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

by
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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 rearrangement, 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 metal site. Those two active sites of bi-functional catalyst should promote the correct combination of hydrogenation, isomerization and limited hydrocracking function, resulting in the maximum yield of product in the lube oil range (2). The kinetics 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 versatility of the hydroconversion process with respect to the variety of feedstock are case to study: i.e. the feasibility of the hydroconversion 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) by using bi-functional catalysts with various acidity at the following operating conditions: temperature: from 380^0 to 410^0 C, pressure: 100 kg/cm^2 and hydrogen 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 and liquid samples, respectively. Liquid product was fractionated to get the following cuts: IBP-380^{0}C and >380^{0}C with 30 theoretical plate fractionator, operating at 4/1 reflux ratio. The >380^{0}C bottom product was treated by dewaxing, using methyl-iso-butyl ketone as a solvent to obtain the lube base stock and wax.

II. EXPERIMENTAL

Three types of feedstocks i.e. non-paraffinic vacuum distillate (NPV), paraffinic vacum distillate (PV) and wax have been used in this experiment. Commercially pure hydrogen was used in all experiment. Small amounts of oxygen were converted to water over deoxo catalyst and water was removed by passage over a silica drier. Bi-functional hydroconversion catalyst with various acidity was used in this experiment.

Dimethyl disulfide was cracked by the hydrodesufurization catalyst (Co-Mo/Al_2O_3) bed into H_2S and CH_4, then entered the catalytic zone of the reactor which is nearly at 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 continous system (Figure 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), gauges for measuring gas flow and pressures, continuous high pressure oil feeding pump. The microreactor was constructed from stainless steel tubing, 220 cc in volume, 19 mm inside diameter and 7 mm out side diameter, with thermocouple well tubing.

Feedstock and hydrogen were fed from the 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 were taken from gas and liquid samples, respectively. Liquid products was fractionated to get the following cuts: IBP-380^{0}C, and >380^{0}C. A 30 theoretical plate fractionator, operating by 4/1 reflax ratio, was used. The >380^{0}C bottom products was dewaxed by solvent dewaxing at temperature of -20^{0}C, using methyl-iso butyl ketone as a solvent, to obtain the lubricant base stock. Viscosity index of lube base stock was analyzed by ASTM-metode D.445.

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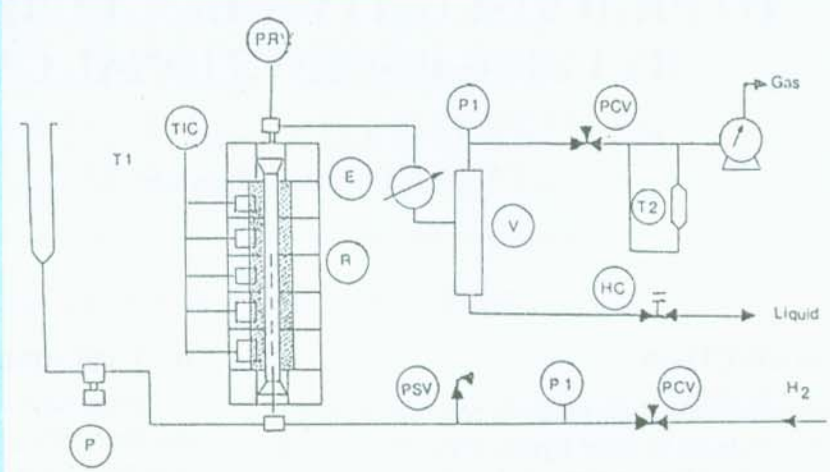
III. RESULTS AND DISCUSSION

Influence of Feedstock Composition

At the operating condition: temperature: from 380^0 to 410^{0}C, total pressure : 1000 kg/cm^2, and H_2/HC = 1000 lt/lt space velocity = 0.88, the selective hydrocracking of nonparaffinic vacuum distillate, paraffinic vacuum distillate and wax have been carried out. And the obtained products are shown on the Figure 2, 3, and 4.

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



E	- Condensor	R	- Contact tube
FT	- Gas meter	T1	- Bath
HC	- Manual valve	T2	- Sample
P	- Adjustable regulator	TIC	- Temperature regulator
PCV	- Pressure regulator	TR	- Temperature recorder
P1	- Pressure gauge	V	- Separator
PSV	- Presure safety valve		

Figure 1
Catatest unit

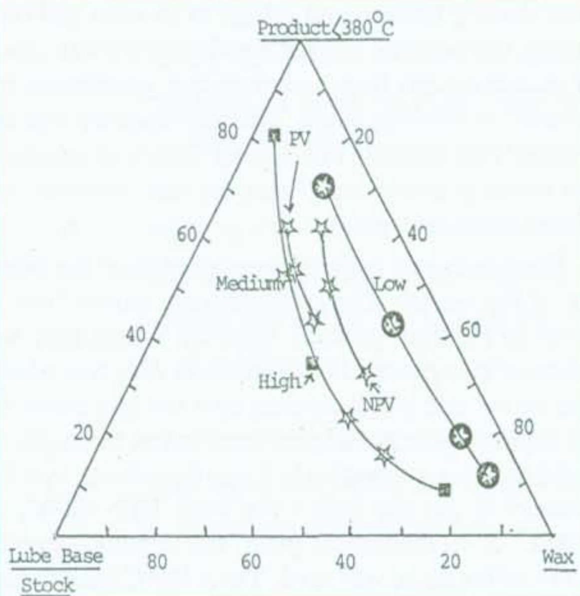


Figure 2
Selective hydrocracking products

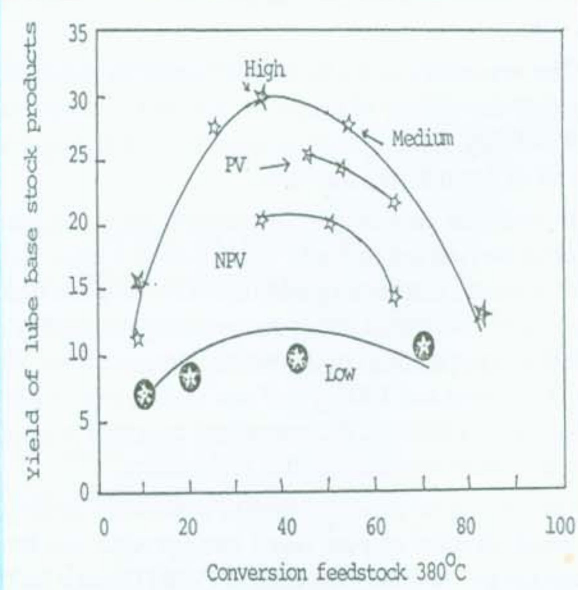


Figure 3
Influence of feedstock convension on the yield of lube base stock products

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are obtained, as shown in Table 1.

In general the viscosity index increases as follows: iso-paraffin > alkyl benzene > alkylcyelohexane (4), thus according to the observed viscosity index of lube base stock products obtained, it suggests that the main hydrocarbons of these lube base stock products are iso-paraffin/alkylcyclohexane, alkyl-cyclohexane/alkylbenzene and alkylbenzene for wax, paraffinic vacuum distillate and non paraffinic feedstock, respectively. And observed yields of the lube base stock products show that the side reactions: i.e. hydrodealkylation, hydrodealkylation/hydrocracking and hydrocracking are dominant for non paraffinic vacuum distallate, paraffinic vacuum distillate and wax, respectively. Thus the reactions of the selective hydrocracking of these three feedsrocks, are as suggested in Table 2.

Influence of Acidity of Bi-functional catalysts.

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

Low acidity of bi-functional catalyst give low yield and low viscosity index of lube base stock products. And both medium and high acidity if 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-funcional catalyst gives 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 weight for medium and high catalyst acidity, respectively.

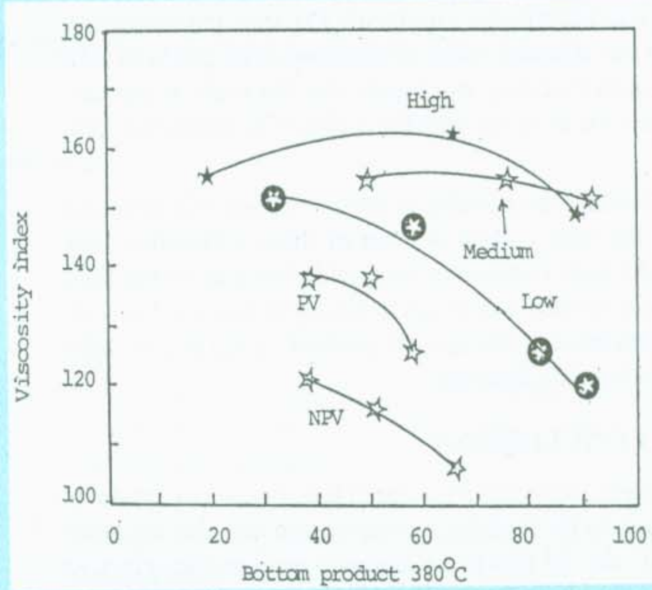

Figure 4
Influence of unconverted feedsrock on the viscosity index of lube base stock products

Table 1
Product yield and viscosity index

	Vacuum distillate		Wax
	Non paraffinic	Paraffinic	
- Yield, wt % on feedstock	20.67	24.67	27.21
- Viscosity index	116	139	158

Table 2
Typical reactions of nasions type of hydrocrading feedstocks

Type of reaction	Vacuum distillate		Wax
	Non paraffinic	Paraffinic	
Hydrogenation/hydrodecyclizatior	Medium to high	Medium	Low
Hydroisomerization	Low	Medium	High
Hydrodealkylation	Medium to high	Medium	Low
Hydrocracking	Low	Medium	High

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In the hydroisomerization and dehydrocyclization reactions of wax using by bi-funcional catalyst, carbonium ion is an intermediate molecule (3), thus the increasing 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.

Because the stability of the carbonium ions decrease with the total carbon number of those carbonium ions (5), 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 used 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 hydrocraking process suggests that a part of condensed aromatic is converted to naphthenes, which are then selectively hydrocracked to single alkylaromatic by metal site and acid-site of bi-funtional catalyst increases cyclization and isomerazition of paraffin-wax to produce single ring alkylnaphthene and isoparaffin.

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