HYDROISOMERIZATION OF PARAFFIN WAX OF SUMATRAN LIGHT WAXY RESIDUE FOR LUBRICATING OIL AND FUEL OILS PRODUCTION USING THE BI -FUNCTIONAL CATALYSTS WITH VARIOUS ACID SUPPORTS.

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ABSTRACT

Paraffin wax (average mol wt 750—850) of Sumatran Light Waxy Residue was hydroisomerized by bi-functional catalyst with various acidic components, using a catetest unit, operated at high temperature and pressure with continous system. The reaction products were distilled at atmospheric pressure to 380°C and the residues subjected to a dewaxing treatment at — 20°C. Based on this separation the reaction products were regarded as pseudo three component systems the component being lubricating oil, unconverted wax and cracked products. The lubricating oils obtained in the experiments have a-viscosity index of 122 — 165. With $M/Al_2O_3—SiO_2$ type catalyst a maximal oil yield of 28,0 per cent wt was obtained with 25 per cent of cracked products. And at 50 percent by wt of feedstock conversion, the smoke point of kerosene and diesel index of gas oil are 34 and 87 mm respectively. The wux contents in the feedstock is an important source for high viscosity index lubricating oil production obtained by hydroisomerization of this wax.

1. INTRODUCTION

There are two ways of producing lube oil base stocks, i.e. the conventional and the selective catalytic hydrocracking. (1)

And for reducing the pour point of lubricating oils, obtained by these two processes, the wax content must be separated on the dewaxing unit. (3)

The separating hydrocracked wax can be hydroisomerized to produce low pour point lubricating oils of high viscosity index and also fuel oils of good quality. (4,5)

Hydroisomerization of separating wax or separating hydrocracked wax (See Figure 1)is a relatively new process, by means of which low pour point lubricating oils of high viscosity index and also diesel fuel and kerosene of good cetane number and smoke points can be produced. (3,6)

The main difficulty encountered in attemps to isomerize high molecular weight paraffins is in preventing excessive cracking to lower molecular weight hydrocarbons of litle value.

The isomerization of petroleum waxes can be carried out at a faster rate and in a simpler and more selective way, with the aid of hydrogenation catalysts on acid supports, if these catalysts are used in the proper temperature range in conjunction with hydrogen under pressure. One such process comprises vaporizing the wax with at least one mole of hydrogen per mole wax with bi-functional catalysts. (7,8)

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Selective hydrocracking of vacuum distillates of Sumatran Light Waxy Crude oil and Kuwait Crude oil for lubricant base stock and fuel oils productions has been done on the previous work. (9)

In order to gain more detailed information, bench-scale hydroisomerization of paraffin wax of deasphalted oil Sumatran Light Waxy Residue was carried out, using the industrial bifunctional catalysts with various acid supports. (M/Al_2O_3-X).

2. EXPERIMENTAL

2.1. Reactants

Feedstock

The feedstock consisted of micro-yellow paraffin wax with a molecular weight range of 750–850, the average carbon atom number range of 50–55, the fusion point about 68°C. The penetration (at 70°C) and the density (at 70°C) are 45 and 0,8261 mm respectively.

The oil content of the wax is about 2,8% wt.

Hydrogen

The hydrogen used contains less than 0,1 per cent volume of impurity (mostly nitrogen).

Catalyst

The catalysts used is the type commonly employed in hydroisomerization of paraffin wax and selective hydrocracking of heavy distillate.

2.2. Procedure

Apparatus

The hydroisomerization experiments was carried out in a micro-catalytic test unit (Catatest Unit), without gas recycle, are shown diagramatically in Figure 2. The volume and inside diameter of the reactor are 220 cc and 19 mm respectively.

The reactor temperature, H_2 injection and liquid product in the high pressure separator are regulated automatically.

Procedure

In the experiment, the catalyst (80 cc) was charged to the reactor and the catalyst unit brought to reaction pressure with hydrogen. In order to remove air from the unit, the hydrogen was blown off and replaced by fresh hydrogen.

The reactor was then heated to about 250°C and kept at this temperature for 2 hours, while hydrogen was recirculated at desired rate. The feed pump was then started and the reaction conditions carefully adjusted in this pre-test period. After the density of the product become constant (abour 5–6 hours), the pre-test period liquid product was removed, then a test run of 10 hours was carried out.

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

Each run, the volume of gas products and the weight of liquid product were recorded.

The operating condition of the experiments are set up in Table 1.

2.3 Method of analysis

250 grams of each liquid product were distilled at atmospheric pressure to get the following cuts: IBP up 80°C, 80-150°C, 150-250°C, 250°-380°C, and the characteristic of cracked products boling below 380°C was determined as follows:

- PONA analysis of cut 80°-150°C - by Mass Spectrometry
- Smoke point of cut 150°-250°C - by the ASTM Method D 1319
- Diesel index of cut 250°-380°C - by the ASTM Method D 161.

- The distillation apparatus has about 30 theoretical plates, operated with 4/1 reflux ratio.
- 50 grams of each distillation residue were dissolved in warm methyl ethyl keton, the weight ratio being 1:5, and the solution slowly stirred and cooled to -20°C, allowing the was to crystallize.
  The solidified mixture was filtered at -20°C by suction, using a filter which was kept at -20°C.
- The oil yield, defined as the weight percentage lubricating oil in the reaction product, can be calculated.
- The viscosity indexes of the obtained lubricating oils were determined according to the ASTM Method D 567-53.

3. Results and discussions

3.1 Relation between the isomerization and cracking reactions

The obtained reaction products may be regarded as pseudo three-component systems of which the component are: lubricating oil, unconverted wax, and cracked products.

The percentages of these components are shown in Table 2 and plotted in a triangular diagram (right-angled) of the isoceles type (Figure 3). In this diagram the ordinate represents the course of isomerization, while the abscissa represents the cracking of the paraffix wax.

It can be seen from Figure 3 that it is possible to draw two following curves:

- Higher curve in obtained from $M/A1_2O_3$-F, $M/A1_2O_3SiO_2$ and $M/A1_2O_3$-B_2O_3 (A) catalysts.
- Lower curve gives the data of the $M/A1_2O_3$ and $M/A1_2O_3$-B_2O_3 (B) catalysts.
- The higher curve has a higher ratio between the isomerization and cracking reaction, or gives a higher selectivity for isomerization reaction for a given cracked products (or conversion level).
  Where for 50% wt of conversion level, the higher and the lower curves give 30% wt and 10% wt of the lubricating oil products respectively.
  There is a higher selectivity of those three catalysts, i.e. $M/A1_2O_3$-F, $M/A1_2O_3$-SiO_2 and $M/A1_2O_3$-B_2O_3 (A), due to the suitable balance of those three bi-functional catalysts, i.e. the ratio between the metal site and the acid site of the catalyst.

3.2. Influence of cracked products on the viscosity index of the lubricating oil product

The influence of cracked products on the viscosity index of lubricating oil products is shown in the Table 2 and Figure 4.

Table 2 shows that there are two different curves as follows:

- The viscosity index of the lubricating oil products increases with the cracked products, i.e. $M/A1_2O_3$ and $M/A1_2O_3$-F catalyst,
- The viscosity index of the oil products has an optimal value at given cracked product, i.e. $M/A1_2O_3$-B_2O_3(A) and $M/A1_2O_3$-B_2O_3 (B) catalysts.
- The $M/A1_2O_3$-SiO_2 catalyst produces the lubricating oil product with the viscosity index nearly constant by increasing the conversion level of level of the feedstock, i.e. for increasing the feedstock conversion from 25,1% wt to 52,5% wt, the viscosity index of the lubricating oil products decrease 2 points only.

The increase of the viscosity index of the oil products with the cracked products indicates that the catalysts (i.e., $M/A1_2O_3$ and $M/A1_2O_3$-F) have the high degree of the isomerization reaction and less degradation (or cracking) of paraffin wax.

Thus for a high conversion level of feedstock, the $M/A1_2O_3$-F and $M/A1_2O_3$-SiO_2 catalysts can produce the high viscosity index of the lubricating oil products.

Generally the heavy feedstock of hydroconversion processes contain an impurity, such as water. The water impurity can remove (or eliminate) fluor (or other halogen) from the catalyst (13) and then balance between the hydrogenation component and acid support of bi-functional catalyst will change. And consequently the activity of the bi-functional catalyst with decrease.

So, the $M/A1_2O_3$-SiO_2 catalyst is the most suitable one for the lubricating oil product by hydroisomerization process of the paraffin wax.

The experimental data are supported by the previous results.(1)

3.3. Influence of the operating temperature on the selectivity of catalyst

The influence of the operating temperature on the ratio between lubricating oil yield and cracked product yield or the selectivity of catalyst will be high of the ratio of activation energy between the Isomerization and the cracking reaction is high too.

The activation energy of these two reactions can be calculated frm the Arrheniuss equation, as follows:

$$k = Ae^{-E/RT}$$

or

$$\log k = -\left(\frac{E}{2{,}302\,R}\right)\left(\frac{1}{T}\right) + 2{,}30 \log A$$

k = yield of the cracked and the lubricating oil products
T = operating temperature, °K
R = universal gaseous constants
E = activation energy, kkal/gmole

Log k = $f\left(\frac{1}{T°K}\right)$ is a straight line, and the value of slope of this line is -E/2,302R or tg = -3/2,302R. The activation energy will be as follows;

$$E = -2{,}302\,R\,tg$$

The calculated activation energies of the isomerization and the cracking reactions are shown on the Table 3.

Table 3 shows that the ratio of activation energy between the isomerization and the cracking reactions are as follows:

- Higher than 1 (one) is obtained from $M/A1_2O_3\text{-}B_2O_3$ (B)
- Lower than 1 (one) is given by $M/A1_2O_3$, $M/A1_2O_3\text{-}SiO_2$ and $M/A1_2O_3\text{-}B_2O_3$ (A).
- And the $M/A1_2O_3\text{-}SiO_2$ gives that activation energy ratio is nearly one.

In the previous chapter is shown that the $M/A1_2O_3\text{-}F$ catalyst is less stable and that the $M/A1_2O_3\text{-}B_2O_3$ (A) catalyst produces a low viscosity index of the lubricating oil products. Thus, the $M/A1_2O_3\text{-}SiO_2$ catalyst is still a more suitable one one comparred with the other form catalysts, i.e.; $M/A1_2O_3\text{-}SiO_2$, $M/A1_2O_3\text{-}B_2O_3$ (A) and $M/A1_2O_3\text{-}B_2O_3$ (B).

3.4. Influence of wax content in the feedstocks on the properties of lubricating oil and cracked products

3.4.1. Lubricating oil products

Paraffin wax of Sumatran Light Waxy Residue, vacuum distillate of Sumatran Light Waxy crude oil and vacuum distillate of Kuwait Crude oil with difference in the wax content have been converted into lube oil product by the hydroconversion process.

Table 4 and Figure 5 show the properties of the oil products for about 50% by weight of feedstock conversion.

It can be seen from Table 4 and Figure 5 that the viscosity index of these lubricating oil products decreases as the wax content in the feedstock declines as follows:

> Paraffin wax — Distillate vacuum of Sumatran Light Wax Crude Oils — Distillate vacuum of Kuwait crude oils.

Thus the results shown the tendency a high viscosity index and the low yield of the lubricating oil products with increasing of the paraffin contents in the feedstocks.

Also, the wax content of the feedstock plays an important role for producing a high quality of lubricant oil product by hydroisomerization process or in other word the hydroisomerizxation reaction is one of the important reactions in the hydroconversion process for lubricating oil production.

There is a decrease of the yield of the lubricating oil products with the paraffin content of the feedstock, due to the high degradation reaction of the paraffinic feedstock compared to the non paraffinic feedstock.

The previous data are similar with those experimental results. (8).

3.4.2. Cracked products

Cracked products of hydroconversion of paraffin wax, vacuum distillate Sumatran Light Waxy Residue and vacuum distillate of Kuwait Crude oil are shown in the Table 6 and the Figure 5 and 7.

Table 5 and Figure 5 and show that the aromatic content of cracked products, i.e. heavy naphtha, kerosene and gas oil products, depend on type of feedstock used; thus, the high wax content of reactants produces the cracked products with less aromatic contents.

In other words, due to the different reaction rate of aromatic production in the cracked products;

> The dehydrocyclization reaction of paraffin wax (in hydroisomerization of paraffin wax), is less rapid than hydrodecyclization reaction of poly aromatic or mixed aromat naphthenic (in hydroconversion of heavy distillate).

As the cracked products of hydroisomerization of paraffin wax contains less aromatic hydrocarbon, the quality of kerosene and gas oil products will be high.

These experimental results are in agreement with the previous data.(4)

4. Conclusions

Hydroisomerization as a process to produce lubricating oil base stock is promising.

The $M/A1_2O_3$-SiO_2 catalyst has a good balance between the hydrogenation site and acid site with less sensitivity to the water impurity of feedstock compared with the other 4 types of catalysts (i.e. $M/A1_2O_3$, $M/A1_2O_3$-F, $M/A1_2O_3$-B_2O_3 (A) and $M/A1_2O_3$-B_2O_3 (B).
The wax contents in the feedstock is an additional source component for lubricating oil base stock as the hydroisomerization converts it to high iso-paraffins.
Optimal operating conditions can certainly be achieved by variation of other parameters, such as pressure, hydrogen/hydrocarbon ratio, spare velocity etc.

These variation will be included in the next programme.

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Operating Conditions

Table 1

Catalyst volume	cc	80
Liquid hourly space velocity		0,5
Pressure	kg/cm^2	125
H_2/Hydrocarbon ratio	lt/lt	1000
Temperature	°C	380°, 390°, 400°, 410°

Product distribution of Hydroisomerization of paraffin wax of Sumatran Light Waxy Residue with various bi-functional catalysts.

Table 2

Type of Catalysts	Operating temp. °C	Properties of reaction rates			
		cracked material	lubricating oil Yield % wt	solid material % wt	Viscosity index of lubricating oil
M/$A1_2O_3$	380	8,1	7,1	84,7	122
	390	20,2	8,2	71,6	132
	400	42,5	9,3	48,2	147
	410	70,0	11,1	19,9	152
M/$A1_2O_3$-F	380	8,3	7,5	84,2	143
	390	20,1	26,5	53,4	147
	400	52,5	27,0	20,5	165
M/$A1_2O_3$-SiO_2	380	9,0	11,5	79,5	151
	390	25,1	28,0	46,9	157
	400	52,5	27,7	19,8	155
M/$A1_2O_3$-B_2O_3(A)	380	9,2	15,5	75,3	150
	390	35,1	29,5	47,4	163
	400	82,0	13,2	4,2	155
M/$A1_2O_3$-B_2O_3(B)	380	9,1	7,5	83,4	141
	390	25,0	14,8	60,2	147
	400	57,5	27,0	15,5	145

Note: M = Metal as hydrogenation component of catalysts.

Table 3

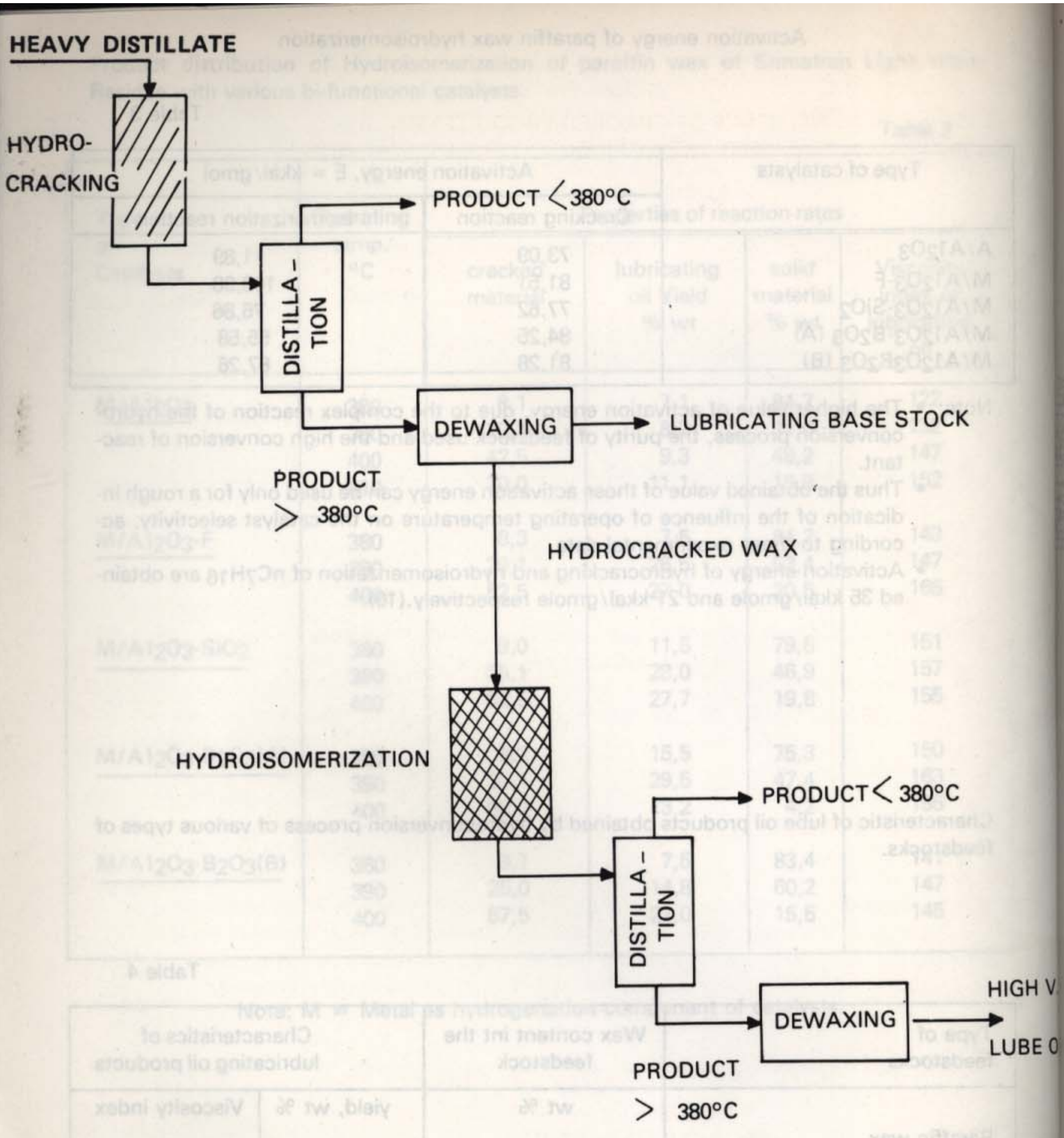
Type of catalysts	Activation energy, E = kkal/gmol	
	Cracking reaction	Isomerization reaction
$A/A1_2O_3$	73,09	11,89
$M/A1_2O_3$-F	81,51	108,98
$M/A1_2O_3$-SiO_2	77,62	76,86
$M/A1_2O_3$-B_2O_3 (A)	84,25	55,58
$M/A1_2O_3B_2O_3$ (B)	81,28	87,26

Note:
- The higher value of activation energy, due to the complex reaction of the hydroconversion process, the purity of feedstock used and the high conversion of reactant.
- Thus the obtained value of those activation energy can be used only for a rough indication of the influence of operating temperature on the catalyst selectivity, according to these experimental data.
- Activation energy of hydrocracking and hydroisomerization of nC_7H_{16} are obtained 35 kkal/gmole and 21 kkal/gmole respectively.(10).

Characteristic of lube oil products obtained by hydroconversion process of various types of feedstocks.

Table 4

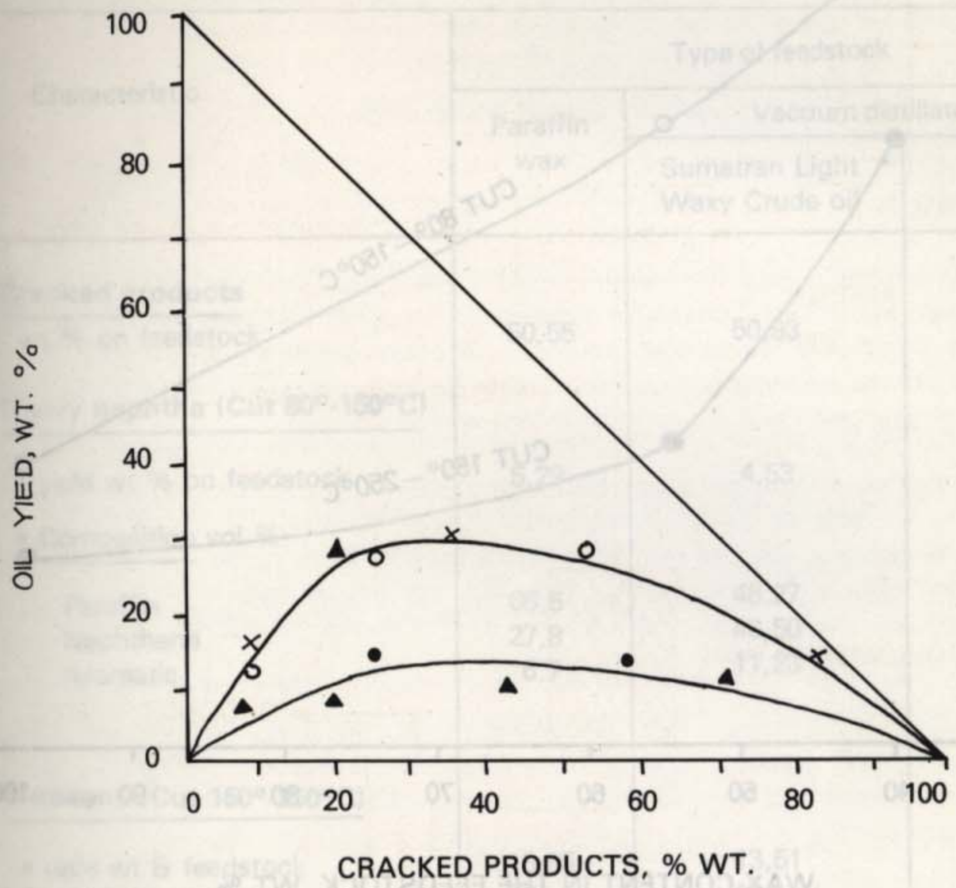
Type of feedstocks	Wax content int the feedstock	Characteristics of lubricating oil products	
	wt %	yield, wt %	Viscosity index
Paraffin wax	97,2	27,0	155
Vacuum distillate of			
• Sumatran Light Waxy Crude Oil	55,0	24,4	139
• Kuwait Crude oil	± 40,0	41	118



HYDROISOMERIZATION OF SEPARATING HYDROCRACKED WAX.

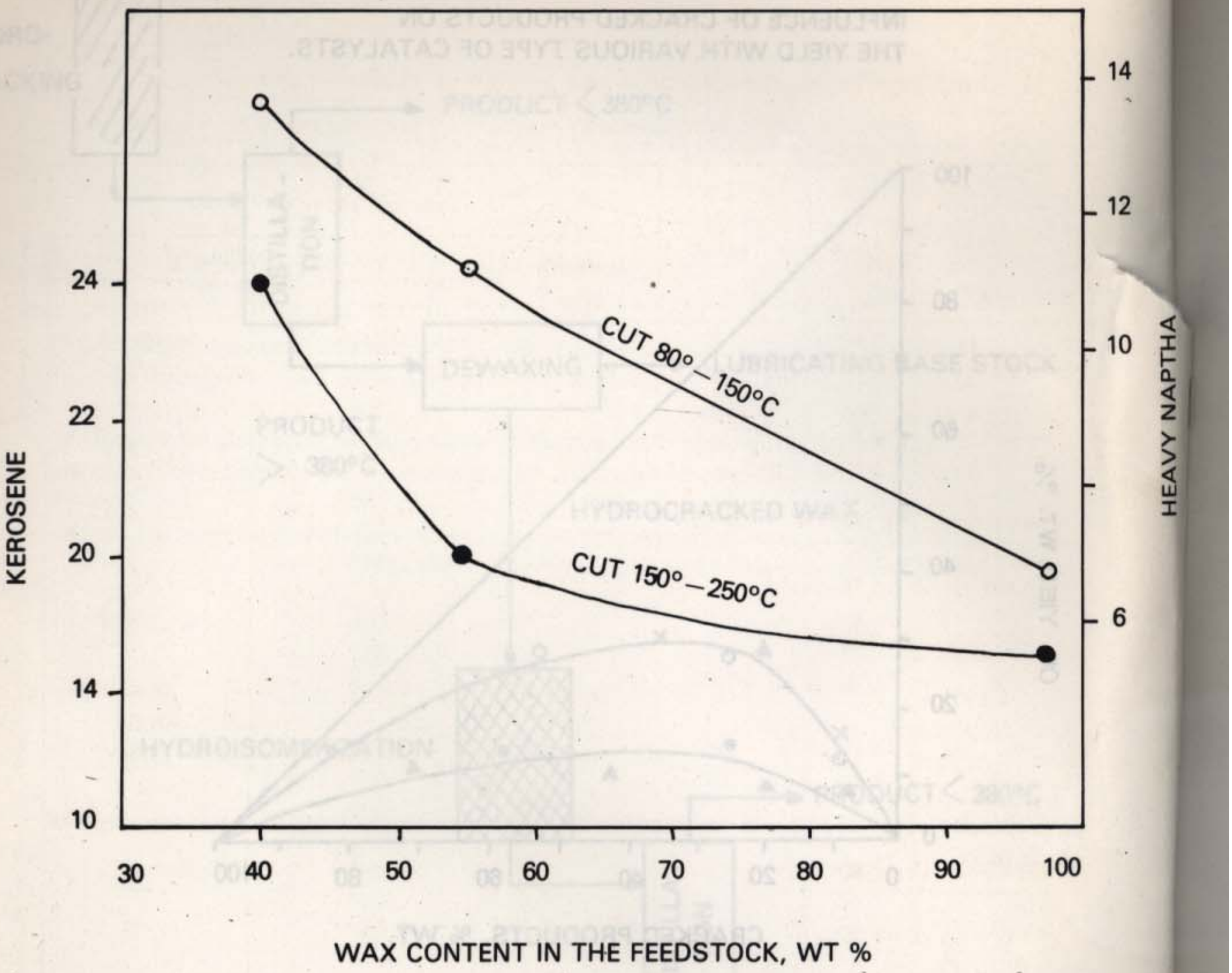
FIGURE : 1

INFLUENCE OF CRACKED PRODUCTS ON THE YIELD WITH VARIOUS TYPE OF CATALYSTS.



NOTE: $M/A1_2O_3$—(Δ); $M/A1_2O_3F$-(Δ)
$M/A1_2O_3$-SiO_2(O); $M/A1_2O_3$-B_2O_3 (A)-(X)
$M/A1_2O_3$-C_2O_3-(B). (O).

FIGURE : 3



INFLUENCE OF WAX CONTENT IN THE FEEDSTOCK ON THE AROMATIC CONTENT IN THE CRACKED PRODUCTS.

Cracked products of hydroconversion process of various types feedstocks

Table 5

Characteristic	Type of feedstock		
	Paraffin wax	Vacuum distillate of	
		Sumatran Light Waxy Crude oil	Kuwait crude oil
Cracked products			
wt % on feedstock	50,55	50,93	50,48
Heavy naphtha (Cut 80°-150°C)			
• yield wt % on feedstock	5,29	4,53	3,57
• Composition vol %			
Paraffin	65,5	48,27	38,4
Naphthene	27,8	40,50	48,0
Aromatic	6,7	11,23	13,6
Kerosene (Cut 150°-250°C)			
• yield wt & feedstock	16,55	13,51	14,09
• Aromatic contents, vol %	15	18	24
Smoke point, mm	34	22,5	17,8
Gas oil (Cut 250°-380°C)			
• yield wt % on feedstock	27,89	31,39	25,81
• Aniline point, °C	95,8	89,4	—
• Diesel index	87,3	74,8	52