

1

3,732,156

## PRODUCTION OF LUBRICATING OILS

Robert Neil Bennett, Ashford, England, and Francis John Morum, West Cross, Wales, assignors to The British Petroleum Company Limited, London, England  
No Drawing. Filed May 20, 1971, Ser. No. 145,492  
Claims priority, application Great Britain, June 1, 1970, 26,307/70

Int. Cl. C10g 13/02, 37/10; C01b 33/28  
U.S. Cl. 208—111

7 Claims

### ABSTRACT OF THE DISCLOSURE

Lubricating oil of improved V.I. and also gasoline are produced by partial hydrocracking of a petroleum feedstock boiling above 350° C. at 300–400° C. and 6900–26,700 kN./m.<sup>2</sup>g. using a catalyst of a hydrogenating metal and a decationised faujasite-type zeolite. Less middle distillate is produced than when using non-zeolite catalysts. The use of a decationised faujasite is necessary, a magnesium faujasite catalyst giving no V.I. improvement.

The hydrogenating metal is preferably a platinum group metal and the preferred conversion is 40–95% wt. of product boiling below 350° C. Products, after dewaxing, of 85–125 V.I. can be produced from feedstocks of 60–80 V.I.

This invention relates to the production of lubricating oils by hydrocatalytic treatment.

As conventionally practised the production of lubricating oils requires the steps of solvent extraction to remove aromatics and improve viscosity index, solvent dewaxing to remove n-paraffins and improve pour point and a finishing treatment to improve colour and colour stability. It is known that the solvent extraction step can be replaced by a hydrocatalytic treatment step using a catalyst of one or more hydrogenating metals on a refractory oxide support. Some breakdown of the feedstock is unavoidable in this hydrocatalytic treatment and gasoline, kerosene and gas oils are also recovered. These lower boiling products contain appreciable amounts of middle distillates as well as gasoline, which is of low octane number, and this type of by-product pattern is not always desirable.

The hydrocracking of petroleum fractions, including those boiling in the lubricating oil boiling range, over catalysts of a hydrogenating metal on a zeolite support has also been proposed. The main product is gasoline of reasonable quality with less middle distillate. With this product pattern, the emphasis has been on maximum conversion and very little attention has been paid to the quality of product material, if any, boiling within the lubricating oil range.

It has now been found that certain zeolite catalysts do improve the viscosity index of lubricating oil fractions and that it is possible to produce, by hydrocatalytic treatment both good quality lubricating oil and good quality gasoline.

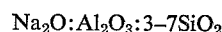
According to the present invention therefore a process for the production of lubricating oil and gasoline comprises contacting a petroleum feedstock boiling above 350° C. at a temperature of 300 to 420° C., a pressure of 6900 to 26,700 kN./m.<sup>2</sup>g. and in the presence of hydrogen with a catalyst comprising a hydrogenating metal and a decationised zeolite of the faujasite type and recovering a product boiling above 350° C. having an improved viscosity index and also a gasoline product boiling below 204° C.

The feedstock to the process is preferably a vacuum distillate boiling within the range 350–600° C. Since lubricating oils are marketed in several grades with relatively narrow boiling ranges, distillation to give relatively

2

narrow boiling range cuts is required at some stage. In the present invention, a wide boiling range cut may be used as feedstock and distillation into narrower cuts given after the hydrocatalytic treatment or distillation may take place before the hydrocatalytic treatment and individual cuts may be hydrotreated. The former route has the advantage of avoiding blocked operation but the latter route has the advantage that optimum hydrotreating conditions may be chosen for each cut. If a vacuum residue fraction is used it should be reasphalted in the normal way.

As indicated above, the nature of the zeolite catalyst is important. The faujasite type zeolite used as starting material preferably has, in its dehydrated form, the formula:



A suitable synthetic zeolite of this type is Zeolite Y. The zeolite is decationised, i.e. a substantial proportion of the metal cations normally present have been removed giving a metal-cation deficiency.

An alternative term in the art is hydrogen zeolite, since it is assumed that when metal cations are removed they are replaced by hydrogen ions. However, since it is not possible to detect the presence of hydrogen ions in zeolites, the precise structure remains in doubt. A cation deficiency can, on the other hand, be readily measured by analysis of the metallic elements present in the zeolite.

This decationisation can be carried out in known manner. Thus, in one common form of decationisation sodium zeolite is base exchanged with ammonium cations. The ammonium form is then heated to drive off ammonia, leaving behind the hydrogen form or decationised zeolite. It is possible that some of the hydrogen ions are also driven off leaving behind free sites in the crystal lattice, but this is not altogether clear. According to the second method the zeolite may be treated with a mineral acid, for example hydrochloric or sulphuric acid, in order directly to decationise the zeolite. A combination of acid treatment and ammonium treatment can also be used.

Preferably the zeolite is decationised to an extent such that at least 50% wt. of the alkali metal cations are absent and more particularly at least 75% wt. It has been known for some time that the presence of alkali metal cations reduces the catalytic activity of zeolites. However, what is surprising in the present context is that other metal cations, which do not impair the hydrocracking activity of the zeolite, nevertheless impair the ability of the zeolite to improve the viscosity index of lubricating oil fractions. Thus one zeolite hydrocracking catalyst uses a magnesium faujasite support and has good activity for cracking and good selectivity for gasoline production. Nevertheless its viscosity index improving characteristics are very much inferior to a catalyst based on decationised faujasite.

The hydrogenating metal on the zeolite is desirably a metal from Groups VI or VIII of the Periodic Table, particularly the latter. Preferably it is platinum group metal, particularly platinum itself or palladium. The metal is preferably added by ion-exchange after decationisation and may be present in an amount of 0.01 to 5% wt., more particularly 0.1 to 2% wt. If present in ion-exchanged form the amount of the metal should obviously not be such as to take up all the metal cation deficiency.

The preferred temperature is 350 to 390° C. and the preferred pressure 10000 to 13,800 kN./m.<sup>2</sup> g. Other process conditions for the hydrocatalytic treatment over the zeolite catalyst may be chosen from the following ranges:

Space velocity, v./v./h.: 0.5 to 3.0 preferably 0.5 to 1.5  
Hydrogen gas rate, mol/m.<sup>3</sup>: 20,000 to 150,000 preferably 25,000 to 100,000

Clearly the conversion should be less than 100% wt. conversion to lower boiling products to give as one prod-

3

uct a lubricating oil fraction boiling above 350° C. The extent of conversion will depend on the relative amounts of gasoline and lubricating oil required and the desired viscosity index of the lubricating oil. Increased conversion increases the viscosity index of the lubricating oil but reduces its yield. The conversion is preferably in the range 40–95% wt. conversion to products boiling below 350° C.

The zeolite catalysts used in the present invention are not permanently poisoned by sulphur and nitrogen compounds in the feedstock, but their activity is lowered. They are also tolerant of H<sub>2</sub>S and NH<sub>3</sub> produced from sulphur and nitrogen compounds by hydrocatalytic treatment, but again these products may reduce the overall activity. It is particularly preferred, therefore, to pretreat sulphur and nitrogen containing feedstocks and to remove H<sub>2</sub>S and NH<sub>3</sub> produced before passing the feedstock to the zeolite catalyst system.

The pretreatment is preferably catalytic hydrogenation. Suitable catalysts comprise one or more hydrogenating metals on compounds thereof chosen from Groups VIA and VIII of the Periodic Table on an acidic refractory oxide support. Suitable metals may be molybdenum together with one or more iron group metals, preferably from 5 to 40% of molybdenum, calculated as the trioxide MoO<sub>3</sub>, and from 1 to 15% of iron group metals, calculated as the divalent oxides (e.g. CoO or NiO). The acidic support may be known catalytic cracking catalyst, for example catalysts of 50–95% wt. of silica and 5–50% wt. of alumina, or a support with more than 50% wt. of alumina and less than 50% wt. of an acidic oxide chosen from oxides or elements of Groups II and III and IV of the Periodic Table, for example boria, silica, titania or zirconia. Thus suitable catalysts may be chosen from the following ranges of composition

	Percent wt.
Ni (as NiO) .....	0–5
Co (as CoO) .....	0–5
Mo (as MoO <sub>3</sub> ) .....	5–30
SiO <sub>2</sub> .....	5–45
Al <sub>2</sub> O <sub>3</sub> .....	45–90

Suitable pretreatment conditions, which are preferably chosen to give minimum breakdown to lower boiling products consistent with adequate sulphur and nitrogen removal, may be chosen from

Temperature, ° C. ....	370 to 460
Pressure, kN./m. <sup>2</sup> gauge .....	6,900 to 20,700
Space velocity, v./v./hr. ....	0.4 to 1.5
Hydrogen gas rate, mols/m. <sup>3</sup> .....	25,000 to 75,000

The product from this pretreatment stage may be de-butanised or topped to about 80° C. before passing to the zeolite catalyst system.

Preferably the sulphur content of the pretreatment stage normally liquid product is less than 500 p.p.m. wt., and the nitrogen content is less than 50 p.p.m. wt. As indicated above H<sub>2</sub>S and NH<sub>3</sub> produced may also be removed in conventional manner. In one hydrocracking system, however the H<sub>2</sub>S and NH<sub>3</sub> are not removed and pass with the pretreatment product to the first of two zeolite catalyst stages, the H<sub>2</sub>S and NH<sub>3</sub> being then removed after the first zeolite catalyst stage. Such a system can be used if desired and, irrespective of whether H<sub>2</sub>S and NH<sub>3</sub> is removed, the zeolite catalyst system can be operated with 2 or more stages. The lubricating oil product can be withdrawn from the system after any of the stages, although clearly, if withdrawn from the first or two zeolite catalyst stages only a portion of the product boiling above 350° C. should be withdrawn as lubricating oil product, the remainder passing to the second stage for further cracking.

The lubricating oil product can be worked up into finished lubricating oil in known manner, e.g. it can be dewaxed and finished with bauxite or clay or by a hydro-

4

finishing treatment. Dewaxing of the feedstock prior to the hydrocracking can be practised but it is not preferred. Starting with wax distillate fractions boiling in the range 350–600° C. and having viscosity indices of 60–80, finished lubricating oil products with viscosity indices of 85–125 can be produced.

The gasoline produced is rich in iso-paraffins and naphthenes and may have a research octane number clear of the order of 85. The amount of middle distillate boiling in the range 200 to 350° C. may be from 5 to 30% wt. of total product, the ratio of 15–200° C. gasoline to 200–350° C. middle distillate being from 1:1 to 10:1.

The invention is illustrated by the following comparative example.

#### EXAMPLE

The feedstock was a Kuwait wax distillate fraction having the following inspection data.

#### ASTM distillation ° C.:

IBP .....	372
5% vol. distilled at .....	456
50% vol. distilled at .....	504
90% vol. distilled at .....	552
FBP .....	578
Specific gravity at 140° F./60° F. ....	0.9079
Sulphur content, percent wt. ....	3.04
Nitrogen content, p.p.m. wt. ....	530
Viscosity index (on dewaxed sample 50) .....	72
Pour point, ° F. ....	100

This feedstock was pretreated over a nickel-molybdenum-silica-alumina catalyst with the following inspection data.

Molybdenum .....	percent wt. ....	11.3
Nickel .....	percent wt. ....	1.8
Silicon .....	percent wt. ....	2.3
Aluminium .....	percent wt. ....	39.3
Pore volume .....	ml./g. ....	0.5
Surface area .....	m. <sup>2</sup> /g. ....	190

The conditions used were:

Temperature .....	° C. ....	393
Pressure .....	kn./m. <sup>2</sup> gauge ..	13,800
Space velocity .....	v./v./hr. ....	0.7
Recycle gas rate (96% volume H <sub>2</sub> ) (scrubbed with water to remove NH <sub>3</sub> ) .....	mol./m. <sup>3</sup> ..	56,400

The product was distilled to remove gas and low boiling hydrocarbon and a portion was analysed to determine the extent of conversion as follows:

#### TBP Distillation:

Product IBP .....	° C. ....	94
IBP–232° C. ....	percent wt. ....	4.5
232–271° C. ....	percent wt. ....	12.8
>371° C. ....	percent wt. ....	82.4

#### Kinematic viscosity of >371° C. fraction at:

100° F. ....	cs. ....	189.7
140° F. ....	cs. ....	31.8
210° F. ....	cs. ....	9.4

Sulphur content .....	p.p.m. wt. ....	220
Nitrogen content .....	p.p.m. wt. ....	32
Viscosity index of >371° C. fraction (on dewaxed sample) .....		87
Pour point .....	° F. ....	105

<sup>1</sup> On dewaxed sample.

The remainder of the product boiling above 94° C. (i.e. free from H<sub>2</sub>S and NH<sub>3</sub>) was passed over a catalyst of palladium on decationised Zeolite Y. For purposes of comparison the same pretreated feedstock was also passed

5

over a catalyst of palladium on magnesium Zeolite Y. Inspection data on the two catalysts were as follows:

	Pd-decati- onised Y	Pd-magne- sium Y
Palladium, percent wt.....	0.53	0.46
Magnesium, percent wt.....	0.03	1.8
Sodium, percent wt.....	0.94	1.25
Silicon, percent wt.....	33.1	25.4
Aluminium, percent wt.....	13.4	17.5
Pore volume, ml/g.....	0.33	0.32
Surface area m. <sup>2</sup> /g.....	676	562

The conditions used and the results obtained with each of the catalysts are set out in Table 1 below:

TABLE 1

	Pd-decationised Zeolite Y				Pd-Mg- Zeolite Y
Hours on stream.....	446-458	514-526	552-564	590-602	625-637
Pressure, kN/m. <sup>2</sup> g.....	10,300	10,300	10,300	10,300	10,300
L.H.S.V., v./v./hr.....	1.0	1.0	1.0	1.0	1.0
Hydrogen gas rate, mol/m. <sup>3</sup> .....	75,000	75,000	75,000	75,000	75,000
Average reactor temperature, ° C.....	350	370	380	390	360
Product recovery, percent wt.....	93	90	85	75	81
T.B.P. distillation data:					
IBP-15° C., percent wt.....	0.3	1.9	2.8	6.9	3.2
15-82° C., percent wt.....	2.8	7.7	16.6	24.4	14.4
82-177° C., percent wt.....	15.7	26.7	30.6	37.1	25.6
177-371° C., percent wt.....	27.1	23.6	22.3	16.7	7.4
Residue >371° C., percent wt.....	54.1	39.8	25.6	12.5	47.3
Solvent dewaxed:					
Residue inspection data:					
Dewaxing yield, percent wt.....	82	85	85	85	87
Yield of dewaxed residue on feed,* percent wt.....	55	44	31	19	45
Kinematic viscosity at 100° F., cs.....	71.85	56.33	46.26	29.43	84.33
Kinematic viscosity at 140° F., cs.....	27.15	22.45	19.18	13.38	30.39
Kinematic viscosity at 210° F., cs.....	8.50	7.54	6.73	5.19	9.16
Viscosity index.....	97	105	108	119	90
Pour point, ° F.....	6	25	10	20	10

\*Yield is on pretreated product >371° C.

The table gives the results on the residue boiling above 371° C. after dewaxing with methyl isobutyl ketone at -18° C.

The results with the decationised Zeolite Y catalyst show that the viscosity indices of the residue boiling above 371° C., after dewaxing, were significantly higher than that of the corresponding, dewaxed, portion of the feedstock (87). The viscosity index increased with increasing conversion being as high as 119 at 390° C. Gasoline yield increased with increasing conversion but the middle distillate yield fell. The 15-82° C. gasoline fraction had a RON clear of 82. The 82-177° C. gasoline fraction had a RON clear of 62.

By contrast the run with the magnesium Zeolite Y catalyst gave only a small increase in viscosity index from 87 to 90. (The decationised Zeolite Y catalyst gave an increase to 95 at 350° C. and to 105 to 370° C., so, by interpolation, the advantage from using the decationised catalyst at the same temperature of 360° C. would have been about 10 numbers).

All viscosity indexes in this specification were obtained using ASTM Test D567. A newer test ASTM D2270 gives different results above 100 VI and had this newer test been used the figures above 100 would have been even higher.

In a further comparative experiment using a catalyst of cobalt and molybdenum oxides on silica alumina (1.75% wt. Co, 12.7% Mo, 9.0% wt. Si) and recovering a dewaxed product boiling above 371° C. with a viscosity index of 119, from a similar Kuwait wax distillate feedstock, the product yield pattern was

	Percent wt.
IBP-15° C. ....	2.77
15-82° C. (RON clear 72) .....	4.72
82-177° C. (RON clear 60) .....	15.45
177-371° C. ....	47.79
Residue >371° C. ....	27.93

6

When using a non-zeolitic catalyst therefore to give a lube oil of 119 VI there is a much greater production of middle distillate and a lesser production of gasoline than when using the decationised zeolite catalyst.

We claim:

1. A process for the production of lubricating oil and gasoline comprising contacting a petroleum feedstock boiling above 350° C. at a temperature of 350 to 420° C., a pressure of 6,900 to 26,700 kN/m.<sup>2</sup> g. and in the presence of hydrogen with a catalyst comprising a hydrogenating metal and a decationised zeolite of the faujasite type so that conversion to material boiling below 350° C. is from 40 to 95% wt., and recovering a product boiling

above 350° C. having an improved viscosity index and also a gasoline product boiling below 204° C.

2. A process as claimed in claim 1 wherein the feedstock is a vacuum distillate boiling within the range 350-600° C.

3. A process as claimed in claim 1 wherein the zeolite is decationised to an extent such that at least 75% wt. of the alkali metal cations are absent.

4. A process as claimed in claim 1 wherein the hydrogenating metal is a platinum group metal present in an amount of 0.01 to 5% wt.

5. A process as claimed in claim 1 wherein the temperature is 350 to 390° C. and the pressure 10,000-13,800 kN/m.<sup>2</sup>g.

6. A process as claimed in claim 1 wherein the feedstock has a viscosity index of 60 to 80 and the product boiling above 350° C. has a viscosity index of 85 to 125.

7. A process as claimed in claim 1 wherein the feedstock contains less than 500 p.p.m. wt. of sulphur and less than 50 p.p.m. wt. of nitrogen.

#### References Cited

##### UNITED STATES PATENTS

3,654,130	4/1972	Voorhies et al. ....	208-57
3,649,518	3/1972	Watkins .....	208-59

DELBERT E. GANTZ, Primary Examiner

G. E. SCHMITKONS, Assistant Examiner

U.S. Cl. X.R.

208-DIG 2, 18