United States Patent Office 3,044,956 Patented July 17, 1962

3,044,956

PROCESS FOR TREATING PETROLEUM RESIDUALS TO REMOVE METAL CONTAMINANTS

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No Drawing. Filed Aug. 7, 1959, Ser. No. 832,130
5 Claims. (Cl. 208—252)

This invention relates to treatment of petroleum residuals and more specifically the present invention is directed towards upgrading the residuals through hydrocracking.

Ordinary petroleum refining procedures result in heavy hydrocarbon fractions which have relatively little economic value. These heavy materials are known as petroleum residuals boiling primarily above 950° F. and most often are contaminated with metals such as nickel and vanadium. It behooves the refiner to upgrade these stocks to materials of greater value and thus avoid their use or sale as low quality residual fuel.

Due to their low hydrogen content and metal contamination the residuals cannot be blended in large amounts into the distillate streams passing to conventional catalytic cracking units producing large amounts of high octane gasoline as, among other things, the silica-alumina catalysts employed in such units would be severely coked and metal contaminated resulting in shorter catalyst life and greater production of undesirable coke and gas. Accordingly, refiners have considered cracking the heavy residuals by thermal operations or by use of catalysts to obtain gas oils which can more readily be used as cracking stocks in gasoline-producing units. Frequently, the gas oil so obtained is of low quality, i.e. it resists further cracking and contains relatively large amounts of sulfur, nitrogen and other contaminants. To obtain gas oils of better cracking characteristics it has often been proposed to crack the residuals in the presence of free hydrogen and a solid hydrocracking catalyst such as cobalt molybdate alumina but again this type of operation leaves much to be desired.

Present procedures for removing metal contaminants from a crude petroleum either result in a substantial loss of hydrocarbon or concentrate the metal-containing compounds in a particular fraction. One of the means presently used to obtain a gas oil cracking charge substantially free of metal contaminants involves distillation of the crude under conditions which prevent undue entrainment of the high boiling metal-containing nitrogen complexes with the result that the metal contaminants concentrate in the heavy residual fractions. When such residuals are hydrocracked by known procedures the metals become further concentrated in the heavy hydrocracked product which causes pitting and corrosion of burners utilizing this material as fuel and, of course, the increase in metals content makes the product even less useful as a cracking stock.

The presence of sulfur and nitrogen in hydrocarbon oils has long been recognized as undesirable. Nitrogen compounds have a poisoning effect as they tend to reduce or destroy catalyst activity. Sulfur compounds are highly objectionable in hydrocarbon oils as they have an unpleasant odor, tend to corrode and often cause sludging. Various methods have been employed with limited success to overcome these problems such as hydrogenation in the presence of sulfur resistant catalysts.

Previous work exemplified by U.S. Patents Nos. 2,729,593 and 2,744,853 has shown that hydrocarbon oils, containing metal contaminants may be demetallized by the use of iodine, aqueous hydrogen iodide and iodine with hydrogen. Treatment of the oil with iodine in the

absence of hydrogen gives a low yield of demetallized oil, when hydrogen is included the demetallization is wasteful of hydrogen as a result of the high hydrogen consumption by the oil. The latter is caused by the high partial pressures of hydrogen required to achieve good demetallization. If the hydrogen partial pressure is lowered, demetallization is poorer and as the partial pressure approaches zero, the yield of product is greatly reduced due to the formation of insoluble sludge.

An object of this invention is to provide a commercially attractive hydrocracking process which can involve hydrogenation, demetallization, denitriding and desulfurization. In the process a petroleum residual is contacted at elevated temperatures with an essentially anhydrous halogen hydride catalyst of a halogen having an atomic number of 35 to 53, i.e. hydrogen iodide and hydrogen bromide, and in the presence of a hydroaromatic material. As a result we obtain a good yield of gas oil which is a high quality catalytic cracking stock for gasoline-producing units and in addition the produced residual oil boiling primarily above 950° F. is relatively free of contaminants and is, therefore, a good furnace fuel. This residual can even be used directly as a feed stock for high-octane gasoline-producing cracking systems especially when blended with straight-run gas oil distillates. When the residual 950° F.+ fraction is to be used as cracking stock, it might be separated or obtained from the hydrocracking step in admixture with the gas oil produced. Also, the heavy fractions of the product exhibit improved hydrogen content as compared with materials derived by hydrocracking of the corresponding feed stock in the absence of the hydroaromatic compound.

In accordance with the present invention petroleum residuals, which are normally solid at room temperature but liquid at treating temperatures, e.g. reduced crude oils, asphalts, tars, vacuum distillation bottoms, etc., boiling primarily above about 950° F. are contacted with a catalytic amount of hydrogen iodide, hydrogen bromide or mixtures thereof and a hydroaromatic compound under conditions such that there is appreciable hydrocracking of the feedstock to gas oil. These feed stocks normally contain metal contaminants, e.g. upwards of about 40 p.p.m. of NiO and more than about 100 or 150 p.p.m. of V_2O_5, and are frequently of high nitrogen or sulfur content. In the 950° F. plus product obtained the nickel contaminant is usually present in amounts not substantially more than about 25 parts as NiO per million while vanadium is usually not present in amounts in excess of about 50 parts as V_2O_5 per million. Advantageously, the NiO and V_2O_5 are less than about 10 p.p.m. and more desirably less than about 1 or 1.5 p.p.m. The residuum from this process may be further upgraded with selected reagents and due to its low metals content provides a relatively non-corrosive fuel or even a cracking feed stock. The process of this invention thus provides a method for removing nitrogen, sulfur and/or metal contaminants from the products of residual oil cracking and supplies a gas oil of good cracking characteristics. Also, this process unexpectedly reduces expensive hydrogen consumption normally associated with hydrocracking processes. When referring to gas oils, we intend the petroleum distillates boiling primarily above about 400° F. usually having a 50 percent distillation point in the range of about 550 to 750° F. and few, if any, components boiling above about 950° F. Gas oils primarily in the approximate 500 or 650° F. to 950° F. range are especially useful in fluid catalytic cracking units.

The catalyst in our process is essentially hydrogen iodide or hydrogen bromide. These can be added as such to the reaction zone or the corresponding elemental halogen, i.e. bromine, iodine, or other materials which give

halogen hydride can be charged. In any event, the halogen hydride is apparently in equilibrium in the reaction zone with elemental halogen and the catalyst may be predominantly the halogen hydride. The catalyst may be contacted with the residual in any convenient manner. The catalyst selected is employed in a substantially anhydrous form although it may be used in solution with alcohol or other solvents. The amount of catalyst utilized normally depends on the characteristics of the residual treated, for instance, the type and amounts of metal contaminants, and the amounts of nitrogen, sulfur, etc. present. The amount of catalyst employed is generally from about .01 to 3 percent by weight of the residual treated with a preferred amount being about .1 to 2 percent.

The hydroaromatic compound can be contacted with the residual oil to be treated in any suitable manner. The agent may be added to the oil prior or subsequent to the addition of the catalyst to the oil. The amount of hydroaromatic compound employed is generally at least about 20% of the residual feed and usually is in a range of from about 50 to 200 percent by weight of the oil treated. The hydroaromatic material can be added as a relatively pure chemical such as Tetralin or Decalin or in admixture with other materials, particularly hydrocarbons. Also, the hydroaromatic material may be a hydrogenated catalytic cycle oil, a hydrogenated lubricating oil extract or other hydrogenated aromatics including naphthenes obtained by hydrogenation of aromatics or by other means. The hydroaromatic material is a liquid at the conditions of our process and acts as a hydrogen donor. When added in admixture with other hydrocarbons the hydroaromatic is usually at least about 40 or 50%, preferably at least about 75% of the mixture.

During our cracking treatment the temperature is about 750° F. to 950° F. with a preferred temperature being about 800 to 850° F. The pressure may vary widely depending on the particular feed stock undergoing treatment and the temperature employed, but it is essential that substantial cracking and conversion to lighter boiling oils occurs. The pressures will generally be elevated and vary from about 600 to 2000 p.s.i.g., with a preferred pressure being about 800 to 1500 p.s.i.g. Our treatment normally takes from about .5 to 3 hours or longer but it is essential that the conditions of temperature and pressure are such that the particular feed stock undergoes substantial hydrocracking during treatment.

The addition of free hydrogen to our hydrocracking

process is normally advantageous as it can increase the liquid product yield and aid in the hydrocracking. Under normal operating conditions it may be desirable to employ hydrogen preferably at a partial pressure of at least about 100 p.s.i.g. There does not appear to be any particular benefit in providing a hydrogen partial pressure in excess of about 1500 p.s.i.g.; the preferred pressure range being from about 300 to 1000 p.s.i.g.

The process of this invention provides a substantial reduction in hydrogen consumption when compared with the amount normally required in the conventional hydrocracking processes. The hydrogen consumption will usually be no more than about 1000 standard cubic feet per barrel of residual treated. Thus, this process allows for a conversion of at least about 20% of the feedstock to a liquid material boiling below about 950° F. while providing substantial reductions in hydrogen consumption.

The following examples will serve to illustrate this invention without necessarily limiting it.

EXAMPLE I

An asphaltic residual from the vacuum distillation of the bottoms from an atmospheric distillation of petroleum crude oil was contacted with Tetralin at about 800° F. and a pressure range of about 1425 to 1540 p.s.i.g. and a hydrogen partial pressure of 500 p.s.i.g. (room temperature) for a period of about one hour. The residual had the following characteristics: specific gravity, 60/60, 1.0021; Con. carbon 20.54; pentane insolubles 14.40; benzene insolubles .23; viscosity, FV at 210° F., of 787.5; NiO, p.p.m., 82; V_2O_5, p.p.m., 244. An analysis of the residual showed the following components: carbon 86.44%; hydrogen 10.78%; sulfur 1.41%; nitrogen .66% and oxygen .766%. The product characteristics are shown in Table I.

EXAMPLES II TO IV

In these examples, the asphaltic oil feed stock of Example I was treated with our catalyst and in the presence or absence of a hydrogen donor and the product characteristics are shown in Table I.

The pertinent product characteristics and the demetallization conversion and hydrogen consumption data that were obtained in the above examples are shown in Table I which follows. The yield data are given on the basis of the asphalt feed, that is on the basis of removal of the donor from the product.

Table I

Example	I	II	III	IV
Run	931-26	931-29	931-31	931-32
Catalyst charged based on asphalt	None	2% I_2	2% I_2	2% I_2
P.s.i.g. H_2 at room temperature	500	500	500	500
Wt. ratio Tetralin: asphalt	1:1	1:1	1:1	None
Feed	(1)	(1)	(1)	(1)
Temp., ° F.	800	800	750	800
Reaction pressure, p.s.i.g.	1,425–1,540	1,160–1,260	1,030–1,060	890–940
Reaction time, hr.	1	1	1	1
Percent Conv. to 950° F. minus material	43	63.3	29.8	67.6
H_2 Cons. (s.c.f./bbl.) at 60° F.			214	706
Total recovery, wt. percent			99.5	101.3
C_4-, wt. percent			1.0	2.7
$C_5-180°$ F., wt. percent	8	[2]12.6	5.7	[2]15.8
180-370° F., wt. percent	Sample lost			
API gravity	Sample lost	40.5	36.0	53.0
FIA:				
Percent O	do	0.7	6.1	2.7
Percent A	do	30.1	31.1	20.6
Br. No.	do	1.4	2.0	6.5
Mol. Wt.	do	125	175	123
Percent S	do	0.18	0.24	0.04
Percent N	do	0.008	0.01	0.034
Percent I_2	do	0.61	0.53	0.43
370-650° F., Wt. Percent	11	12.0	4.7	21.4
Mol. wt.	220	203	198	204
API gravity	26.8	26.3	26.0	30.5
Br. No.	17.2	6.1	7.4	7.9
FIA:				
Percent O	too dark	54.9	31.0	
Percent A			25.0	

See footnotes at end of table.

Table I—Continued

Example	I	II	III	IV
An. Pt., ° F	123.4	109.9		121
Percent C	86.51	87.96	86.84	87.50
Percent H	11.85	11.48	11.38	12.17
Percent N	0.22	0.09	0.07	0.16
Percent S	1.00	0.54	0.91	0.55
Percent I_2		0.35	1.26	0.74
650–950 ° F., wt. Percent	18	29.5	18.4	27.4
Mol. wt	389	396	Sample lost	423
API gravity	20.1	18.9	do	18.6
Br. No	19.0	16.9	do	31.4
An. Pt., ° F	163.0		do	176.0
Percent C	86.59	87.02	do	87.50
Percent H	11.69	11.14	do	11.39
Percent S	1.04	0.62	do	0.70
Percent N	0.47	0.34	do	0.38
Percent I_2		0.07	do	<0.02
950 ° F.+, wt. Percent	54	32.2	69.2	24.4
Percent C	87.48	87.87	87.55	88.24
Percent H	10.01	10.93	10.98	9.96
Percent S	1.24	0.91	0.76	1.05
Percent N	0.84	0.61	0.46	0.61
Percent I_2		0	0.20	0.02
p.p.m. NiO	113	<0.44	6.8	1.6
p.p.m. V_2O_5	300	0.91	15.4	1.8
Con. Carbon	27.25	22.42	16.46	
Sp. Gr. 60/60	1.0317	1.0350	0.9839	1.0061
C_5 Insol				
Solids, Wt. Percent	3	4.5	1.0	8.0
Percent Ni	.011	0.147	0.264	.091
Percent V	.008	0.293	0.594	.180
Percent I_2		0	trace	0.63
Percent N	0.88	3.81	7.24	2.62

[1] Asphaltic feed same in all examples.
[2] Analysis is for IBP-370° F. fraction.

Examples I, II and IV can be compared since they were conducted at 800° F.; the lower pressure in Example IV was due to the absence of donor. Example I which lacks the catalyst but had the donor gave a lower conversion to gas oil and poorer metals, sulfur and nitrogen removal. When Example IV, having the catalyst but no donor, is compared with Example II conducted in accordance with our invention, it is seen that Example IV gave materially less metals removal, particularly as the amount of metals reported in the 950° F.+ fraction of Example II could permit use of the material as catalytic cracking feed stock while the metals content of the same fraction of the product in Example IV would make the fraction much less suited for this use. Moreover, the solids from the run of Example IV was almost double that of Example II. Also, the sulfur and nitrogen removal in Example II was better than in Example IV and the 950° F.+ product from the former had almost 10% more hydrogen which, along with the low metals content, should give good cracking characteristics.

We claim:

1. A process for treating petroleum residuals boiling primarily above 950° F. and containing metal contaminants consisting essentially of contacting under essentially anhydrous conditions said residual in a zone under hydrocracking conversion conditions so that there is a conversion of at least about 20 percent of said residual to liquid products boiling below about 950° F., at a temperature from about 750° F. to 950° F. and at a hydrogen partial pressure of at least about 100 p.s.i.g. with a catalytic amount of halogen hydride of a halogen having an atomic number from 35 to 53 and with a hydroaromatic material in an amount of at least about 20% based on the residual, and separating from the hydrocracked product a gas oil fraction and a material boiling primarily above about 950° F.

2. A process for treating petroleum residuals boiling primarily above 950° F. and containing metal contaminants consisting essentially of contacting under essentially anhydrous conditions said residual in a zone under hydrocracking conversion conditions so that there is a conversion of at least about 20 percent of said residual to liquid products boiling below about 950° F., at a temperature from about 750° F. to 950° F. and at a hydrogen partial pressure of at least about 100 p.s.i.g. with a catalytic amount of hydrogen iodide and with a hydroaromatic material in an amount of at least about 20% based on the residual, and separating from the hydrocracked product a gas oil fraction and a material boiling primarily above about 950° F.

3. A process for treating petroleum residuals boiling primarily above 950° F. and containing metal contaminants consisting essentially of contacting under essentially anhydrous conditions said residual in a zone under hydrocracking conversion conditions so that there is a conversion of at least about 20 percent of said residual to liquid products boiling below about 950° F., at a temperature from about 800 to 850° F. and at a hydrogen partial pressure from about 300 to 1000 p.s.i.g., with a halogen hydride of a halogen having an atomic number from 35 to 53 which is present in amounts of from 0.01 to 3 percent of the residual and with a hydroaromatic material which is present in an amount of from 50 to 200 percent of the residual and separating from the hydrocracked product a gas oil fraction and a material boiling primarily above about 950° F.

4. The process of claim 3 where the hydroaromatic compound is Tetralin.

5. A process for treating petroleum residuals boiling primarily above 950° F. and containing metal contaminants consisting essentially of contacting under essentially anhydrous conditions said residual in a zone under hydrocracking conversion conditions so that there is a conversion of at least about 20 percent of said residual to liquid products boiling below about 950° F., at a temperature from about 800 to 850° F. and at a hydrogen partial pressure from about 300 to 1000 p.s.i.g., with hydrogen iodide which is present in amounts of from 0.01 to 3 percent of the residual and with a hydroaromatic material which is present in an amount of from 50 to 200 percent of the residual and separating from the hydrocracked product a gas oil fraction and a material boiling primarily above about 950° F.

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UNITED STATES PATENTS

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