SELECTIVE HYDROCRACKING OF HEAVY DISTILLATE TO HIGH VISCOSITY INDEX OF LUBE BASE STOCK USING BI-FUNCTIONAL CATALYSTS*)

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ABSTRACT

Selective hydrocracking of heavy distillate to high viscosity index of lube base stock has been carried out at the operating conditions: temperatures: 380° –410° C, pressure: 100 kg/cm², H_2/HC = 1000 lt/lt with bifunctional catalysts having various acidity using a Catatest unit operated with a continuous system.

I. INTRODUCTION

Hydroprocessing is the catalytic reaction of hydrogen with petroleum or other hydrocarbon materials. It may be carried out for a variety of objectives, including: saturation of olefins or aromatics, molecular rearangement, or removal of impurity(1).

Selective hydrocracking is one of this hydroprocessing to convert higher-boiling distillate to lube base stock using a bi-functional catalyst containing both acid site and metalsite. Those two active site of bi-functional catalyst should promote the correct combination of hydrogenation, isomerization and limited hydrocracking function, resulting the maximum yield of product in the lube oil range(2). The kinetic of this selective hydrocracking greatly depends on the operating conditions: such as feedstock composition, type of catalyst, temperature, pressure, hydrogen to hydrocarbon ratio and space velocity(6).

The verstability of the hydroconversion process with respect to the variety of feedstock and case to study: i.e. the feasibility of obtaining lube base stock from heavy distillate.

In order to gain more information, an experiment has been carried out to study the selective hydrocracking of vacuum distillate (paraffinic and non-paraffinic) and wax using bi-functional catalysts with various acidity at operating conditions: temperature: from 380° to 410°C, pressure: 100 kg/cm² and hydrogene to hydrocarbon ratio: 1000 lt/lt. A Catatest unit operated in a continuous system was used in this experiment.

Gas and liquid product samples were taken from gas liquid samplers respectively. Liquid product was fractionated to get the following cuts: IBP-380°C and > 380°C with the 30 theoretically plate, operating by 4/1 reflux ratio, was used. The > 380°C bottom product was dewaxed by solvent dewaxing, using methyl-iso-butyl ketone as a solvent to obtain the lube base stock and wax.

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II. EXPERIMENTAL

Three types of feedstocks i.e. non-paraffinic vacuum distillate (NPV), paraffinic vacuum distillate (PV) and wax, were used in this experiment. Commercially pure hydrogen was used in all experiment. Small amount of oxygen were converted to water over a Deoxo catalyst and water was removed by passage over a silica drier. Bi-functional hydroconversion catalysts with various acidity has used in this experiment. Dimethyl disulfide was cracked by the hydro-desulfurization catalyst ($Co\text{-}Mo/Al_2O_3$) into H_2S and CH_4 in the catalytic zone of the reactor which is nearly the same level as that in the recycle gas, used in the actual refinery.

The experimental was carried out in a Catatest Unit which can be operated in a continuous system (Fig. 1). The reactor assembly consisted of a microreactor placed in an electric furnace and joined to an inlet and outlet fittings, temperature control panel (not shown), gauses for measuring gas flow and pressures, continuous high pressure oil feeding pump. The microreactor was constructed from stainless steel tubing, 220 cc volume, 19 mm inside diameter and 7 mm outside diameter couple well tubing.

Feedstock and hydrogen were fed from bottom part of the reactor. The products were moved from the cooler to the high pressure receiver, where they were separated into gas and liquid products. Gas was released after its volume was measured by a wet gas meter. Gas and liquid products samples taken from gas and liquid samplers respectively. Liquid product was fractionated to get the following cuts: IBP-380°C, and > 380°C, with the 30 theoretically plate operating by 4/1 reflux ratio, was used The > 380°C bottom product was dewaxed by solvent dewaxing at temperature −20°C, using methyl-iso butyl ketone as a solvent, to obtain the lubricant base stock and wax. Viscosity index of lube base stock were analyzed by ASTM-metode D.445.

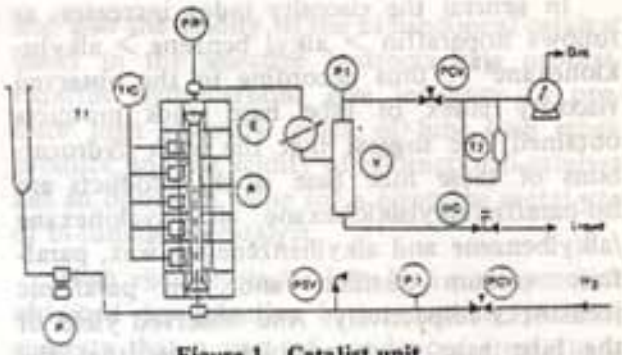

Figure 1. Catalist unit.

E – Condenser
FT – Gas meter
HC – Manual valve
F – Adjustable regulator
PCV – Pressure regulator
PI – Pressure gauge
PSV – Pressure safety valve
R – Contact tube
T1 – Bath
T2 – Sample
TIC – Temperature regulator
TR – Temperature recorder
V – Separator

III. RESULTS AND DISCUSSION

A. Influence of Feedstocks Composition

At the operating conditions: temperature: from 380° to 410°C, total pressure: 1000 kg/cm², and H_2/HC = 1000 lt/lt space velocity = 0.88, the selective hydrocracking of non-paraffinic vacuum distillate, paraffinic vacuum distilate and wax have been carried out. And the obtained products are shown on the Figs. 2, 3 and 4.

Yield and viscosity index of lube base stock products increase with paraffinic content of the feedstocks as follows was > paraffinic vacuum distillate > non paraffinic vacuum distillate. And the ± 50% by weight of feedstock conversion, yield and viscosity index of lube base stocks products are obtained, as follows.

	Vacuum distillate		Wax
	Non parafinic	Parafinic	
Yield, wt % on feedstock	20.67	24.57	27.21
Viscosity index	116	139	158

In general the viscosity index increases: as follows isoparaffin > alkyl benzene > alkylsiklohexane[4], thus according to the observed viscosity index of lube base stock prouucts obtained, the suggest that the main hydrocarbons of these lube base stocks products are iso-paraffin/alkylsiklohexane, alkyl-cyclohexane /alkylbenzene and alkylhenzene for wax, paraffinic vacuum distillate and non paraffinic feedstocks respectively. And observed yield of the lube base stock products show that the side reactions: i.e. hydrrodealkylation, hydrodealkylation/hydrocracking and hydrocracking are dominant for non-paraffinic vacuum distillate, paraffinic vacuum distilat and wax respectively. Thus the reactions of the selective hydrocarcking of these tree feedstocks, it suggests as follows.

Type of reaction	Vacuum distillate		Wax
	Non-paraffinic	Paraffinic	
Hydrogenation/ Hydrodecyclization	medium to high	medium	low
Hydroisomerization	low	medium	high
Hydrodealkylation	medium to high	medium	low
Hydrocracking	low	medium	high

B. Influence of the acidity of the bi-functional catalysts

The selective hydrocracking of wax using three bi-functional catalysts with difference in acidity, has been carried out, and the observed products are shown on the Figs. 2, 3 and 4.

Low acidity of bi-functional catalyst gives low yield and low viscosity index of lube base stock products. And both medium and high acidity of bi-functional catalysts produce high yield and high viscosity index of lube base stock products for low feedstock conversion: i.e. ± 35%. But high acidity of bi-functional catalyst gives the higher feedstock conversion and consequently low selectivity for lube base stock production compared with the medium acidity of this bi-functional catalyst for high operating temperature: i.e. 62% compared with 82% by wt for medium and high catalyst acidity respectivelv

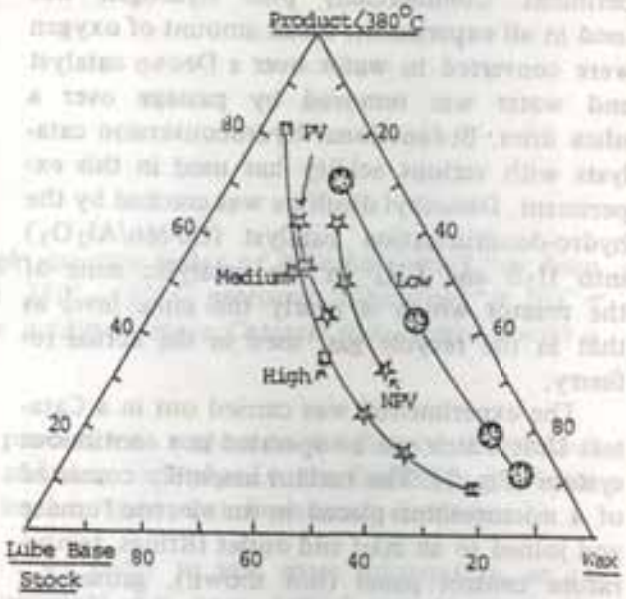

Figure 2. Selective hydrocracking products.

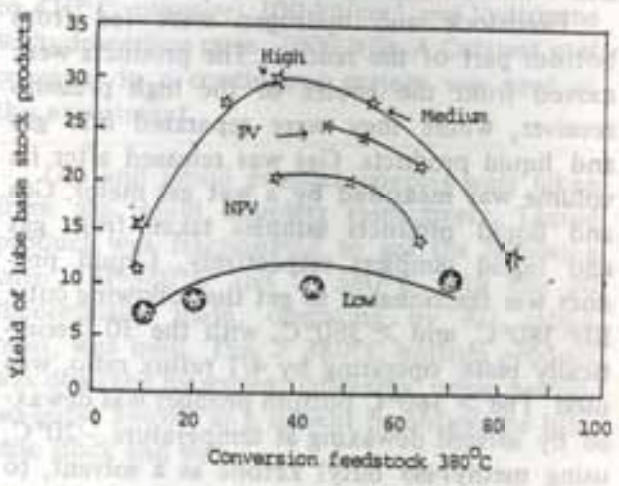

Figure 3. Influence of feedstock conversion on the yield of lube base stock products.

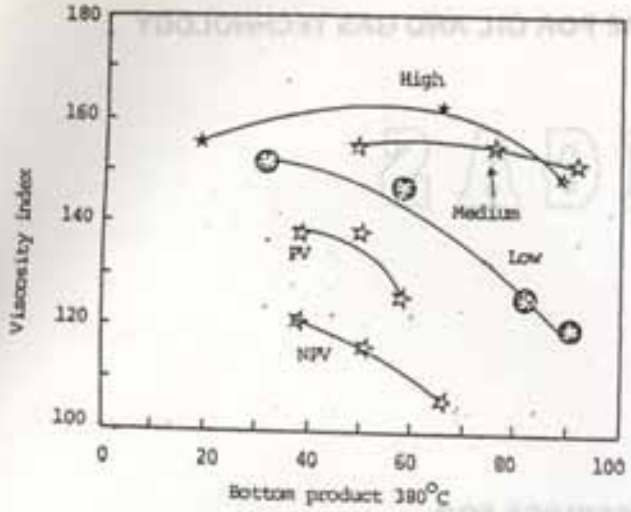

Figure 4. Influence of unconverted feedstock on the viscosity index of lube base stock products.

In the hydroisomerization and dehydrocyclization reactions of wax using bi-functional catalyst, carbonium ion is an intermediate molecule[3], thus the increasing of yield and viscosity index of lube base stock products with the catalyst acidity, it suggests that the yield of this carbonium ion increases with the acidity of bi-functional catalyst.

And due to the stability the carbonium ion decrease with the its total carbon number of those carbonium ions[5], thus the high carbonium ion yield obtained by the high catalyst acidity, has a high tendency to crack to low carbonium ion as a source light products, such as gas naphtha and middle distillate.

IV. CONCLUSIONS

Yield and viscosity index of lube base stock products depend on the feedstock composition and also the acidity of the bi-functional catalyst useds in the selective hydrocracking process. Paraffin hydrocarbons give tendency to produce high viscosity index of lube base stock product, and the acidity of bi-functional catalyst has an optimum value for a given the metal-site of bi-functional catalyst.

High viscosity index lube base stock product obtained by selective hydro-cracking process, suggests that a part of condenced aromatic is converted to naphthenes, which are then selectivity hydrocracked to single alkylaromatic by metal site and acid-site of bi-functional catalyst increases cyclization and isomerization of paraffin-wax to produce single ring alkyl naphthene and iso-paraffin.

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