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G. H. CLOUD

2,366,490

PRODUCTION OF DIESEL FUELS

Filed Feb. 18, 1942

2 Sheets-Sheet 1

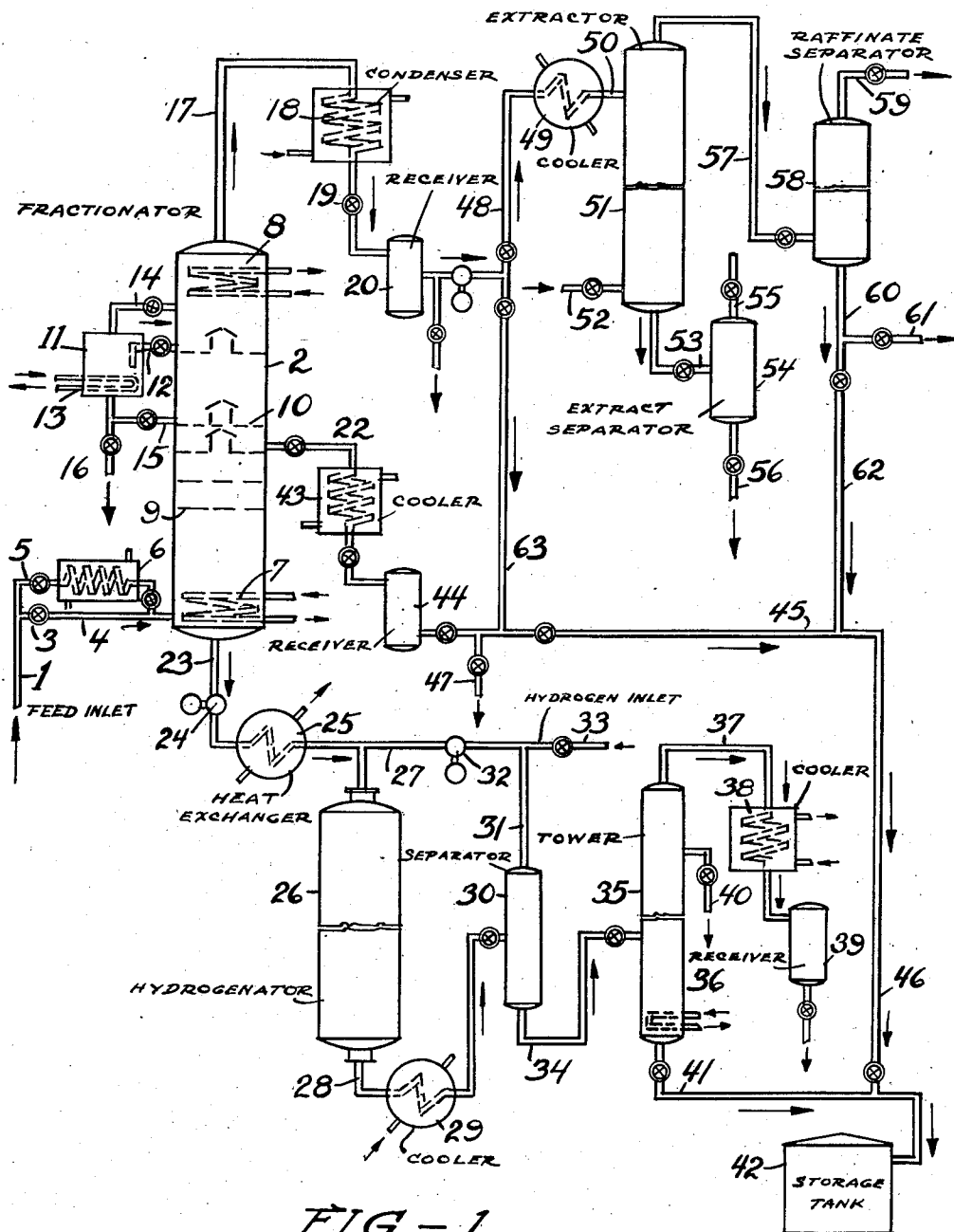


FIG. -1

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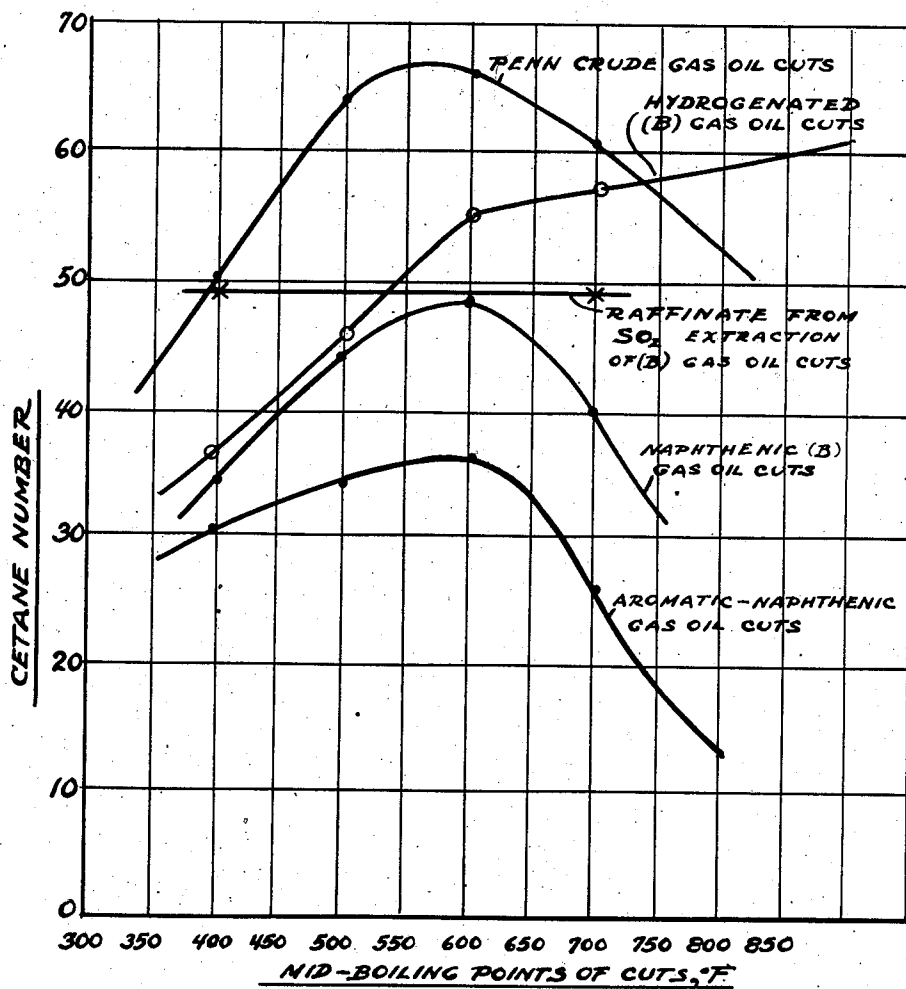


FIG.-2

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UNITED STATES PATENT OFFICE

2,366,490

PRODUCTION OF DIESEL FUELS

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4 Claims. (Cl. 196-13)

This invention relates to a method for preparing high ignition quality Diesel fuels.

In order to insure continued development of Diesel engines, it is essential to have methods for economically making available larger quantities of fuels having high ignition quality. Straight run gas oil distillates from highly paraffinic crudes meet the requirements of modern Diesel engines, but it has become increasingly difficult to obtain the straight run distillates of high ignition quality for it requires diversion of the paraffinic base gas oils from their use as superior cracking stocks in the preparation of high anti-knock gasolines. Also, the high cetane paraffinic stocks available have high cloud and pour points which hamper their use in areas where temperatures drop much below the freezing point of water. On the other hand, more abundant types of crude oils and cracked distillates are too low in ignition quality, with cetane numbers in the range of 30 to 45, to meet even current recommendations of Diesel engine manufacturers.

The refiner of Diesel fuels is confronted with the problem of providing Diesel fuels which meet the requirements of ignition quality and at the same time have high heating values in terms of B. t. u. per gallon in order to put the operation of a Diesel engine at its best advantage in fuel economy.

The present invention is concerned with a treatment of petroleum gas oils to obtain efficiently therefrom Diesel fuels of highly improved ignition quality, high heating value, and low pour points.

Although there has been a good deal of investigation of special refining processes, such as solvent extraction and hydrogenation for obtaining improved Diesel fuels, these processes have been given only limited application commercially on account of their costliness. Solvent extraction, as it hitherto has been recommended for application to Diesel fuels, results in high treating losses. Most of the aromatic extract obtained in a selective solvent extraction of a total gas oil distillate has very little practical value in commercial products, being usable only in low price products, such as bunker fuel oil. Hydrogenation, as it has been proposed, was found to be excessively expensive for the improvement gained

considering the cost of hydrogen and equipment used.

In accordance with the present invention, it has been found that certain selected fractional cuts of petroleum gas oils respond best to a solvent extraction, others more advantageously to a hydrogenation, while still others practically require neither treatment in achieving the object of economically preparing the improved Diesel fuels.

The definition of the term gas oil as used herein conforms with the authoritative A. S. T. M. designations (D288-28T and D288-36T), and is descriptive of a liquid petroleum distillate having a viscosity and boiling range intermediate between kerosene and lubricating oil.

The procedure of the invention will be described with reference to the accompanying drawings which illustrate a diagrammatic flow plan of a plant for carrying out the desired steps, as shown in Fig. 1.

Referring to the drawings, a gas oil distillate or fraction is represented as passing from feed inlet 1 into a fractionator 2. The gas oil fraction charge may be in the form of vapors directed past valve 3 thru line 4 into the fractionator, or the gas oil may be in the form of a distillate which may be directed past valve 5 with valve 3 closed, then thru preheater 6 into the fractionator.

The fractionator 2 is of any conventional type for making a fairly close fractionation of the gas oil fraction into a number of cuts. The fractionator may be equipped with a heating coil 7 or similar reboiling means at its base and with a cooling coil 8 or similar condensing means in the uppermost section. In the interior of the fractionator are disposed baffle plates 9 and reflux condensate collecting pans 10 or equivalent means for dephlegmation of the gas oil vapors ascending in the fractionator. Also, there may be attached to the fractionator a side stream stripper 11 to receive a side stream from line 12 and with a heat exchanger 13 for making a closer fractionation of an individual cut. The vapors separated in the stripper may be returned therefrom to the fractionator by valve control line 14 and the stripped condensate may be returned to another part of the fractionator as, for example, thru line 15, or be withdrawn thru line 16.

The lowest boiling cut of the gas oil may be withdrawn from an upper part of the fractionator and, as illustrated, may be withdrawn from the fractionator as an overhead vapor thru line 17 to be conducted to the condensing coil 18 and from there be led thru valve 19 into receiver 20. For the present purposes, the lowest boiling cut of the gas oil, such as collected in receiver 20, should boil predominantly below 550° F. It may be cut to have an end boiling point in the range of about 450° F. to 550° F., and in some instances, somewhat higher.

The side stream stripper 11 may be used to separate a stripped fractional condensate boiling in the range of about 450° F. to 550° F.

An intermediate reflux condensate boiling preferably in the range of about 550° F. to 650° F. may be withdrawn from the fractionator as a side stream thru line 22.

The heaviest cut of the distillate boiling above about 600° F. and predominantly from about 600° F. or 650° F. to 750° F. may be withdrawn from the bottom section of the fractionator thru line 23.

As will be later shown, it is highly desirable to separate from the total gas oil distillate the described heavy cut boiling above 600° F. for hydrogenation because this heavy cut is the most responsive to the hydrogenation treatment for improvement.

The fraction of the gas oil distillate boiling below 550° F. has relatively low ignition quality and does not respond satisfactorily to hydrogenation, but is the most suitable part of the gas oil distillate for treatment by solvent extraction for a good increase in cetane number by removal of aromatic compounds.

The heart cut or intermediate reflux condensate boiling in the range of 550° F. to 650° F. is given the least improvement by either solvent extraction or hydrogenation.

To proceed with the treatment of the heavy gas oil cut withdrawn from the base of fractionator 2 thru line 23, this material is passed by pump 24 thru heat exchanger 25 for regulating the temperature of the oil as it is conducted into the hydrogenation reactor 26. This reactor is made to contain a suitable hydrogenation catalyst for contact with the oil in the presence of hydrogen supplied by line 27.

Suitable conditions for the hydrogenation are as follows: The reaction mixture is maintained at a temperature in the range of about 700° F. to 850° F. and under a superatmospheric pressure ranging from 50 to about 250 atmospheres. Hydrogen gas is supplied to the reactor at the rate of about 4,000 to 15,000 cu. ft./bbl. of oil. The contact catalyst is of the type immune to sulfur poisoning and comprises an oxide or sulfide of the 6th group metals, usually chromium, molybdenum, or tungsten, alone or mixed with oxides or sulfides of other metals, such as nickel sulfide, zinc oxide, magnesium oxide, aluminum oxide, and the like. The space velocity is from about 1 to 3 volumes of liquid oil per unit volume of catalyst per hour. As the temperature is increased, the space velocity in general is proportionately increased. The reaction is predominantly a hydrogenation but a small amount of conversion to lower boiling hydrocarbons may occur, but it is preferred to restrain the splitting reaction so that less than about 10% of lower boiling hydrocarbons are formed from the heavy gas oil cut in the hydrogenation.

The products are withdrawn from the reactor

thru line 28 to be passed thru a cooler 29 into a gas separator 30. Hydrogen gas from the separator is recycled by line 31 and booster pump 32. Make-up hydrogen gas is added thru line 33. The separated liquid products are withdrawn from the separator thru line 34 to be discharged into a rerun fractionator 35 for removal of low boiling products. At the base of fractionator 35 is a re-boiling heat exchanger 36. Overhead vapors are led from the fractionator thru line 37 into the condenser coil 38, thence to receiver 39. A side stream may be removed from the fractionator thru line 40. The high boiling hydrogenated product is withdrawn from the fractionator by line 41 to be sent therethru to storage tank 42.

The intermediate high ignition quality fraction of the gas oil withdrawn as a side stream from fractionator 2 is run by line 22 into cooling coil 43 and from there into the receiver 44. Any desired amount of this intermediate cut may be passed by lines 45 and 46 to be combined with the hydrogenated heavy cut. Any remaining amount of the intermediate cut may be withdrawn for separate storage by line 47.

Any desired portion of the light fraction of the gas oil separated in fractionator 2 and collected in receiver 20, as described, may be passed thru line 48 by pump 49 thru a pre-cooler 49 and by line 50 into extractor 51. A selective solvent is fed into the extractor by line 52. The extract phase is withdrawn from the extractor by line 53 into a separator 54. Vapors of the solvent are removed from the separator 54 by line 55 and extracted hydrocarbons are withdrawn from the separator 54 by line 56 to be sent to another unit for processing in order to recover useful high anti-knock gasoline or solvent ingredients which are highly aromatic. The raffinate is removed from the extractor by line 57 to separator 58 for complete removal of extracting solvent which is led away from the separator 58 thru line 59. The purified raffinate may be removed by withdrawal line 60 to be run to storage by line 61 and any desired portion thereof may be sent thru lines 62 and 46 for blending with the intermediate gas oil cut and with the heavy hydrogenated oil. If the high degree of improvement obtained thru the solvent extraction of the light cut is unnecessary, and nevertheless if it is desired to lower the viscosity of the final Diesel fuel product, any desired amount of the light cut may be sent from receiver 20 by way of lines 63, 45, and 46, to be mixed with the hydrogenated heavy cut.

For the solvent extraction of the light gas oil cut, either a vapor-liquid or liquid-liquid extraction may be employed, but it is generally more convenient to employ the latter, using liquefied sulfur dioxide or similar selective solvents, such as furfural, glycol ethers, or the like. As an illustration of the solvent extraction procedure, the light gas oil distillate is intimately contacted in an extraction vessel as, for example, in a countercurrent extractor tower illustrated in the drawing at a temperature sufficiently low to maintain the solvent in liquid phase, for example, in treating with liquid SO₂, the temperature was maintained at about 0° F. to 20° F. The extract mixture of the solvent and extract in solution gravitates to the bottom of the extractor, and in the extract separator the solvent is expelled by vaporization. The separated solvent may then be recovered for recycling. The raffinate mixed with a relatively small amount of the solvent is freed of the solvent in the separator 58.

Pertinent data on various gas oil distillates and their fractionated cuts are summarized in the following table:

TABLE 1

A = typical straight run paraffin base (Penna.) gas oil
B = typical straight run naphthenic base gas oil
C = typical cracked gas oil

	Boiling range, ° F.	Aniline point, ° F.	° A. P. I. gravity	B. t. u. per gal.	Conradson carbon, per cent	Saybolt U. vis. @ 100° F.	Cetane number	Pour point, ° F.
A cuts:								
(1)-----	350-450	153	47.6	132,000	.03	30.0	51	0
(2)-----	450-550	171	44.2	134,500	.02	35.0	64	0
(3)-----	550-650	188	37.6	137,700	.01	46.0	87	30
(4)-----	650-750	206	32.0	141,000	.07	122.0	61	25
A total-----	350-750	182	39.7	137,700	.03	39.0	63	10
B cuts:								
(1)-----	350-450	127	39.4	136,000	.01	30.0	34	0
(2)-----	450-550	134	32.5	141,400	.04	36.0	44	0
(3)-----	550-650	138	26.5	144,400	.06	51.0	47	0
(4)-----	650-750	152	20.8	148,380	.39	220.0	40	5
B total-----	340-750	136	28.9	142,500	.08	43.0	40	0
C cuts:								
(1)-----	350-450	119	36.3	139,000	.01	31.0	31	0
(2)-----	450-550	120	28.3	142,800	.07	37.0	33	0
(3)-----	550-650	112	21.0	148,300	.67	57.0	37	0
(4)-----	650-750	120	14.8	151,380	.67	376.0	26	0
C total-----	440-760	115	23.2	146,500	.11	48.0	28	0

The foregoing inspection data illustrates how in all common varieties of gas oils the heart cut boiling within the approximate limits of 550° F. to 650° F. has been found superior to other portions of the gas oil in ignition quality and to compare favorably with the other portions on heating value and low carbon residue formation. Although the heaviest cut boiling above about 600° F. has the best heating value, in general it forms carbon residue to the greatest extent, has a relatively low ignition quality, and is high in pour point. The lightest cut also has very low ignition quality.

The relationship between the boiling points of the various gas oil components and their ignition quality is brought out graphically in the chart of Fig. 2. In this chart are shown the cetane numbers corresponding to the mid-boiling points of separate cuts derived from the three typical gas oils on which inspection data is given in Table 1. Also, in this chart is shown the relationship of cetane number to boiling points of representative hydrogenated type B gas oil cuts and of raffinate fractions from an SO₂ extraction of the B type crude gas oil.

The relationship between ignition quality and volatility is strikingly changed when the cuts of the gas oil have been hydrogenated as is shown in the following tabulated data for a representative gas oil originally of type B (mixed naphthene base crude):

TABLE 2

Hydrogenated gas oil cuts from mixed-naphthene base crude (B)

	Boiling range, ° F.	° A. P. I. gravity	B. t. u. per gal.	Conradson carbon, per cent	Saybolt U. vis. @ 100° F.	Cetane number	Pour point, ° F.
Cuts:							
(1)-----	350-450	41.0	135,000	.002	30.0	37	0
(2)-----	450-550	36.0	138,800	.001	35.0	44	0
(3)-----	550-650	32.9	142,000	.001	50.0	55	0
(4)-----	650-750	33.0	142,300	.02	83.0	57	-5
Total-----	375-715	35.7	140,400	.02	39.0	51	0

The data in Table 2 proves how the heaviest cut of a gas oil responds best to improvement by hydrogenation and how the lighter cuts are not very susceptible to improvement by hydrogenation.

As a matter of fact, the improvement of the lightest cuts by hydrogenation is too small to be worth the expense.

TABLE 3

Hydrogenated naphthene base gas oil cuts

Hydrogenated cut	Boiling points, ° F.			Cetane number
	Initial	Mid	Final	
80% overhead-----	412	474	566	46
85% overhead-----	412	478	580	47
90% overhead-----	418	486	596	47
95% overhead-----	418	486	618	48
80-85% overhead cut-----	576	590	610	58
85-90% overhead cut-----	588	610	630	59
90-95% overhead cut-----	604	642	662	59
Total hydrogenated gas oil-----	408	493	682	49

Thus it can be seen that the heaviest fraction amounting to between about 10% to 30% of a gas oil is given a maximum improvement in ignition quality by hydrogenation. The lightest overhead cuts of a gas oil are given very little, if any, improvement in ignition quality by hydrogenation. These facts clearly indicate that there is a considerable advantage to be gained in subjecting the heaviest fraction alone to hydrogenation and eliminating the expense of hydrogenating the lower boiling fractions of the gas oil. Moreover, by restricting the hydrogenation to the heaviest cuts of gas oils, one obtains gas oil fuel components of highest heating value from the part of gas oil which in many instances is not adapted for use in a Diesel fuel on account of its high

carbon residue formation and tendency to foul the engine. Also, hydrogenation of the naphthenic heavy stock does not appreciably increase its pour point.

Results on the solvent extraction of different cuts fractionated from gas oils are illustrated by the following example:

EXAMPLE

A type "B" gas oil was fractionated to obtain light and heavy cuts. Extractions of the total gas oil and of the cuts were carried out with liquefied SO₂, phenol, and furfural solvents. Representative specific results from an SO₂ extraction using 85% by volume of solvent at temperatures in the range of about 14 to 20° F. were obtained as shown in the following tabulated data:

TABLE 4

Solvent treated gas oil cuts from mixed naphthene base crude (B)

Diesel fuel tested	Raffinate yield, per cent	Cetane number
Initial untreated B gas oil.....		40
Raffinate of total gas oil.....	80.0	49
Raffinate of lowest boiling fraction.....	79.1	50
Raffinate of highest boiling fraction.....	77.9	49

From a comparison with representative results in Table 1 and Fig. 2, it can be seen that the lowest boiling fraction of the gas oil responds to the solvent treatment far better than the highest boiling fraction for ignition quality improvement. The cetane number gained for the lightest fraction amounts to about 15 cetane numbers whereas for the highest boiling cut the cetane number gain is hardly significant, particularly in comparison to the improvement by hydrogenation; and on the heart cut, the solvent treatment gives no practical improvement.

By correlating the foregoing results, it becomes evident that with the procedure of the present invention, a gas oil is improved with considerable advantage if it is first divided into cuts so that the lightest cut of the gas oil may be subjected to the solvent extraction and the heaviest cut may be subjected to hydrogenation, while the middle cut, if desired, may be left untreated or be subjected to any other suitable treatment.

This invention makes commercially feasible the preparation of superior Diesel fuels from all types of gas oil distillates which are petroleum fractions boiling intermediate kerosene and lubricating oil. In general, the gas oil distillates have boiling ranges of from about 350° F. to 750° F. The distillates to be processed may be procured from paraffin base, naphthene base, asphalt base, or mixed base crudes by straight distillation. They may be obtained as reflux condensates from cracking processes provided the cracking is not so severe as to excessively degrade the gas oil by making it extremely aromatic. From practical considerations, the best results are obtained by treating gas oils having aniline points within the approximate limits of 100 to 175, which includes the usual run of gas oils derived from naphthene base crudes, mixed base crudes, some asphalt base crudes, and many recycle oils from cracking units.

It is to be understood that the gas oil cuts treated by the method described to obtain an improved Diesel fuel may be derived from a number of gas oil distillates; for example, the paraffin base intermediate gas oil cut may be combined with a hydrogenated heavy cut from a naphthene base gas oil. The distillation characteristics of gas oils may vary somewhat depending upon the exact type of fractionating device

and the particular kind of oil distilled, so that the initial and end boiling points of the gas oils and of their fractions are variable to some degree.

In commercial distillation practice, it is to be expected that the boiling range of one cut overlaps to some extent the boiling range of an adjacent cut. For instance, the heart cut of the gas oil in general has a mid-boiling point within the limits of about 550° F. to 600° F. but the initial boiling point of this cut may be regarded to be as low as 500° F. and its end point as high as 650° F. As a rule, the mid-boiling point of the heart cut tends to be closer to 600° F. for oils of relatively low aniline point, whereas for oils of relatively high aniline point the heart cut of maximum cetane number has a mid boiling point closer to 550° F. The proportion of the heart cut varies and increases in quantity with increase in the aniline point. As already indicated, a point is reached at which less advantage is obtained in separating out the heart cut and it is better to divide the gas oil into only two fractions for improvement, i. e., a light fraction for solvent extraction and a heavy fraction boiling above 600° F. for hydrogenation. The isolation of the heart cut with separate treatments of the lighter and heavier cuts is most advantageous when the gas oil has an aniline point in the range of about 130° F. to 175° F.

With the present procedure, less than about 30% of a typical gas oil requires improvement by solvent extraction. Characteristically, from about 80% to 95% of the light gas oil fraction subjected to the solvent extraction treatment boils within the range of 450° F. to 550° F., and this light fraction may be identified, also, as having a mid-boiling point within the limits of 450° F. to 550° F. The heart cut fractions having peak cetane numbers which make them suitable for use without solvent extraction treatment often comprise from about 20% to 30% of the total gas oil. Thus, the present procedure makes it possible to obtain the desired high ignition quality Diesel fuels with greatly reduced expense of treatment. Furthermore, with the described operations, the resulting Diesel fuels have satisfactory high flash points and proper viscosities to meet all common specification requirements, such as a minimum flash point of 150° F. and S. U. viscosity ranging from about 32 to 75 seconds at 100° F.

Following the preparation of the Diesel fuel by the selective treatments described, there may be incorporated into the fuel various addition agents, such as ignition promoters, cold starting agents, pour point depressants, viscosity modifiers, dyes, corrosion inhibitors, anti-oxidants, or other additives which serve to improve various qualities of the fuels.

It is not intended that the invention be limited to the specific examples given for the sake of illustration. Modifications which come within the spirit of the invention are intended to be included within its scope.

I claim:

1. In a process of producing a Diesel fuel of high ignition quality, the steps comprising separating a petroleum gas oil into a light fraction, an intermediate fraction, and a heavy fraction, removing aromatic hydrocarbon components of the light fraction by selective solvent extraction, hydrogenating the heavy fraction, and combining the light fraction separated from aromatic components with said intermediate fraction and with the hydrogenated heavy fraction.

2. In a process for preparing a Diesel fuel of high ignition quality, the steps comprising fractionating petroleum gas oil to separate therefrom a light fraction boiling below 550° F. and a heavy fraction boiling predominantly above 600° F., treating said light fraction with a selective solvent for aromatic hydrocarbons to obtain a raffinate of increased cetane number, hydrogenating said heavy fraction to obtain a hydrogenated heavy gas oil fraction boiling above 600° F. of increased cetane number, and combining said raffinate with said hydrogenated heavy fraction to obtain the Diesel fuel.

3. A process for preparing a Diesel fuel of high ignition quality, high heating value, and low pour point, which comprises fractionating naphthene base petroleum gas oils which have aniline points in the range of about 130° F. to 175° F. into light fractions boiling below 550° F., intermediate fractions boiling in the range of 500° F. to 650° F., and heavy fractions boiling above 600° F., removing aromatic components of the light frac-

tions by selective solvent extraction, hydrogenating the heavy fractions, and combining a portion of the light fractions, separated from extracted aromatic components thereof, with a portion of said intermediate fractions and a portion of the hydrogenated heavy fractions.

4. In a process for preparing a high quality Diesel fuel, the steps which comprise fractionating from petroleum gas oil having an aniline point in the range of 100° F. to 175° F. and a mid-boiling point in the range of 550° F. to 650° F. a light fraction boiling below 550° F. and a heavy fraction boiling above 600° F., treating said light fraction with a selective solvent for aromatic hydrocarbons to obtain a raffinate of increased cetane number, hydrogenating said heavy fraction to obtain a hydrogenated heavy gas oil fraction boiling above 600° F. of increased cetane number, and combining said hydrogenated heavy gas oil fraction with said raffinate to obtain the Diesel fuel of high quality.

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