United States Patent Office 3,654,130 Patented Apr. 4, 1972

3,654,130

PREPARATION OF HIGH V.I. LUBE OILS

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No Drawing. Filed Nov. 10, 1969, Ser. No. 875,509
Int. Cl. C10g 23/02, 37/06
U.S. Cl. 208—57 4 Claims

ABSTRACT OF THE DISCLOSURE

High boiling hydrocarbon feeds are converted to high V.I. lube oils in high yields by hydrotreating in a first stage over a hydrogenation catalyst under conditions adapted to saturate the polynuclear aromatic hydrocarbons therein and then hydrocracking in a second stage over a faujasite-base catalyst, such as Pd on H-faujasite, under conditions such that less than 15% conversion to products boiling below 650° F. occurs and polynuclear naphthenes are converted to single ring naphthenes, and paraffins are isomerized to branch-chain structure.

BACKGROUND OF THE INVENTION

This invention relates to the preparation of high V.I. lubricating oils by two-stage hydroprocessing.

The characteristics of satisfactory lubricating oils and specific types of lubricating oils are known in the art. To provide lubricating oils which can be used for known and ever-changing specific purposes and have acceptable characteristics, the refining processes generally require a careful selection of the crude base stock and an elaborate combination of refining steps sufficient to produce the desired product.

It is desirable therefore to be able to supply the demands of the consumer by utilizing as broad a feed spectrum as possible and particularly less desirable feeds in a refining process which minimizes the refining steps necessary to obtain a desired valuable product such as lubricating oil of high V.I. in good yields.

It is known that improved lubricating oils can be prepared by a plural stage hydrogenation process in which lubricating oil fractions are subjected to hydrogenation under different conditions prior to the hydrogenation designed to open the naphthene rings in polycyclic naphthenes. Such a process is taught by U.S. Patent 2,915,452 issued Dec. 1, 1959, to Fear which uses any suitable metallic hydrogenating catalyst in each stage, although cobalt molybdate is preferred.

This process is limited in that its feedstocks are restricted to lubricating oil fractions and the catalysts used in the second stage are insufficiently selective to give a large yield of high V.I. oil.

SUMMARY OF THE INVENTION

It has now been found that high boiling oils from various crude sources may be converted in high yields to high V.I. lubricating oils by subjecting the high-boiling feed to a simple first stage hydrogenation employing conventional catalysts and conditions that maximize hydrogenation of condensed ring aromatics and that minimize hydrocracking of the hydrocarbon feed and hydrogenated product. This is followed by a second stage which employs a faujasite-base catalyst impregnated with hydrogenating components under conditions for selectively converting polycyclic naphthenes to single ring naphthenes and isomerizing any paraffins present and in which conditions are so chosen that less than 15% (preferably less than 10%) conversion to 650° F. and lighter products are obtained.

PREFERRED EMBODIMENTS

The charge oil which is subjected to the hydrogenation according to the invention is a petroleum feedstock having a Saybolt Universal viscosity at 100° F. of at least 50 seconds and more preferably at least 100 seconds. Usually the petroleum oil will not have a viscosity of more than 300 Saybolt Universal seconds at 210° F. Preferably less than 5 volume percent of the charge oil has a boiling point below 700° F.

The first stage hydrogenation is performed at a temperature in the approximate range from 650–725° F. Preferably the pressure is within the approximate range of 1500 to 5000 p.s.i.g. The liquid hourly space velocity (v./v./hr.) is preferably within the range of 0.2 to 2. The hydrogen feed rate is preferably 2000 to 10,000 s.c.f./bbl.

The first stage hydrogenation is necessary in order to convert aromatic compounds, which would otherwise form undesirable products in the subsequent hydrogenation, into compounds which do not form undesirable products in the subsequent step, e.g. polynuclear naphthenes.

The catalyst in the first stage is preferably one or more of the metals cobalt, molybdenum, nickel or tungsten, preferably mixtures such as the sulfides of NiW, NiMo, CoMo, or CoW or mixtures thereof on a carrier such as bauxite, alumina, silica, silica-alumina, etc. A preferred catalyst is the sulfide of NiW on Al_2O_3.

The second stage is carried out under less severe conditions of temperature, preferably between 450 and 650° F. The feed rate should also be higher, being between 0.5 and 5 v./v./hr. Pressure and recycle gas rate are about the same as in the first stage.

During the second stage hydrogenation, conversion to products boiling below 650° F. is kept below 15% (preferably below 10%) while the polynuclear naphthenes are converted largely to single-ring naphthenes, including those polynuclear naphthenes which existed in the original feed stock and those formed in the first stage. As is well known the conversion of polynuclear naphthenes to single ring naphthenes results in a large increase of the V.I. of the product. Also in the second stage the normal paraffins are extensively isomerized to branch chain structure to increase lube yield and to increase the V.I. of the product.

The product effluent of the two-stage process of this invention is separated by distillation into desired fractions, e.g. 320° F. and lighter (if any), 320–550° F., 550–650° F., 650–800° F. and 800° F. and higher. The fraction boiling 650–800° F. may be recycled to the first stage for further V.I. improvement. The 650–800° F. fraction and the 800° F.+ fractions are usually combined and dewaxed to produce the desired high V.I. lubricating oil. Removal of the waxy material in desired amounts is accomplished by any of the well-known techniques used to give desired low pour point oils. Dewaxing to obtain exceptionally low pour points is essential for some lubes and may be accomplished with one or more steps of solvent extraction with a solvent such as propane, methyl ethyl ketone, toluene and others with suitable chilling and filtering between steps followed by recovery of the solvent by distillation. This dewaxing step is part of this invention only to the extent required to obtain desired pour point lube oils.

If desired the combined dewaxed fraction may be further upgraded by treating it with anhydrous HF as described in U.S. 3,463,724 issued Aug. 26, 1969 to Langlois et al. or with any of the treating agents disclosed in Table I of column 4 of said patent or with any other similar treating agent known in the art.

In carrying out this invention any suitable equipment arrangement may be used for contacting the oil with the catalyst in the presence of excess hydrogen in either stage. For example the catalyst may be maintained as one or more fluidized beds, gravitating beds, or fixed beds of small particles, through which the oil and hydrogen are passed, upflow or downflow, concurrent or countercurrent. A slurry of catalyst in oil may also be used. Usually the catalyst is in the form of small pellets or rod-like extrusions contained in a reactor as a plurality of fixed beds and the oil and hydrogen are passed together downflow through the beds at controlled temperature, pressure and flow rates. The effluent is cooled to separate product oil from hydrogen-rich gas which is recycled. Where desired the hydrogen sulfide and ammonia produced in the first stage may be removed from the hydrogen stream prior to processing the lube fraction over the second stage faujasite catalysts system.

The two major differences between the first and second stages are (1) the use of a faujasite-base catalyst in the second stage, impregnated with hydrogenation components, such as the sulfides of Ni-W, Ni-Mo, Co-W, Co-Mo or the platinum group metals; (the preferred catalyst is a noble metal such as platinum or palladium on H-faujasite), and (2) maintaining a conversion of less than 15% to products boiling 650° F. and below. This latter factor is highly important because when the conversion goes above about 15% the V.I. of the 650° F. and higher fraction and particularly the 850° F. and higher fraction decreases substantially.

The new concept of this invention, the method of using it, and the advantages obtained thereby may be best explained and understood by means of the following examples.

Example 1

A mixture (boiling 650° F.+) of 60% deasphalted oil and 40% heavy vacuum gas oil both from a West Texas Sour crude was first processed at non-conversion conditions, 680° F., 2500 p.s.i.g., 0.25 v./v./hr. with 4000 s.c.f. H_2 per bbl. of feed over an Ni-W-Al_2O_3 catalyst (sulfided) to saturate the aromatics present in the feed. The product was stabilized at atmospheric conditions and the stabilized product was passed over Pd on hydrogen-

faujasite catalyst at similar conditions except for temperature and feed rate. The following data were obtained:

	1st stage	2d stage			
		Catalyst			
	Ni-W-alumina	Ni-W-alumina	Pd-H-faujasite		
Run	1	2	3	4	5[1]
Process conditions:					
Temperature, ° F	680	770	500	600	575
Pressure, p.s.i.	2,500	2,500	"	2,500	"
Gas rate, s.c.f./bbl.	4,000	4,000	"	4,000	"
V/v./hr.	0.25	0.53	1.6	2.8	3.6
Lube yield, 650° F.+, wt. percent	95	73.1	93.0	91.7	[2] 70.7 (68.5)
Lube inspections:					
650–800° F. fraction, wt. percent		16.6	9.6	9.7	[2] 11.9
°API		31.3	29.6	29.6	"
V.I. (waxy)		91	76		"
800° F.+fraction, wt. percent		56.5	83.4	82.0	[2] 56.6
°API	28.1	30.5	29.0	31.0	30.0
V.I. (waxy)		114	102	111	93
V.I. (est. on DWO)		102	90	99	81
VSU at 100° F.		620	790	778	1,220
VSU at 210° F.		71.5	89.8	90.0	96.8
N^2, p.p.m.	7	"	"	1.7	"
S, p.p.m.	16	"	"	1.0	"

[1] 800° F.+fraction, from previous 2 runs with Pd on faujasite catalyst, used as feed.
[2] Original feed basis, only 2.8 wt. percent of recycle feed was converted to 650–800° F. lube fraction.

The above data show that very high V.I. oils can be obtained by a two-stage process in which a faujasite-base catalyst is used in the second stage provided the conversion to 650° F. and lighter products be kept under 15%. If a non-zeolitic catalyst is used in the second stage high V.I. oils can be obtained only at a sacrifice in yield. (Compare column 2 with columns 3 and 4.) When the conditions in the second stage are set so that substantial cracking to lighter products occurs both yield and V.I. of the lube oil product decrease (see column 5 as compared to column 2). Obviously the V.I. level of the 650–800° F. fraction can be increased by recycling with the result that the V.I. will be 91 or greater, in which case dewaxing of the combined fractions gives greater overall lube yield of excellent V.I.

The nature and advantages of the present invention having thus been fully set forth and specific examples of the same given, what is claimed as new, useful and unobvious is:

1. A process for producing lubricating oils having a high V.I. from petroleum oil feedstocks which are characterized in that less than 5 volume percent of the oil has a boiling point below about 700° F. as well as having a Saybolt Universal Viscosity at 100° F. of at least 50 seconds which comprises contacting said oil in a first stage with hydrogen and a first stage metallic hydrogenation catalyst comprising metals or sulfide of metals selected from the group consisting of cobalt, molybdenum, nickel, tungsten and mixtures thereof on a non-zeolite carrier selected from the group consisting of alumina and silica-alumina at a temperature of about 650° to 725° F., a pressure within the approximate range from 1500 to 5000 p.s.i.g. and a liquid hourly space velocity within the approximate range from 0.2 to 2 v./v./hr. so as to hydrogenate aromatics contained within said oil to naphthenes and subsequently contacting at least a portion of the product effluent from said first stage in a second stage with hydrogen in the presence of a second stage catalyst which is different than the said first stage catalyst under less severe conditions of temperature and liquid hourly space velocity than are used in the said first stage so that conversion to products boiling below 650° F. in said second stage is below about 15%, said second stage conditions including a temperature of about 450 to 650° F. and a liquid hourly space velocity of about 0.5 to 5 v./v./hr. and said second stage catalyst comprising a faujasite zeolite impregnated with a metallic hydrogenation component comprising metals or oxides or sulfides of metals selected from the group consisting of cobalt,

nickel, molybdenum, tungsten, the Platinum Group metals and mixtures thereof.

2. The process of claim 1, in which the first stage catalyst comprises a sulfided nickel-tungsten on alumina.

3. The process of claim 1 in which the second stage catalyst comprises palladium on the hydrogen form of faujasite.

4. The process of claim 1 in which the second stage catalyst comprises a faujasite zeolite impregnated with the sulfide of a mixture of metals selected from the group consisting of nickel-tungsten, nickel-molybdenum, cobalt-tungsten and cobalt-molybdenum.

References Cited

UNITED STATES PATENTS

2,915,452	12/1959	Fear	208—57
3,494,854	2/1970	Gallagher et al.	208—59

HERBERT LEVINE, Primary Examiner

U.S. Cl. X.R.

208—15, 111, 143, DIG. 2