• INFLUENCE OF THE PARTICLE SIZE OF CATALYST ON THE HYDROCRACKING OF VACUUM DISTILLATE INTO MIDDLE DISTILLATE AND LUBRICANT BASE STOCK

by

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ABSTRACT

In order to obtain more data on the hydrocracking catalysts, an experiment has been carried out to study the hydrocracking of vacuum distillate into middle distillate with operating conditions : temperature : from 390^0 to 420^{0}C; LHSV : from 0.45 to 0.90; pressure : 125 kg/cm^2 and H_2/HC ratio : 1000 lt/lt by using two Ni-Mo/Al_2O_3-SiO_2 catalysts with various particle sizes using a Catatest unit operated in a continuous system.

Gas product sample was analysed by using a gas-liquid chromatography. The liquid product were fractionated and bottom products was dewaxed by solvent dewaxing.

Based on the experimental data show that :

- *By increasing the operating temperature, LHSV, and decreasing of the particle size of the Ni-Mo/Al_2O_3-SiO_2 catalyst, the conversion rate, the quality of the middle distillate, and the lubricant base stocks products increase, but the selectivity of these products will decrease.*
- *At operating conditions T = 400^{0}C, P = 125 kg/cm^2; LHSV = 0.45; and H_2/HC ratio : 1000 lt/lt, the conversion rate, smoke point of kerosene, diesel index of gas oil, viscosity index of lubricant base stock decrease from : 54.08 to 50.08 % by weight; from 22 to 16 mm, from 62.0 to 57.7 and from 133 to 118 for the low particle size and high particle size of the Ni-Mo/Al_2O_3-SiO_2 catalyst respectively.*
- *The apparent activation energy of vacuum distillate is obtained 28.717 and 23.720 kcal/mol for the low particle size and the high particle size of the Ni-Mo/Al_2O_3-SiO_2 catalyst respectively.*

I. INTRODUCTION

Hydrocracking of heavy petroleum converts the undersirable hydrocarbons and other compounds, contained in the original feedstock into hydrocarbon distillates possesing properties which make them suitable for blending into lubricant base stock or fuels. (Beuther, H., et.al., 1961; Watkins, C.H., and Webb, T.A., 1968).

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. (Myers, C.G., et.at., 1962).

Mechanism of hydrocracking process is the formation of the carbonium ion as an intermediate molecule, which then gives the final products, characterized by a majority of branched paraffin isomers

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and the virtual absense of small fragments (methane and ethane). (Coonradt, H.L., and Garwood, W.E., 1961).

The kinetic of hydrocracking process greatly depends on the operating conditions, such as hydrocarbon composition of feedstock, type of catalyst, pressure, temperature, hydrogen-hydrocarbon ratio. (Voorhiers, A., et.al., 1962; Rapp, L.M., and Van Driesen, R.P., 1965).

The versatility of hydrocracking process with respect to the variety of feedstock characteristics gives rise to an interesting case to study : i.e. Hydrocracking of vacuum distillate of Minas waxy residue; Hydroisomerization of paraffin wax, and Influence of the catalyst acidity or the hydrocracking of Minas vacuum distillate. (Nasution, A.S., 1975, 1980, 1984).

In order to gain more data on the hydrocracking process, an experiment has been carried out to study the influence of the particle size of catalyst on the hydrocracking of vacuum distillate into middle distillate and lubricant base stock with the operating conditions : Temperature from 390° to 420°C, Pressure : 125 kg/cm^2; H_2/HC ratio : 1000 lt/lt and LHSV : from 0.45 to 0.90 using Ni-Mo/Al_2O_3-SiO_2 catalysts. A catalytic activity test unit operated in a continuous system was used in this experiment.

II. EXPERIMENTAL

A. Reactants

Vacuum distillate with boiling range 350° – 550°C has been used as feedstock at this experiment. The asphaltene content of this feedstock is 0.05% by weight.

The electrolytic hydrogen has been purified from oxygene compound by passing this hydrogen into Deoxo catalyst and then followed by drying in the molecular sieve. The purified hydrogen has a purity 99.5% by volume.

Ni-Mo/Al_2O_3-SiO_2 catalyst is the type commonly employed in hydrocracking process of heavy distillate.

B. Procedure

1. Apparatus

The hydrocracking of vacuum distillate was carried out in a catalytic activity test unit which can be operated in continuous system (Fig. 1). The volume and inside diameter of reactor are 220 cc and 19 mm respectively. The reactor temperature is regulated automatically.

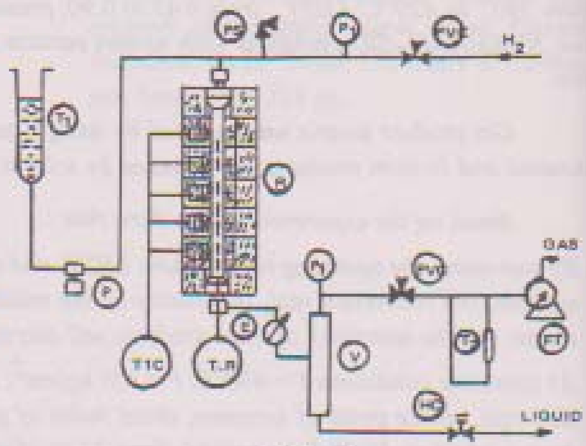

Figure 1
Catatest Unit

E – Condenser
FT – Gas meter
P – Pump
PVC – Pressure regulator
P_1 – Pressure gauge
PS – Pressure safety valve
R – Constant tube
T_1 – Batch
T_2 – Sample
T1C – Temperature regulator
TR – Temperature recorder
V – Separator

2. Procedure

80 cc of the catalyst was charged to the reactor and the catatest unit brought to the operating pressure with hydrogen. The reactor was then heated to about 250°C and kept at this temperature for two hours, while hydrogen was recirculated at desired rate. The feed pump was then started and the operating conditions carefully adjusted in this pretest period. After the density of the product become constant, the pre-test period liquid product was removed; then a test run of ten hours was carried out.

Gas and liquid product samples were taken from gas an liquid samples respectively and these products were then analysed.

C. Method of Analysis

Liquid products were fractionated to get the following cuts : IBP-80°–150°C, 250°–380°C, where by distillation apparatus; with the 30 theoretically plate, operated by 4/1 reflux ratio, was used.

The > 380°C bottom product was dissolved in methyl-ethyl ketone, the weight ratio being 1 : 5; and the solution slowly stirred and cooled at -20°C, allowing the wax to crystallize. The solidified mixture was filtered at -20°C. By suction, using a filtered which was kept at -20°C. The oil yield; defined as the weight percentage lubricant base stock in the reaction product, can be calculated. Hydrocarbon composition, smoke point, diesel index, and viscosity index of cuts : 80°–150°, 150°–250°, 250°–380°C and lubricant base stock respectively, are determined.

III. RESULTS AND DISCUSSIONS

Experimental data of hydrocracking of distillate vacuum are shown in Fig. 2, 3, 4, 5, 6, 7, 8 and 9.

These experimental data will be discussed in two following topics :

. Distribution of hydrocracked products

. Characteristics of hydrocracked products.

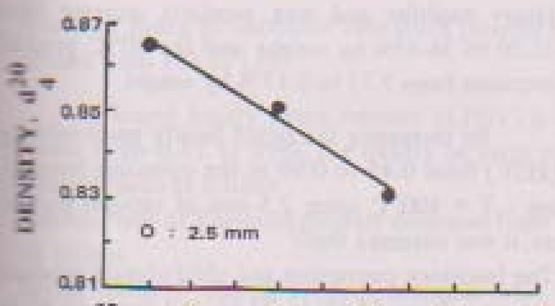

Figure 2

Influence of feedstock conversion on the density of liquid product using 2.5 mm of catalyst particle size

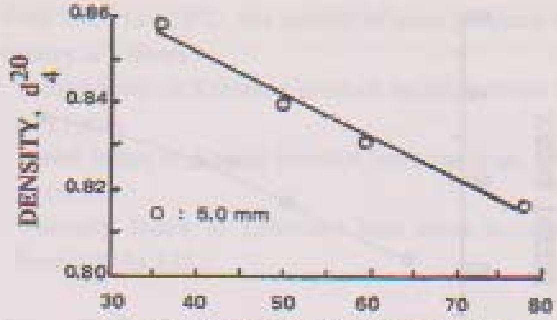

Figure 3

Influence of feedstock conversion on the density of liquid product using 5.0 mm of catalyst particle size

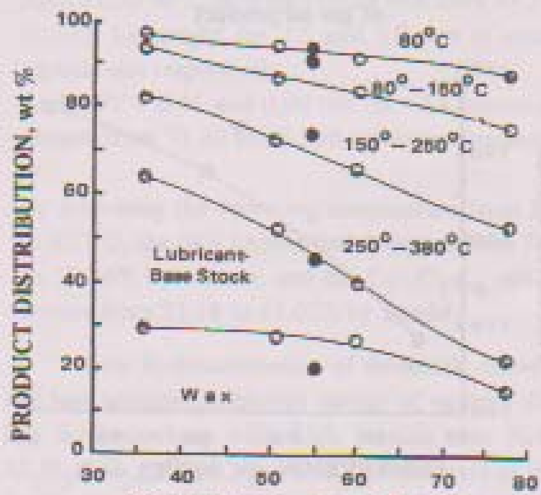

Figure 4

Influence of feedstock conversion on the distribution of hydrocracked products

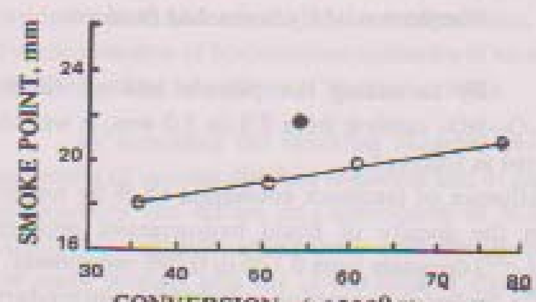

Figure 5

Influence of feedstock conversion on the smoke point of kerosene product

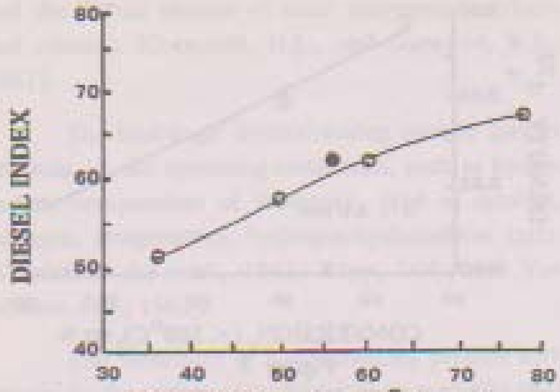

Figure 6

Influence of feedstock conversion on the diesel index of gas oil product

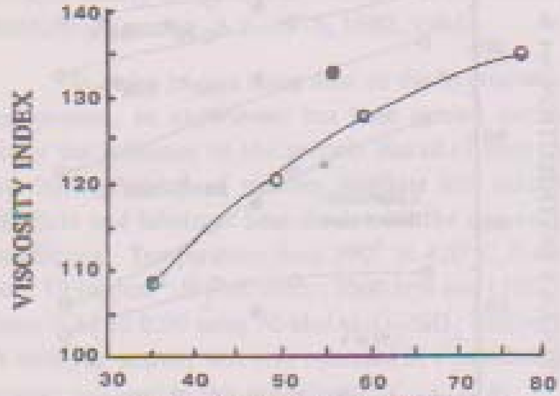

Figure 7

Influence of feedstock conversion on the viscosity index of lubricant base stock product

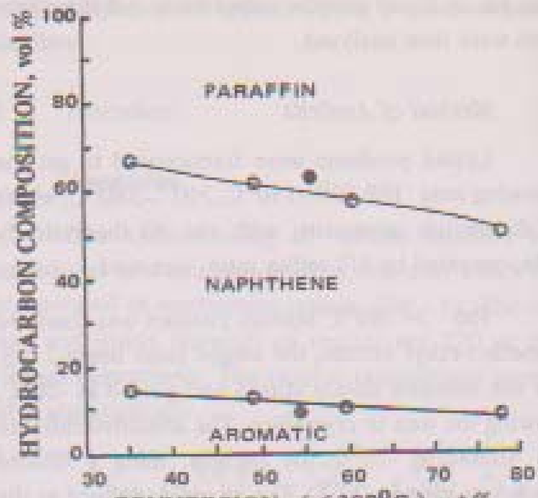

Figure 8

Influence of feedstock conversion on the hydrocarbon composition of heavy naphtha product

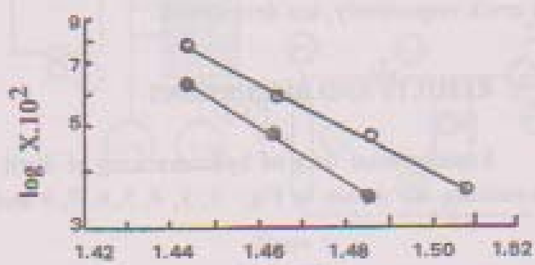

Figure 9

Arrhemius Plot of hydrocracking of vacuum distillate

A. Distribution of Hydrocracked Products

By increasing the particle size of Ni-Mo/ Al_2O_3-SiO_2 catalyst from 2.5 to 5.0 mm, it was observed as follows :

. Influence of feedstock conversion (X % by weight) on the density of liquid hydrocracked products (d_4^{20}) decreases from 0.120 to 0.098 respectively.

. The feedstock conversion and yield of main products (kerosene, gas oil and lubricating base stock) decrease from 54.19 to 50.08 and from 69.96 to 58.90 % by weight respectively.

. Heavy naphtha and wax products increase from 22.39 to 36.45% by weight and the 80°C product increases from 7.75 to 5.17 % by weight.

By increasing the liquid hourly space velocity (LHSV) from 0.45 to 0.90 at the operating temperature : T = 400°C using 2.5 mm of catalyst particle size, it was obtained that :

. The feedstock conversion and yield of main products decrease from 54.19 to 33.66 and from 69.86 to 49.73 % by weight respectively.

. Heavy naphtha and wax products increase from 22.39 to 46.48 % by weight, but the 80°C product decrease from 7.75 to 4.69 % by weight.

By increasing the operating temperature from 390° to 420°C, it was found as follows :

. The feedstock conversion and the middle distillate product (kerosene and gas oil) increase from 35.35 to 78.05 from 27.98 to 54.12 % by weight respectively. And lubricant base stock product decrease from 35.74 to 5.47 % by weight.
. Heavy naphtha and the 80°C products increase from 3.07 to 12.75 and from 4.78 to 11.25 % by weight respectively. And wax product decreases from 28.88 to 16.41 % by weight.
. If the feedstock conversion (X) is proportional with the rate constant (k) of vacuum distillate hydrocracking, the apparent activation energy (E) of this vacuum distillate hydrocracking can be calculated by using the Arrhenius equation. The apparent activation energy is obtained 28.717 and 23.720 kcal/mole for low particle size and high particle size of the $Ni\text{-}Mo/Al_2O_3\text{-}SiO_2$ catalysts respectively.

B. *Characteristics of Hydrocracked Products*

1. Main Products

By increasing of particle size of the catalyst from 2.5 to 5.0 mm, the quality of main products decrease as follows :

. Smoke Point of Kerosene product decreases from 22 to 19 mm.
. Diesel Index of Gas-oil product decreases from 62.0 to 57.7
. Viscosity Index of Lubricant base stock product decreases from 133 to 118.

If liquid hourly space velocity (LHSV) is increased from 0.45 to 0.90, the quality of main products decreases as follows :

. Smoke Point of Kerosene product decreases from 22 to 18 mm.
. Diesel Index of Gas-oil product decreases from 62 to 42.5
. Viscosity Index of Lubricant base stock product decreases from 133 to 106.

By increasing of the operating temperature from 390° to 420°C, the quality of main products increases as follows :

. Smoke Point of Kerosene product increases from 18 to 21 mm.
. Diesel Index of Gas-oil product increases from 50.5 to 68.1
. Viscosity Index of Lubricant base stock increases from 109 to 135.

2. By Product

Hydrocarbon compositions of heavy naphtha products are obtained as follows :

. (N + 2A) content and the $C_3+/C_1\text{-}C_6$ ratio increases from 71.30 to 72.80% by volume and from 33.27 to 62.58% by weight for 2.5 and 5.0 mm of catalyst particle size respectively.
. At LHSV = 0.45 and 0.90 the (N + 2A) content increases from 71.30 to 83.30% by volume respectively.
. By increasing the operating temperature from 390° to 420°C, the (N + 2A) content decreases from 78.99 to 59.96% by volume, and the $C_3+/C_1\text{-}C_6$ ratio increases from 22.18 to 63.02% by weight.

Low hydroconversion of feedstock molecules and low apparent activation energy of vacuum distillate hydrocracking with high particle size $Ni\text{-}Mo/Al_2O_3\text{-}SiO_2$ catalyst show that diffusion rate of these feedstock molecules appears as a rate control or determinated rate of this hydrocracking reaction. (Thomas, J.M., and Thomas, W.J., 1967).

At high liquid space velocity (LHSV) or short residence time of feedstock in the catalyst zone, the hydroconversion of hydrocarbon molecules of vacuum distillate will be low. (Scott, J.W., et.al., 1960).

By increasing the operating temperature, the molecules of vacuum distillate feedstock and of cracked products can diffure into micropores of $Ni\text{-}Mo/Al_2O_3\text{-}SiO_2$ catalyst, where these molecules encounter many strongly acid site of this catalyst. (Sullivan, R.F., et.al., 1961).

Thus a high severity of vacuum distillate hydrocracking is low particle size of the catalyst, low

liquid hourly space velocity and high operating temperature. At this operating condition, hydroconversions of molecules of distillate vacuum will be proceeded as follows :

. Hydrogenation of high aromatic into naphthene rings and followed by hydrodecyclization of these naphthene rings into alkyl appendages or side chains on other less densed centred molecular structures. In some cases this gives high viscosity-index of lubricant base stock, with a downward hook in their viscosity-temperature curve at low temperature. (Billon, A., et.al., 1969).

. Hydroisomerization and hydrodestruction of hydrocarbons of vacuum distillate feedstock with formation of high quality of lighter fuel oil fraction such as kerosene and gas oil. But (N + 2A) content of heavy naphtha decreases. (Breimen, F., 1957).

IV. CONCLUSIONS

By increasing the operating temperature and decreasing the particle size of Ni-Mo/Al_2O_3-SiO_2 catalyst, the conversion rate of vacuum distillate, the quality of the middle distillate, and the lubricant base stock products increase, but the selectivity of these main products will decreases.

At the operating conditions : Temperature : 400°C, Pressure : 125 kg/cm^2, H_2/HC ratio : 1000 lt/lt and liquid hourly space velocity : 0.45 the conversion rate of vacuum distillate with low particle size and high particle size of Ni-Mo/Al_2O_3-SiO_2 catalyst, is obtained as follows :

. Conversion rate	: From 54.08 to 50.08% by weight.
. Yield of main products	: From 69.86 to 58.90% by weight.
. Smoke Point of kerosene	: From 22 to 19 mm.
. Diesel Index of gas oil	: From 62.0 to 57.7
. Viscosity Index of Lubricant base stock	: From 133 to 118.
. (N + 2A) content of heavy naphtha	: From 71.3 to 72.8% by volume.

The apparent activation energy of vacuum distillate hydrocracking is found : 28.717 and 23.720 kcal/mole of the Ni-Mo/Al_2O_3-SiO_2 for low particle size and high particle size of catalysts respectively.

Based on these experimental data, it can be concluded that the particle size of the Ni-Mo/Al_2O_3-SiO_2 catalysts, the liquid hourly space velocity and the operating temperature are, an important variable on the performance of hydrocracked products.

Optimal operating conditions can certainly by achieved by variation of other parameters, such as pressures, H_2/HC ratios and type of the catalyst.

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