HYDROCONVERSION OF HEAVY DISTILLATE INTO LUBE BASE STOCK USING BI-FUNCTIONAL CATALYSTS*

by

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ABSTRACT

Hydroconversion process replaces the furfural stage and dewaxing part of conventional process of lube base stock production. To study the ability of this hydroconversion process to weed low viscosity index component out of heavy distillate fraction to produce high viscosity index lube base stock, an experiment has been carried out on the hydroconversion of three feedstock types, i.e.: non-paraffinic vacuum distillate (NPVD), paraffinic vacuum distillate (PVD) and paraffin-wax (WAX), using three bifunctional catalysts having low, medium and high acidities. The experiment was done at the following operating conditions: temperature from 380° to 420°C, pressure: 100 kg/cm^2 and H_2/HC ratio: 1000 L/L using a Catatest Unit operated in continuous system.

The experimental data shows that at 50% by wt. feedstock conversion, the yields and viscosity index of lube base stock product are 20.7% by wt. and 118; 25.5% by wt. and 136; and 29.5% by wt. and 164 for NPVD, PVD and wax feedstocks, respectively. Lube base stock products of wax feedstock are 149, 156 and 164 for low, medium and high acidity bifunctional catalysts, respectively. By conventional process, PVD feedstock produces 10-15% by wt. lube base stock with viscosity index lube of 90 to 100.

The high viscosity index of lube base stock product, obtained by hydroconversion process, suggests that a part of condensed aromatics is converted into naphthenes, which are then selectively hydrocracked into single alkyl aromatics by both the metal site and acid site of the bifunctional catalyst. With medium and high acidity bifunctional catalysts, isomerization and cyclization of wax feedstock into isoparaffins and single ring alkyl-naphthene will be more pronounced compared to low acidity bifunctional catalyst. Selective hydrocracking of aromatic-naphthene ring of vacuum distillate feedstock into single ring alkyl-aromatic is quite dominant with medium acidity catalyst.

I. INTRODUCTION

In the 21st century, increasing quality demands of lubricating oils will require that lube refineries have increased access to sophisticated models of lube refining, the most up to date process design, and the best use of catalysis in order to make these high quality lubes at minimal cost.

Hydroconversion is well established process in the refining industry. It has been widely employed for many years in fuel manufactures, and it is currently experiencing a growing use in lube manufacture. Bifunctional catalyst, associating a hydro-dehydrogenating function of NiMo or NiW sulfides with acidic support (silica-alumina, zeolite) are widely used[1]. On these catalysts, the transformation of hydrocarbons involves reaction steps both on hydrogenating sites (hydrogenation and dehydrogenation), and on hydrogenating and acid sites (rearrangement, splitting, cracking)[2].

Hydroconversion process converts the undesirable components of heavy distillate feed such as polycondensed aromatics and naphthenes, and normal paraffins or slightly branched paraffins into valuable lube molecules with suitable high viscosity index of preferred hydrocarbon-structures molecular lube oil [3]. This process replaces the furfural stage and dewaxing part of conventional process of lube base stock production[4]. An average growth rate of 4% per year of lube oils utilization by

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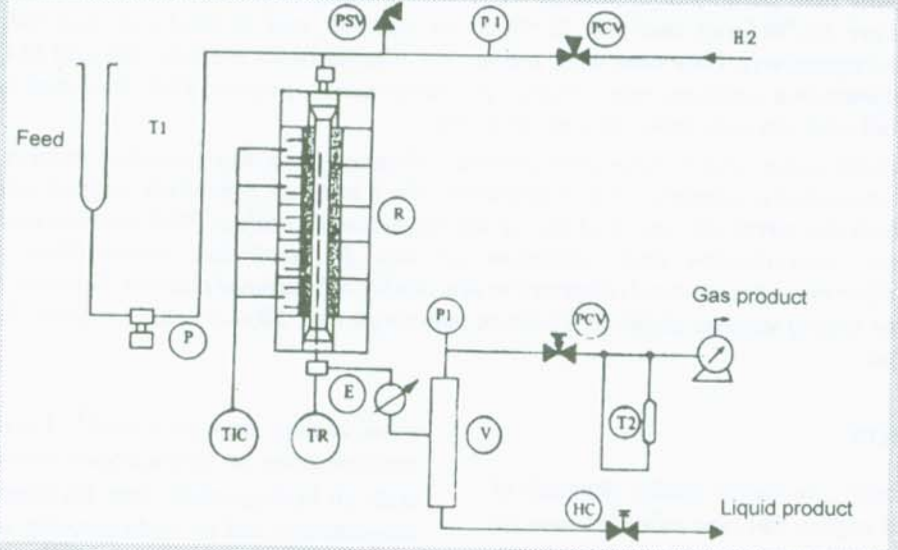
industry is projected to reach about 16% by the year 2000[5].

The aim of this work is to study the ability of this hydroconversion process to weed low viscosity index component out of heavy distillate fraction to produce high viscosity index lube base stock. An experiment has been carried out on the hydroconversion of three feedstocks i.e. non-paraffinic vacuum distillate, paraffinic vacuum distillate and paraffin-wax, using three bifunctional catalysts having low, medium and high acidities. The experiment was carried out at the following operating conditions: temperature from 380° to 410°C, pressure: 100 kg/cm^2 and H_2/HC ratio: 1000 L/L using a Catatest Unit operated in continuous system.

II. EXPERIMENTAL

Three types of feedstock i.e. non-paraffinic vacuum distillate (NPV), paraffinic vacuum distillate (PV) and paraffin wax (WAX), have been used in this experiment. Commercially pure hydrogen and three industrial bifunctional hydroconversion catalysts with high, medium and low acidity, respectively, have been used to treat the feedstocks.

The experiment was carried out in a Catatest Unit which can be operated in a continuous system. (Fig 1).



F	Condensor
FT	Gas meter
HC	Manual valve
P	Adjustable flow pump
PCV	Pressure regulator
P1	Pressure gauge
PSV	Pressure safety valve
R	Reactor
T1	Batch
T2	Gas sample
TIC	Temperature regulator
TR	Temperature recorder
V	Separator

Figure 1
Catatest unit

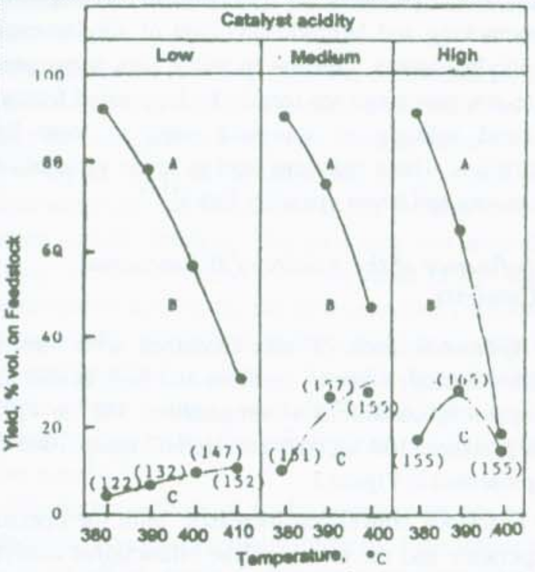


Figure 2
Product distribution of hydroconversion process of wax feedstock with low, medium and high acidities bifunctional catalysts
Note: () = Viscosity Index
A = Products 380 °C, B = Wax, C = Lube base stock

Tabel 1
Yield and Viscosity Index of Lube Base Stock Product at 50% vol. feedstock conversion

	Lube Base Stock Product	
	Yield, vol. % on feedstock	Viscosity Index
Feedstock	20.7	118
• Non-Praffinic		
Vacuum Distillate		
Vacuum Distillate		
• Paraffinix	25.6	136
Vacuum Distillate		
• Wax	29.5	164
Bifunctional		
Catalyst		
• High Acidity	29.0	164
• Medium Acidity	29.5	156
• Low Acidity	10.5	149

The microreactor was constructed from stainless steel tubing, 220 cc in volume, 19 mm inside diameter and 7 mm outside diameter 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 samplers, respectively. The liquid product was fractionated to get the following cuts: IBP-380°C, and > 380°C, with at 30 theoretical plate fractionator, operating at 4/1 reflux ratio. The > 380°C bottom product was dewaxed by solvent dewaxing at a temperature of -20°C, using methyl isobutyl ketone as the solvent, to obtain the lube base stock and wax. Lube base stock viscosity index was analyzed by ASTM- D.445 method.

III. RESULT AND DISCUSSION

A. *Influence of Feedstock Conversion*

Observed data on the hydroconversion of non-paraffinic (NPV) and paraffinic (PV) vacuum distillates, and paraffin-wax (WAX) using medium acidity of bifunctional catalyst at the operating conditions: temperatures from 310° to 410°C, total pressure: 100 kg/cm2, and H2/HC ratio: 1000 L/L are shown in Figure 2.

Feedstock conversion increases the operating temperature. Viscosity index of lube base stock products decreases feedstock conversion for two vacuum distillate feedstocks (NPV anda PV), but an optimum value is observed for wax feedstock. Yield and viscosity index of lube base stock products increase with paraffin content of feedstock i.e. wax > paraffinic vacuum distillate > non-paraffinic vacuum distillate. Yield and viscosity index of lube base stock products at 50 wt. % of feedstock conversion are as shown in Table 1.

The high viscosity index lube base stock products of hydroconversion of those three feedstock types with medium acidity bifunctional catalyst suggests that the undesirable component of the feedstock has been converted into the preferred lube oil molecular structures such as highly branched paraffins, single ring aromatics with long aliphatic chain, and naphthenes with a single ring

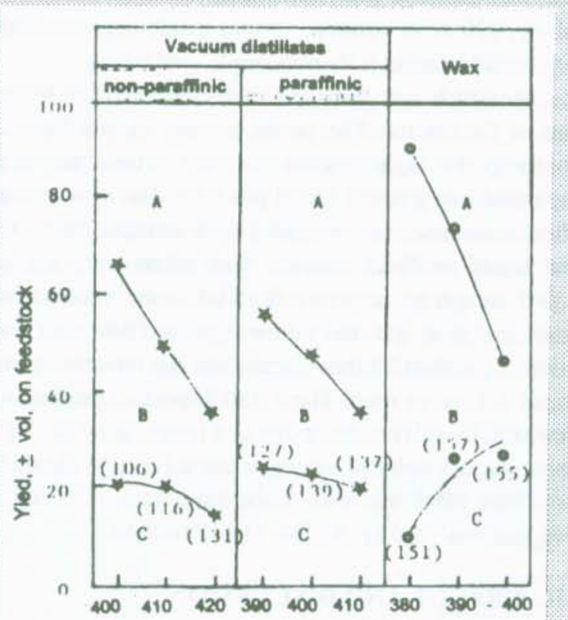


Figure 3
Product distribution of hydroconversion process of two vacum distillates and wax feedstocks with medium acidity bifunctional catalyst. Note () = Viscosity Index,
A = Products 380 °C,
B = Wax C = Lube base stock

having branched aliphatic long chains. Saturation of aromatics, opening of some of the naphthenes rings and isomerization of paraffins occur with the following reaction mechanisms[1,2]:

- The partial hydrogenation of polycyclic aromatic rings over hydrogenation function catalyst, followed by rapid splitting of the saturated ring to form substitute monocyclic aromatic by both hydrogenation and acidic functions of the bifunctional catalyst.
- With bifunctional catalyst, normal paraffins or slighty branched paraffins hydroisomerized into highly branched isoparaffins over bifunctional catalyst.

At high operating temperature it appears that the cracking of products can continue to produce lower molecular weight products, such as paraffin and isoparaffin hydrocracking and hydrodealkylation of alkylaromatics and alkylnaphtenes, whereas at fairly high temperature, single-aromatic rings are readily hydrogenated followed by rapid splitting of saturated rings to form light isoparaffins. These reactions lead to lower yield of lube base stocks and lower viscosity index[3,6].

A. *Influence of the Acidity of Bifunctional Catalysts*

Hydroconversion of wax feedstock with three bifunctional catalysts (low, medium and high acidities) at the operating conditions of temperature: 380° to 410°C, total pressure: 100 kg/cm^2 and H_2/HC ratio: 1000 L/L are presented in Figure 3.

Feedstock conversion increases both the operating temperature and the acidity of the bifunctional catalysts. The optimum yields of lube base stock products are observed with medium and high acidity bifunctional catalysts. Viscosity index of lube base stock products increases the acidity of the bifunctional catalyst; influence of feedstock conversion on the viscosity index of lube base stock products with various catalyst acidities are observed as follows: an optimum for high acidity, nearly constant for medium acidity, and decreasing for low acidity. Yield and viscosity index of lube base stock products at 50 wt. % on feedstock are presented in Table 1.

Conversion of normal paraffin or slightly branched paraffin of wax feedstock over bifunctional catalyst into high viscosity index lube base stock product suggests that the wax isomerization and cyclization have taken place by the following steps:

- Long chain normal or slightly branched paraffins are dehydrogenated over a metal function to form olefins. The olefins diffuse to the acid sites where they are protonated to form carbonium ions.
- Skeletal isomerization and or cyclization of these carbonium ions occur quickly within the pores of the acid support. It increases the acidity of catalyst support. The isomerized carbonium ions donate protons back to the acid support, and produced isoolefin then crack through b-scission to lower molecular weight

products or transfer back the protons to another olefin.

- The isoolefins resulting form the carbonium ions are then hydrogenated over the same metal function used for the hydrogenation reaction into isoolefins.

A higher ratio of intermediate to low molecular weight paraffins was also found in the product from the medium acidity catalyst. This indicates less secondary splitting, presumably also a consequence of the higher hydrogenation activity of the hydrogenating component in more rapidly converting cracked products to more stable paraffins. This property is desirable for minimizing the ratio of gas to liquid products during hydrocracking and thus leading to less hydrogen consumed in reactions of this type [1,2].

The higher activity of acidic components can be advantageous, however, in maintaining the high iso/normal ratio of paraffins, made during hydrocracking. The use of lower acidic components can lead to lower iso/normal paraffins ratios and producing low viscosity index lube base stock[6].

The key steps appear to be in the competitive rates of cracking and olefin hydrogenation. These rates are governed by a complex combination of support acid strength, support pore size constraints, and diffussion parameters. Proximity of the acid and metal sites of bifunctional catalyst is also important as the proper balance between the number of metal sites and the number of acid sites. If the diffusivity of the isoolefin is much faster than the isoolefin cracking rate (or correspondingly the isocarbonium ions cracking rates), then a high branched isoparaffins yield is possible.

Production of lube base stocks from fuels hydrocracker bottoms is another route to lubes that would become attractive in the near future. The growing interest for lubes manufactures stems from the several advantages hydrocracking offers versus solvent processing: higher lubes yields, broaden feedstock flexibility, and high quality lube base stock as the main drivers of these implementations[3,7].

III. CONCLUSION

Hydroconversion process converts the undesirable components of feedstock into lube oil molecular structures with high viscosity index as well as valuable light products (naphtha and middle distillate). Such incentives as crude flexibility and high quality stocks for multigrade automotive engine oils appear to be the main drivers of these implimentations.

At 50% by wt. feedstock conversion, the yield and viscosity index of lube base stock products are 20.7% wt. and 118; 25.5 % by wt. and 139; and 29.5 % by wt. and 164 for non-paraffinic (NPV) and paraffinic (PV) vacuum distillate, and wax feedstocks respectively. By conventional process, PVD feedstock produces lower lube base stock products; i.e. yield of 10-15% by wt. and viscosity index of 90-100. Yield and viscosity index of lube base stock products of wax feedstock increase acidity of bifunctional catalyst.

The key steps appear to be in the competitive rates of cracking and olefin hydrogenation. These rates are governed by complex combination of support acid strength, support pore size constrains, and diffusion parameters. The preferred catalysts are bifunctional containing both a metal function and an accompanying acid function that have been properly tailored to balance the metal function. The growing interest for lubes manufactures stems from several advantages hydrocracking offers versus solvent processing: converts undesirable components to lubes rather than removing them, permits lube production from low quality, cheaper crudes, while producing higher quality lube oils.

The extereme versalitity of hydrocracking with respect to its ability to process a wide variety of difficult feedstock into a wide variety of desirable products suggests that unconverted feedstock of hydrocracking process, such as from Pertamina Dumai and Balikpapan Refineries could be seriously considered as a potential source of lube base stock for which Indonesia is still in great need.

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