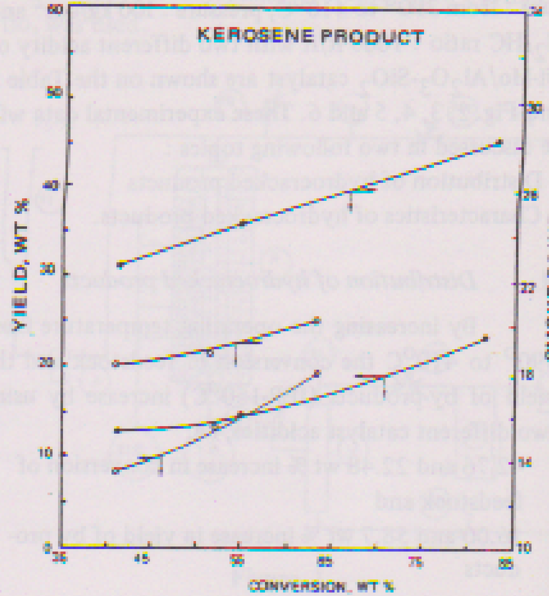

Figure 4

A plot of yield and smoke point of kerosene product against conversion

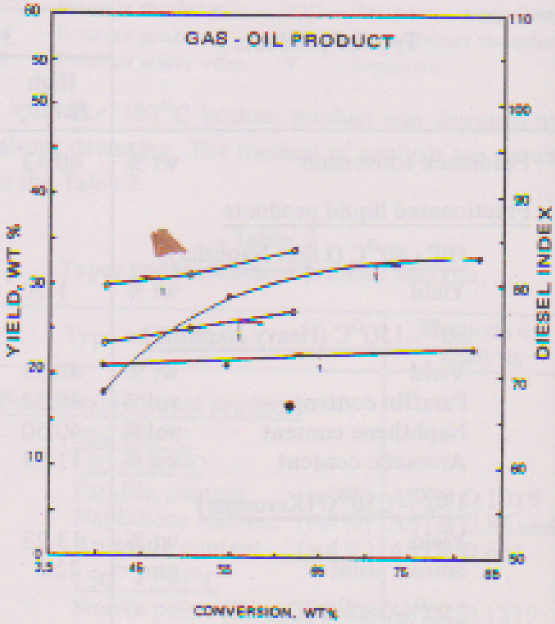

Figure 5

A plot of yield and diesel index of gas-oil product against conversion

carbonium ion in the hydrocracking of Minas vacuum distillate increase with the acidity of catalyst (4). As the consecutive reaction is a typical of hydrocracking process, thus the yield of the intermediate products will decrease with the feedstock conversion (5). So hydrocracking of Minas vacuum distillate with low acidity of $Ni\text{-}Mo/Al_2O_3\text{-}SiO_2$ catalyst will produce a high selectivity of middle distillate products.

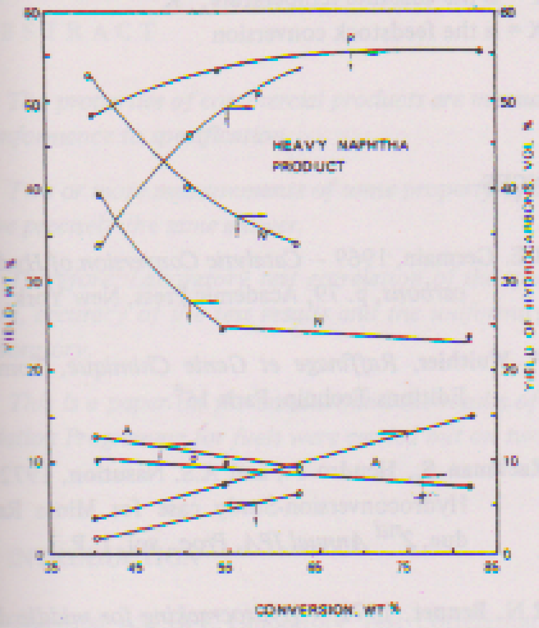

Figure 6

A plot of yield and yield of hydrocarbons product against conversion

Note : P = Paraffin, N = Naphthene, A = Aromatic

2. *Characteristics of hydrocracked products*

The quality of the middle distillate products (kerosene and gas-oil) increases by increasing the operating temperature from 390° to 410°C, i.e.; 5.6 and 4.0 points increase in smoke point of kerosene, and 10.2 and 10.5 points increase in diesel index of gas oil by using the high and the low catalyst acidity respectively.

High paraffin content and low naphthene plus aromatic content was observed by increasing the operating temperature from 390° to 410°C; i.e.; 6.97 and 19.91 vol % increase in paraffin content; 16.97 and 18.71 vol % decrease in naphthene plus aromatic content; for the high acidity and the acidity of the $Ni\text{-}Mo/Al_2O_3\text{-}SiO_2$ catalysts respectively.

High quality of kerosene and gas-oil products, produced by high acidity of $Ni\text{-}Mo/Al_2O_3\text{-}SiO_2$ catalyst, suggest that the aromatic saturation of hydrocracked products, obtained by Ni-Mo-metal site of this hydrocracking catalyst increases with the feedstock conversion. (6)

High paraffin content and low naphthene and aromatic content in the heavy naphtha products, by using the high acidity of $Ni\text{-}Mo/Al_2O_3\text{-}SiO_2$ catalyst, suggest that the decyclization of naphthene and aromatic rings into paraffin, increase with high acid strength of this catalyst. (7)

IV. CONCLUSIONS

The quality and the yield of middle distillate product depended on the operating temperature and the acidity of the catalyst i.e. high quality and low selectivity of middle distillate at high operating temperature and high catalyst acidity. And low acidity of $Ni\text{-}Mo/Al_2O_3\text{-}SiO_2$ catalyst can produce a high selectivity of middle distillate.

The apparent activation energies of hydrocracking of Minas vacuum distillate are E = 32.114 and 21.641 kcal/mole for high acidity and low acidity catalysts respectively.

At the operating conditions : temperature : 400°C, pressure : 100 kg/cm² and H_2/HC ratio : 1000 lt/lt, the feedstock conversion, yield and smoke point of kerosene, and yield and diesel index of gas-oil are as follows :

High acidity of catalyst : 54.38 wt %; 15.46 wt %, 24.0 mm, 21.59 wt %, and 79.2

Low acidity of catalyst : 50.38 wt %; 13.51 wt %, 19.0 mm; 31.90 wt %, and 74.8

Optimal composition of hydrocracking catalyst of Minas vacuum distillate into middle distillate, can be certainly be achieved by variation of other parameter, such as the variation of the type and the composition of the active metal site of hydrocracking catalysts.

Notation

A = is the pre-exponential factor
E = is the apparent activation energy kcal/mole
k = is the rate constant
R = is the gaseous constant
T = is the absolute temperature, ^{o}K
X = is the feedstock conversion

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