HYDROCRACKING OF VACUUM DISTILLATE AND LUBRICANT BASE STOCK PRODUCTION *)

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Abstract

Hydrocracking of vacuum distillate for middle distillate and lubricant base stock production has been carried out with temperature (from 400° to 420°). Hourly Liquid Space Velocity (from 0.422 to 0.88), Pressure (100 kg/cm2) and H_2/Hydrocarbon ratio (1000 lt/lt), by using a Catatest unit apparatus.

1. Introduction.

Hydrocracking is probably the most versatile of modern petroleuem processes. This versatility has been achieved by the development of specific families of cátalysts, of processing schemes designed to allow these catalysts to function efficiently, and optimal refining relationships between hydrocracking and other refining processes.

Hydrocracking is distinguished by its objective of producing products of significantly lower-molecular weight than that of the feed, and involves correspondingly large hydrogen consumption.

Hydrocracking catalysts are be-functional, containing both hydrogenating and cracking sites. The best choise of catalysts for a specific objective requires a particular balance between these two functions.

The kinetic of hydrocracking process with respect to the variety of feedstock characteristics gives rise to an interesting case to study, i.e. the feasibility of obtaining lube base stock and fuel oil from Minas Waxy Residue, MWR because the high wax content of the latter respresents the point of difficulty when the conventional process is to be used.

A case study for MWR to the production of 100,000 MT/y lubricant base stock and 180,000,T/y middle distillate has been made (1). The economic calculation, base on literature and other reliable data, show the advantage of hydrocracking compared to conventional processing.

And research on hydrocracking of Minas, vacuum distillate for fuel oil and lubricant base stock production has been carried out (2).

In order to gain more detail information, bench scale hydrocracking of a non paraffine vacuum distillate was carried out for middle distillate and lube oil production.

Research on the hydrocracking of vacuum distillate is practically free of asphaltene, its negative effect upon the catalyst performance does not arise in this case.

2. Experimental

The feedstocks used have characteristics, shown in Table 1. The dimethyl-disulfide contained less than 4 per cent or impurity; this was blended with the vacuum distillate

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of Minas and Kuwait crude oils, as much as 2 wt % on feedstock. The hydrogen used contained less than 0.1 per cent volume of impurity(mostly nitrogen). The catalyst used was of the type commonly employed in hydrocracking of heavy distillate but with less acidic properties. The hydrodesulfurization catalyst (for obtaining the H2S and CH4 from dimethyl disulfide) was Co-Mo/Al2O3 catalyst.

The hydrocracking experiments were carried out in a micro-catalyst activity test unit (Catatest), without gas recycle, shown diagrammatically in Figure 1. The volume and inside diameter of the reactor are 200 cc and 19 mm respectively. The reactor temperature, H2—injection and liquid product in the high pressure separator were regulated automatically. The liquid products were fractionated to get the following cuts: IBP—80°C, 80°C—150°C, 150°C—250°C, 250°C—380°C, whereby distillation apparat;us, with the 30 theoretically plate, operating by 4/1 reflux ratio, was used.

The 380°C bottom product was dewaxed by solvent dewaxing. The operating conditions and the method of analysis are shown on the Tables 2 and 3.

3. Results and Discussion

The hydrocracking of vacuum distillate has been studied in the temperature range of 400° to 420°C under 100 kg/cm2 (Table 4).

As the operating temperature is increased from 400°C to 420°C, the conversion of feedstock is to rapid, i.e. the conversions of feedstock at 400°, 410°C are 33.66; 50.20 and 62.60 wt % respectively.

The selectivity of middle distillate product i.e. kerosene and gas oil is constant at 400° and 410° C of working temperature, but this selectivity with decrease about 4% by increasing the temperature from 410° to 420° C. Yield of wax product decreases from 45.44 to 23.37 wt.% by increasing of the operating temperature from 400° to 420°C.

These results suggest that at high working temperature, the large molecules of feedstock can diffuse into micropores, which they encounter more strong acid sites (5). As result feedstock conversion goes up and the selectivity of middle distillate products decreases.

The Arrhenius equation of constant rate can be written as follows:

$$k = A\, e^{-E/RT} \quad \text{or}$$

$$\log k = \left(\frac{E}{2.303R} \right) \frac{1}{T} + 2.303 \log A$$

By plotting log k versus (1/T°K), the value of slope log k = f (1/T°K) is equal to -(E/2.303R), and than the activation energy of hydrocracking of Kuwait vacuum distillate is E = 22 kcal/gmol (Figure 2).

The hydrocracking of vacuum distillate has been studied in the liquid hourly space velocity (LHSV) range of 0.42 to 0.88, which the experimental data are set up on the Table 4.

The decreasing of feedstock conversion as the LHSV which increased from 0.422 to 0.63 is less significant than when increasing the LHSV from 0.63 to 0.88 (See Table

4). But by increasing of LHVS from 0.42 to 0.88 the selectivity of the middle distillate production will increase from 82.04 to 85.65 by wt. % (or about 4,4 %).

By increasing of LHVS from 0.42 to 0.88 the wax product will increase from 20.16 to 45.44 wt %. It seems that the decreasing of feedstock conversion rate with LHVS, due to the reducing of the contact time of the hydrocracking reaction, and consequently for a consequtif hydrocracking reaction, the selectivity of the middle distillate product will increase.

4. Characteristics of products

By increasing of operating temperature from 400° to 420°C, the smoke point of kerosene only 2 point compared with 6.5 point as the decreasing of LHVS from 0.88 to 0.42 (Table 4 and Figure 3).

Thus the effect of operating temperature is less significant compared with the effect of LHVS on the smoke point and aromatic content of kerosene products (Table 4 and Figure 3).

The increasing of diesel index of gas oil product is 13.5 point (Table 4 and Figure 4).

. increasing of operating temperature from 400° to 420°C.
. and decreasing of LHVS from 0.88 to 0.42.

So, the influence of operating temperature is less than the effect of LHSV, too.

The influence of working temperature is nearly the same with the effect of LHVS on the viscosity index (VI) of lubricant base stock (Table 4 and Figure 5) i.e.

. V.I. increase is 25 and 27 point by increasing of working temperature from 400° to 420°C and reducing of LHVS from 0.88 to 0.42.

But the effect of these two operating process i.e. Temperature and LHVS on the yield of lubricant base stock product is not the same, i.e. (Figure 5).

The yield of lubricant base stock product will decrease from 20.90 to 14.03 wt % for raising the operating temperature from 400° to 420° C and this yield with increase from 20.90 to 20.65 wt % for decreasing of LHSV from 0.88 to 0.22.

5. Conclusion

Based on data the quality and the quantity of hydrocracking product depended on the operating temperature and feedstock rate (LHSV).
And the influences of temperature and LHSV on the percentage of wax products is nearly the same.

The hydrocracking or a non paraffine vacuum distillate can produce a high enough quality and quantity of middle distillate and lubricant base stock.

Base on the experimental data, the optimum operating conditions is as follows:

. LHSV = 0.88, Temperature = 410°C, H2/HC ratio = 1000 lt/lt and Pressure = 100 kg/cm2.

Optimal operating conditions can certainly be achieved by variation of other parameter, such as pressure, hydrogen/hydrocarbon ratio and type of catalyst.

Notation

A = is the pre-exponential factor
E = is the activation energy-kcal/mole
k = is the rate constant
R = is the gaseous constant
T = is the absolute temperature — °K

Literature cited

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Table 1
Characteristic of feedstock used

Characteristics		
Boiling range	°C	350–550
Yield on crude oil	wt %	23
Density	$d_{4}15$	0,932
Average molecular weight		425
Viscosity at 98, 90C	cSt	13
Pour Point	°C	42
Sulphur content	wt %	2.8–3.0
Nitrogen content	ppm	900–1100
Asphaltene content	wt %	0.05

Table 2
Operating Condition

Operating Conditions		
Catalyst volume	°C	80
Liquid Hourly Space Velocity		0.42; 0.63 0.88
Pressure	kc/cm^2	100
Temperature	°C	400°; 410°; 420°
Hydrogen to Hydrocarbon ratio	1t/1t	1000
Operating time	hour	200

Table 3
Types and methods of product analysis

No.	Products and type of analysing	
1.	Gas product	
2.	Liquid product	
	Fraction of distillation:	
	IP – 80°	
	Yield	wt %
	Density at 20°C	
	80 – 150°C (naphtha)	
	Yield	wt %
	Density at 20°C	
	Paraffin component	vol %
	Olefin component	vol %
	Naphthene component	vol %
	Aromatic component	vol %
	150 – 250°C (Kerosene)	
	Yield	
	Density at 20° C	
	Aromatic content	vol %
	Smoke point	mm
	250 – 380°C (Gas oil)	
	Yield	
	Density at 20°C	
	Aniline	°C
	Diesel Index	
	380°C	
	Yield	wt %
	Products of dewaxing:	
	Lube	
	Yield	
	Density at 70°C	
	Viscosity at 37.8°C,	cSt
	Viscosity at 98.9°C,	cSt
	Pour point	°C
	Wax	
	Yield	wt %
	Melting point	°C

Table 4
Effect of operating temperature and of Hourly Liquid Space Velocity (LHSV) on the hydrocracked products

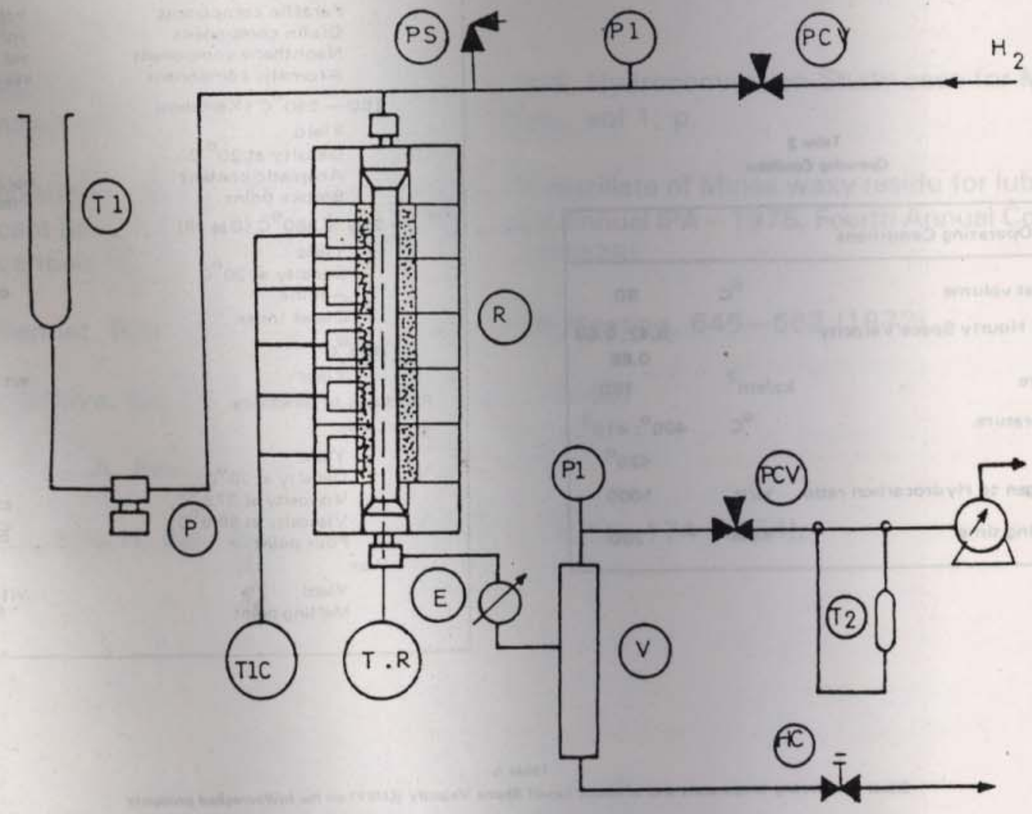
		Operating temperature °C			LHSV		
		400°	410°	420°	0.42	0.63	0.88
Conversion ∠380°C,	wt %	33.66	50.20	62.60	55.11	49.52	33.66
Kerosene (150–250°C),	wt %	8.66	14.25	22.90	16.61	14.75	8.66
Smoke point	mm	15.0	16.0	17.0	21.5	17.0	15.0
Aromatic content	vol %	30.5	28.0	26.0	16.1	24.2	30.5
Gas oil (250 – 380°C),	wt %	20.17	28.90	28.5	28.60	26.79	20.17
Diesel Index		42.5	50.5	56.0	62.0	52.0	42.5
Lube oil	wt %	20.90	20.67	14.03	24.65	20.70	20.90
Viscosity Index		106	116	131	113	118	106
Wax	wt %	45.44	29.13	23.37	20.16	29.78	45.44
Selectivity							
Kerosene + gas oil	wt %	85.65	85.96	82.11	82.04	83.89	85.65

Figure 1

CATATEST UNIT

Working pressure : 150 bars-Working temperature : 550°C

Liquid flow : 750 cc/h-Contact tube capacity : 220 cm^3



E – Condenser
FT – Gas meter
HC – Adjustable flow pump
PCV – Pressure regulator
P1 – Pressure gauge
PSC – Pressure safety valve

R – Contact tube
T1 – Batch
T2 – Sample
TIC – Temperature regulator
TR – Temperature recorder
V – Separator

Figure 2

A plot of log k_1 against $1/T°K$.

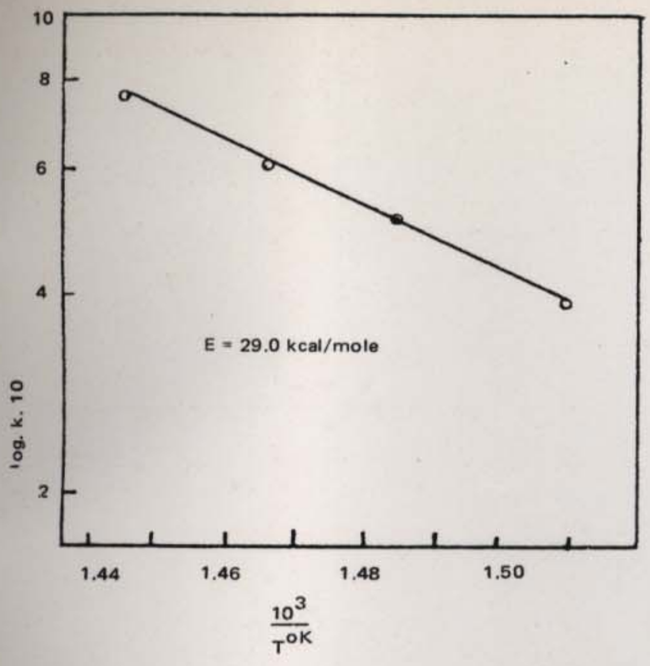


Figure 3

A plot of yield and smoke point against conversion for kerosene product.

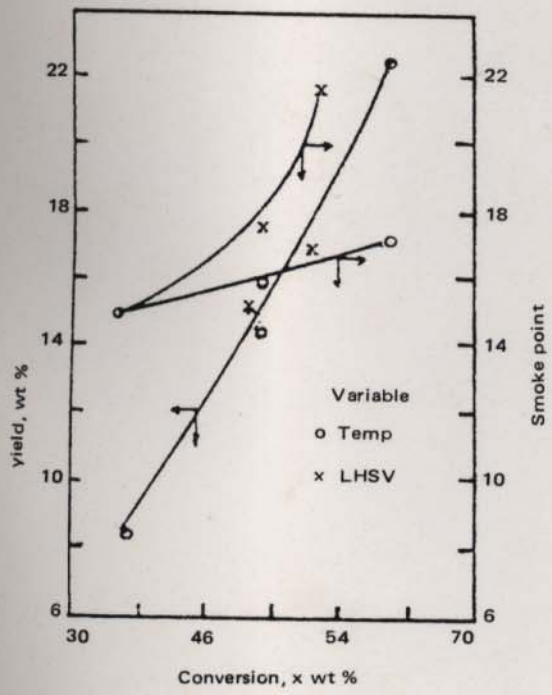


Figure 4

A plot of yield and Diesel Index against conversion for diesel oil product.

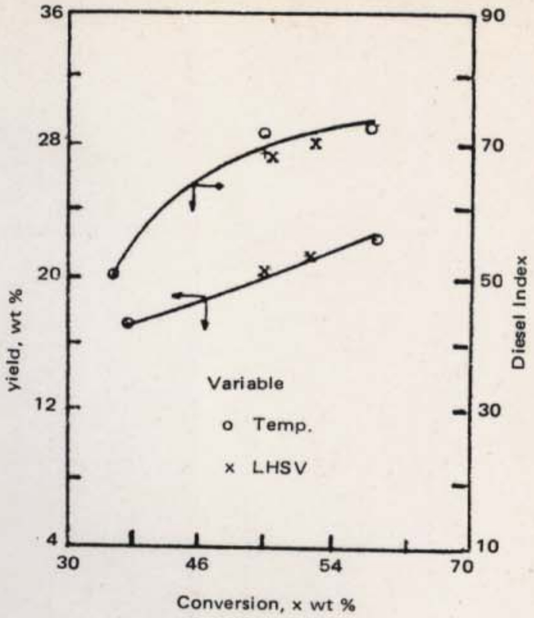


Figure 5

A plot of yield and viscosity index against conversion for lube base stock product.