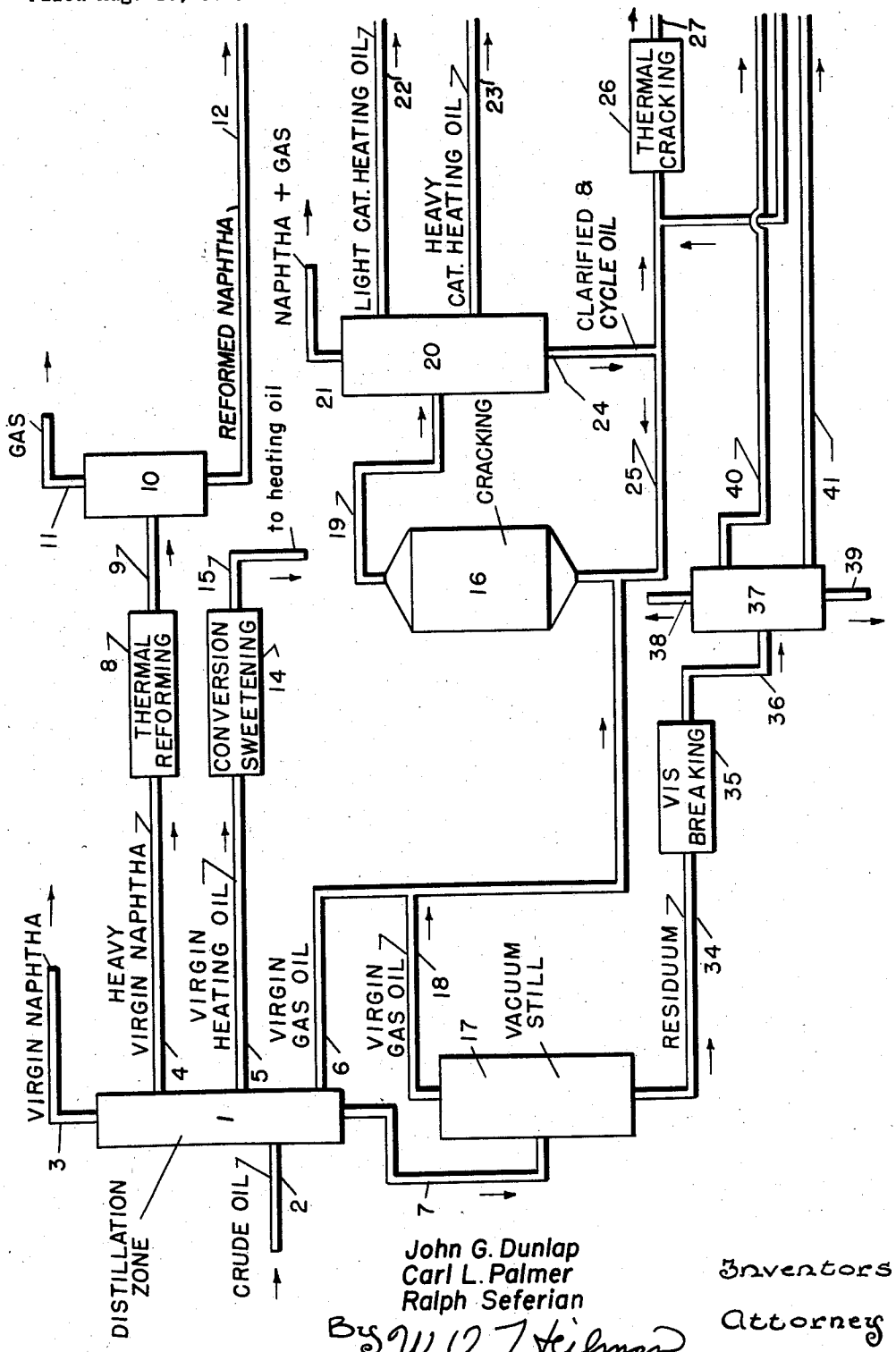
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INTEGRATED HYDROFINING PROCESS

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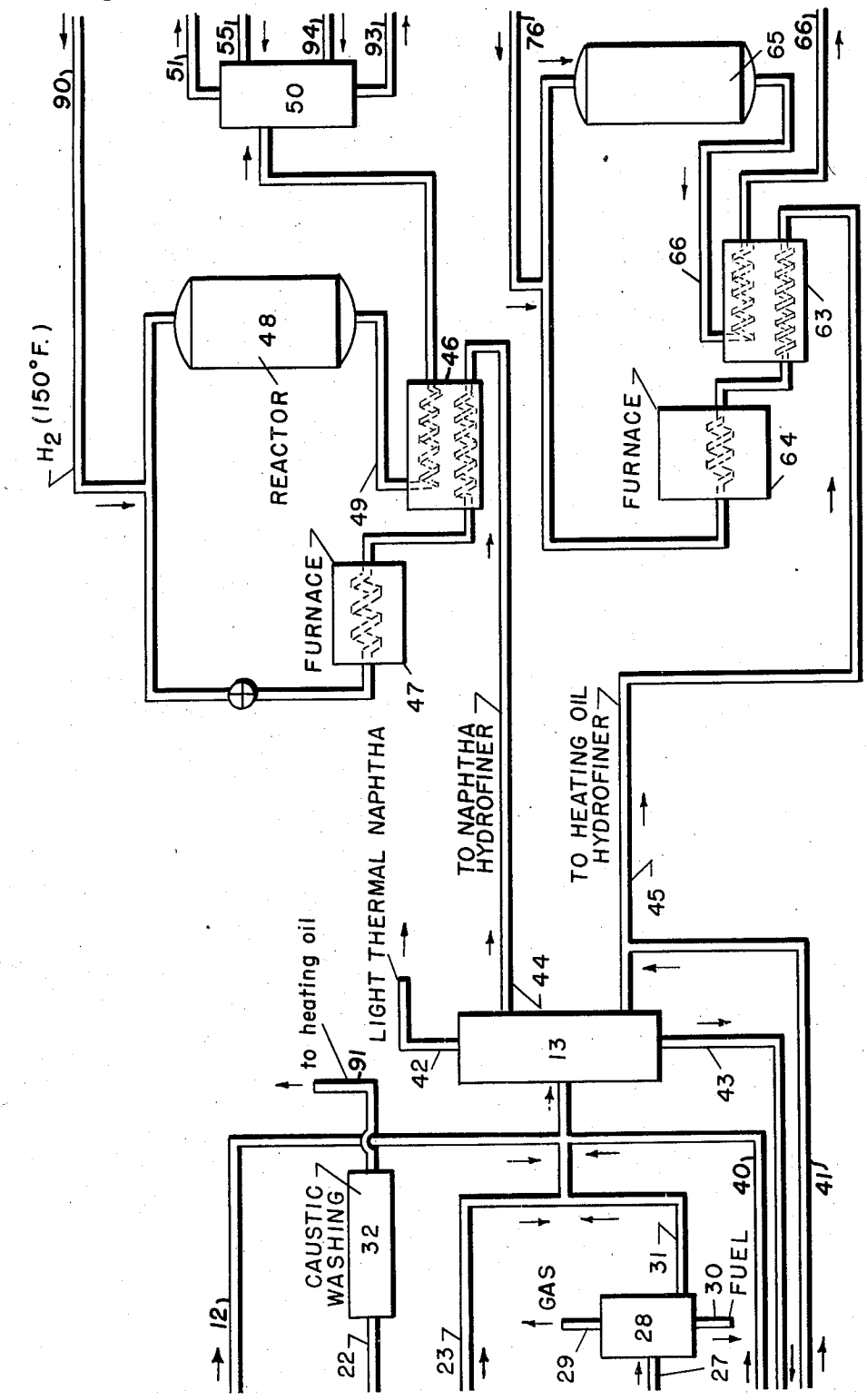
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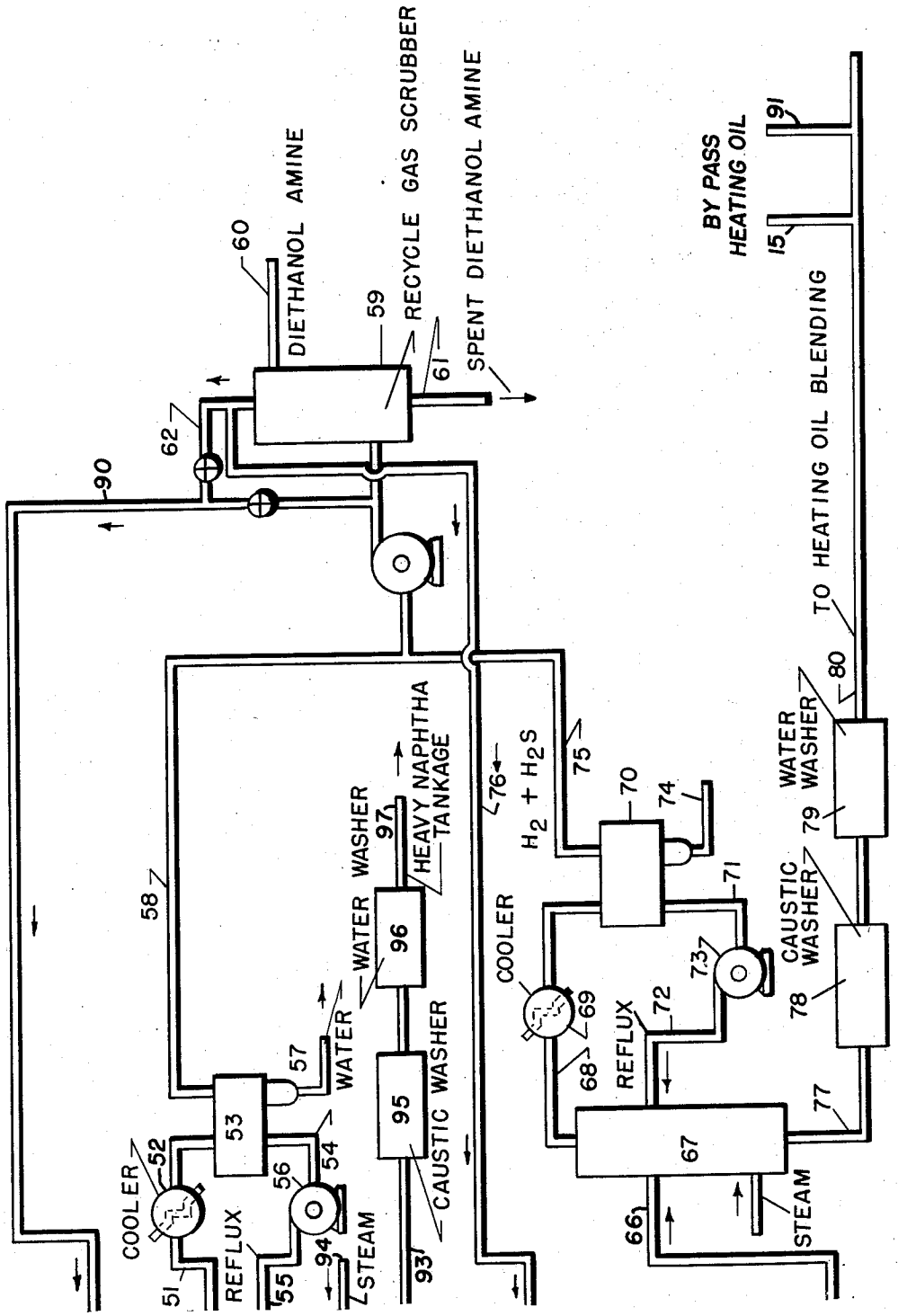
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INTEGRATED HYDROFINING PROCESS

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2,906,694

INTEGRATED HYDROFINING PROCESS

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4 Claims. (Cl. 208—97)

The present invention is concerned with an improved hydrofining operation for the production of high quality petroleum oil products. The invention is particularly concerned with an integrated hydrofining process for the production of high quantity petroleum oils boiling in the motor fuel boiling range and in the heating oil boiling range. A particular adaptation of the invention relates to the production of a high quality blended heating oil product wherein virgin heating oil constituents are blended with a portion of cracked heating oil constituents which have been mildly hydrofined.

As pointed out, the invention is particularly concerned with an integrated process for the production of high quality motor fuels and heating oil products. The invention is more particularly concerned with the production of improved hydrocarbon mixtures known as "heating oils" of the nature employed in various burner systems, as diesel fuels, or as domestic and industrial heating oils. Heating oils may be derived from petroleum by a variety of methods including straight distillation from crude petroleum oil, and thermal or catalytic cracking of various petroleum oil fractions. Heretofore, in the art, heating oil blends comprised a relatively large proportion of virgin heating oil as compared to cracked heating oils. However, due to the desirability of virgin heating oils as feed stocks to various cracking operations, as for example, a fluid catalytic cracking operation, the blends comprise an increasing proportion of cracked heating oil fractions as compared to virgin stocks. Virgin heating oil fractions are also very desirable as diesel oil products which further decreases their availability for heating oil blends.

It is known in the art that heating oils consisting completely or in part of catalytic cracked stocks are characterized by an undesirable instability giving rise to the formation of sediment. It is also known that when cracked heating oils are blended with sweetened virgin heating oils, certain undesirable characteristics are increased due to their incompatibility. As a result, such blended fuel oils tends to cause clogging of filters, orifices, or conduits associated with the burning systems in which they are employed.

It is also known in the art that when a virgin heating oil is blended with a cracked heating oil, the carbon residue of the blend in many cases exceeds the carbon residue of either the virgin heating oil or the cracked heating oil. This carbon residue is an indication of the extent the blended heating oil will carbonize the burners, particularly a rotary burner in actual use and to some extent determines the burning characteristics and desirability of the fuel.

In order to improve the quality of blended heating oils, various processes have been practiced in the art. It is known in the art to process a virgin heating oil by a caustic wash if the oil be relatively sweet. On the other hand, if the virgin heating oil has a relatively high mercaptan content so as to render it sour, the oil is processed by a doctor treat or an equivalent sweetening

operation. On the other hand, light cracked heating oils in many operations merely require a caustic wash. However, the conventional procedure is to secure the cracked heating oil from a relatively severe cracking operation in which case it is necessary to acid treat the cracked heating oil followed by a caustic wash in order to control the carbon residue. This latter operation is not desirable since acid treatment polymerizes many desirable constituents resulting in a loss in yield. Furthermore, the sludge is expensive and difficult to handle.

In accordance with the present invention, a high quality motor fuel may be secured and the instability of catalytically cracked heating oils overcome by subjecting the selected fractions to hydrofining operations. Heating oil blends which may be processed by the hydrofining operation of the present invention are particularly hydrocarbon mixtures of which more than about 10%, preferably from about 15% to 60% by volume consist of stocks derived from cracking operations. More precisely still, the finished blends may be characterized as petroleum fractions containing a proportion of cracked stocks greater than 10%, preferably from about 15% to 60% by volume, and falling within A.S.T.M. specification D–396–48T for fuel oils (grades Nos. 1 or 2). Inspections of a typical heating oil blend are for example:

Gravity, °A.P.I.	34.5
Distillation, A.S.T.M.:	
Initial, B.P., ° F.	363
10% @ ° F.	438
50% @ ° F.	504
90% @ ° F.	583
Final, B.P., ° F.	640
Flash, ° F.	158
Color, Tag Robinson	15
Viscosity, SSU/100° F.	34.7
Pour point, ° F.	0
Sulfur, wt. percent	.37
Suspended sediment, mgs./100 ml.	1.0
Carbon residue on 10% residum, percent	.08
Corrosion, 1 hr. @ 212 ° F.	pass
Diesel index	48.2
Aniline point, ° F.	140

The process of the present invention may be fully understood by reference to the drawing illustrating one embodiment of the same.

Referring specifically to the drawing, a crude oil fraction is introduced into atmospheric distillation unit 1 by means of feed line 2. Temperature and pressure conditions in zone 1 are adjusted to remove overhead by means of line 3 a low boiling virgin naphtha (boiling range about 100° F. to 300° F.). A heavy virgin naphtha is removed as a side stream by means of line 4, a heating oil fraction by means of line 5, and a virgin gas oil fraction by means of line 6. The heavy virgin naphtha fraction boils in the range from about 275° F. to 430° F. The virgin heating oil boils in the range from about 400° F. to 550° F., while the virgin gas oil boils in the range from about 550° F. to 900° F. A residuum fraction is removed as a bottoms by means of line 7.

The heavy virgin naphtha is introduced into a thermal reforming zone 8 wherein it is subjected to pressures in the range from about 900 to 1100 lbs. per sq. in. and to temperatures in the range from about 950° F. to 1100° F. The reformed product is removed from zone 8 by means of line 9 and introduced into a fractionating zone 10 wherein temperature and pressure conditions are adjusted to remove overhead by means of line 11 gaseous constituents boiling below the motor fuel boiling range. A reformed naphtha having an end point of about 430° F. is removed as a bottoms from distillation zone 10 by

means of line 12 and passed into a prefractionation zone 13.

The virgin heating oil removed by means of line 5 is passed to a sweetening zone 14 wherein the sulfur constituents are converted to disulfides by conventional chemical treating processes. The sweetened heating oil is removed from zone 14 by means of line 15 and blended into the heating oil pool secured as hereinafter described. The virgin gas oil stream segregated by means of line 6 is passed into a catalytic cracking zone 16 wherein the same is subjected to temperatures in the range from about 900° F. to 1100° F. and to pressures in the range from 15 lbs. to 200 lbs. per sq. in. in the presence of a cracking catalyst, as for example alumina on silica.

The residuum removed from zone 1 by means of line 7 is passed to a vacuum distillation zone 17 wherein temperature and pressure conditions are adapted to remove overhead by means of line 18 gas oil constituents boiling up to about 1150° F. These constituents are blended with the gas oil constituents removed from zone 1 by means of line 6.

Cracked products are removed overhead from the cracking zone 16 by means of line 19 and passed to a distillation zone 20. Temperature and pressure conditions in zone 20 are adjusted to remove overhead by means of line 21 a catalytic cracked naphtha and lower boiling constituents. This stream is subsequently treated to segregate hydrocarbon constituents boiling in the motor fuel boiling range from the lower boiling hydrocarbon gases. A low boiling catalytic heating oil (about 400° F. to 580° F.) is removed by means of line 22, while a high boiling catalytic heating oil (about 550° F. to 650° F.) is removed by means of line 23. A heavy clarified or cycle oil is removed by means of line 24. A portion of this oil is recycled to zone 16 by means of line 25, while the remainder is passed to a thermal cracking zone 26.

Thermal cracking zone 26 is maintained at a pressure of about 1,000 lbs. per sq. in. and at a temperature of 980° F. A cracked product is removed from zone 26 by means of line 27 and passed to a distillation zone 28 wherein temperature and pressure conditions are adjusted to segregate low boiling hydrocarbon constituents which are removed by means of line 29. A heavy fuel fraction is removed by means of line 30. A fraction boiling in the range of about 400° F. to 650° F. is removed by means of line 31 and passed to prefractionator 13 along with the heavy catalytic heating oil segregated by means of line 23.

The light catalytic heating oil removed by means of line 22 is passed to caustic treating zone 32 wherein the same is treated with caustic (about 5–15° Bé.). The caustic treated oil is removed by means of line 91 and blended with the heating oil pool secured as described.

The residuum from zone 17, segregated by means of line 34, is passed to a visbreaking unit 35. Temperature in zone 35 is in the range from about 800° F. to 1000° F., while the pressure is in the range from about 200 to 600 p.s.i.g.

The visbroken product is removed by means of line 36 and passed to a distillation zone 37. Temperature and pressure conditions in zone 37 are adjusted to remove overhead by means of line 38 hydrocarbon constituents boiling below the gasoline boiling range. A heavy fuel fraction is removed as a bottoms stream by means of line 39. A hydrocarbon fraction boiling in the range from about 100° F. to 430° F. is removed by means of line 40 and passed to prefractionator 13. A heavy hydrocarbon fraction boiling in the range from about 400° F. to 650° F. is removed by means of line 41.

Temperature and pressure conditions in prefractionator 13 are adjusted to remove overhead by means of line 42 a light thermal naphtha having a final boiling point of about 300° F. A heavy fraction boiling above about 650° F. is removed by means of line 43 and recycled to thermal cracking zone 26. A heavy naphtha fraction boiling in the range from about 275° F. to 430° F. is removed as a side stream by means of line 44, while a heating oil fraction boiling in the range from about 400° F. to 650° F. is segregated as a side stream by means of line 45 and combined with the heating oil fraction segregated in zone 37 by means of line 41. In accordance with the present invention the naphtha fraction segregated by means of line 44 is passed through a heat exchanging zone 46, passed through a furnace 47 and introduced into hydrofining zone 48 and contacted with a hydrofining catalyst, preferably cobalt molybdate on alumina. The temperature in zone 48 is about 600° F. while the pressure is about 200 lbs. per sq. in. The feed rate is about 8 volumes of oil per volume of catalyst per hour. The catalyst comprises about 10–15% cobalt molybdate on alumina. The hydrofined naphtha product is removed from the bottom of zone 48 by means of line 49 and passed into a stripping zone 50. Steam is introduced by means of line 94.

Temperature and pressure conditions in zone 50 are adjusted to remove overhead by means of line 51 hydrogen, hydrogen sulfide, and low boiling hydrocarbon constituents. This stream is passed through a cooler 52 and introduced into a distillate drum 53. Condensed constituents are removed by means of line 54 and reintroduced as reflux into zone 50 by means of line 55 and pump 56. Condensed water is removed from zone 53 by means of line 57. Gases comprising hydrogen and hydrogen sulfide are removed from zone 53 by means of line 58 and introduced into a hydrogen sulfide removal zone 59. In zone 59, these gases are treated with a solvent such as diethanolamine, which is introduced into zone 59 by means of line 60. The spent diethanolamine containing hydrogen sulfide is removed by means of line 61, while the hydrogen containing gases are removed overhead by means of line 62 and preferably recycled to reactor 48 by means of line 90. A portion of the recycle gas is purged to prevent the buildup of inert materials. The spent diethanolamine is regenerated by steam stripping out the hydrogen sulfide. The solution is then recycled to the gas scrubber by means of line 60.

The hydrofined naphtha is removed from zone 50 by means of line 93 and passed to a caustic washing zone 95. The caustic washed hydrofined naphtha is then water washed in zone 96 and passed to naphtha storage by means of line 97.

The heavy heating oil fraction removed from prefractionator 13 by means of line 45 is passed through a heat exchanging zone 63, furnace 64, and introduced into hydrofining zone 65. The temperature in zone 65 is about 600° F. while the pressure is about 200 lbs. per sq. in. The catalyst preferably comprises about 10% molybdenum oxide on alumina. The feed rate is about 16 volumes of oil per volume of catalyst per hour.

The hydrofined product is removed from the bottom of zone 65 by means of line 66 and passed into the stripping zone 67. Temperature and pressure conditions in zone 67 are adjusted to remove overhead by means of line 68 low boiling hydrocarbon gases, hydrogen and hydrogen sulfide. These gases are passed through a cooler 69 and into a distillate drum 70. Condensed constituents are removed by means of line 71 and reintroduced as reflux into zone 67 by means of line 72 and pump 73. Water is removed from zone 70 by means of line 74.

Hydrogen and hydrogen sulfide are removed overhead from zone 70 by means of line 75 and treated in zone 59 as heretofore described. Hydrogen is segregated from zone 59 by means of line 76 and recycled to zone 65. A refined heating oil fraction is removed as a bottoms stream from zone 67 by means of line 77, caustic treated in zone 78, water washed in zone 79 and withdrawn by means of line 80. This stream is blended with bypassed virgin heating oil which is introduced by means

of line 15 and with the caustic washed light catalytic heating oil which is introduced by means of line 91.

It is essential, in practicing the present invention, that the hydrofining operation conducted on the respective oil streams be "mild hydrofining operations." This is to be distinguished from conventional hydrogenation operations heretofore practiced in the art. Such hydrogenation operations have been employed at pressures from about 200 to 500 lbs. per sq. in., at feed rates of about .5 to 2.0 volumes of feed per volume of catalyst per hour. Relatively high rates of hydrogen recycle have been employed as for example, 2,000 to 4,000 standard cu. ft. per barrel in order to prevent carbonization of the catalyst. Likewise, very active catalysts have been used which are effective for desulfurization. Under these conditions hydrogen consumption has generally been in the range of 150 to 600 standard cu. ft. per barrel of feed. This relatively high consumption of hydrogen in the past has made the process expensive to operate, so that its application heretofore has been limited to the treatment of relatively high sulfur stocks which could not be readily desulfurized by any other available treating operation. The catalyst heretofore employed has been a cobalt molybdate supported on a carrier, as for example alumina.

Due to the fact that the sulfur content of heating oils is relatively low, since the cracking operation desulfurized to a great extent, conventional hydrofining operations have not been necessary in the processing of cracked heating oils. On the other hand, when conventional hydrogenation operations, as described above, were employed in the processing of cracked heating oils for improving the carbon residue, these conventional operations were found entirely unsatisfactory, since they actually increased the carbon residue and further impaired the quality of the fuel. On the other hand, when employing the mild hydrofining process of the present invention, unexpected desirable results are secured with a higher quality blended fuel oil product.

The "mild hydrofining" conditions of the present invention may be secured by lowering the temperature, increasing the feed rate per volume of catalyst or by using a less active catalyst. In accordance with the present invention, the temperatures used are in the range from about 400° F. to 700° F., preferably in the range from about 500° F. to 650° F. Pressures employed are in the range from 50 to 250 lbs. per sq. in. The feed rates, in accordance with the present process, are in the range from about 1–16 volumes of liquid per volume of catalyst per hour. Preferred feed rates are in the range from 4–12 v./v./hr. The hydrogen in the gas to the hydrofining unit may vary from about 50 to 100%, by volume. This means that, for example dilute hydrogen from a hydroformer can be used in the hydrofining process. A particularly desirable method of hydrofining in accordance with the present process is to recycle appreciable quantities of hydrogen to the hydrofining unit in order to completely prevent carbonization of the catalyst.

The catalyst utilized in the present operation may comprise known hydrofining catalyst, as for example cobalt molybdate on a carrier as for example alumina, providing other operating conditions are adjusted to secure a "mild hydrofining" process. The preferred catalyst, however, of the present invention comprises molybdenum oxide on a carrier preferably alumina. The amount of molybdenum oxide employed is about 5% to 13% by weight based upon the weight of the alumina. The catalyst is prepared by known methods, such as by impregnation of the alumina with a water-soluble molybdenum salt, followed by heating to convert this salt to molybdenum oxide, or by coprecipitation of aluminum and molybdenum hydroxides by addition of an ammoniacal solution of ammonium molybdate to an acid solution of an aluminum salt followed by water washing and by heating to convert to the oxides.

It is to be understood that the mild hydrofining conditions of the present invention are secured by the adjustment of the above designated operating conditions. For instance, if a relatively high liquid feed rate is used as compared to the amount of catalyst present, the higher temperature range may be employed. On the other hand, if a very active catalyst is used, it is desirable to use a relatively high feed rate or to use a relatively low temperature. The mild hydrofining conditions of the present invention are measured by the amount of hydrogen consumption per barrel of oil feed. As pointed out heretofore in the art, conventional hydrofining operations utilized for the desulfurization of certain stocks are conducted under conditions whereby the hydrogen consumption ranges from 150 to 600 standard cu. ft. of hydrogen per barrel of oil. These operations used heretofore in the art secured a substantial sulfur reduction (50 to 90%). In accordance with the present process, operating conditions are adjusted so that the hydrogen consumption in standard cu. ft. per barrel does not exceed 60 and is preferably less than 40. Furthermore, the extent of the sulfur reduction when utilizing the mild hydrofining conditions of the present invention does not exceed about 35% and preferably does not exceed about 20%.

By operating as described, a high quality hydrofined naphtha is secured as well as a high quality heating oil blend. In accordance with the present invention, particular fractions bypass the heating oil hydrofining operation which fractions comprise the virgin heating oil constituents and the light or low-boiling catalytic heating oil constituents. By practicing the present invention, integrated facilities for the treatment and recycling of the hydrogen is secured. Furthermore, the stripping of hydrogen and hydrogen sulfide is secured in a single high pressure vessel. Another advantage is that the naphtha is heated in a high pressure furnace to maintain a homogeneous phase thus prevent furnace and reactor coking. Furthermore, all the heat requirements are applied to the oil, thus avoiding the necessity of heating the hydrogen in separate facilities. It is also within the scope of the present invention to vary the hydrogen sulfide content of the recycled hydrogen by selective bypassing of a portion of the hydrogen around zone 59 in order to control catalyst activity. A purge is provided on the recovery stages of the process in order to control the quality of the stripper bottoms.

What is claimed is:

1. Integrated process for the production of high quality petroleum products which comprises introducing a thermally reformed naphtha boiling in the range from about 100° F. to 450° F. into a product fractionator, introducing a heavy catalytic heating oil boiling in the range from about 550° F. to 650° F. into said product fractionator, separating a heavy residual fraction from a catalytic cracking operation, thermally cracking said fraction, distilling said latter fraction to segregate an oil boiling in the range from about 400° F. to 650° F., introducing said latter stream into said product fractionator, introducing a naphtha secured from a visbreaking operation into said product fractionator, maintaining the pressure and temperatures in said product fractionator to segregate a petroleum oil boiling in the motor fuel boiling range and to segregate a petroleum oil boiling in the heating oil boiling range, mildly hydrofining said oil boiling in the motor fuel boiling range in an initial hydrofining zone, removing the hydrofined product from said initial hydrofining zone and separating normally liquid hydrocarbons from normally gaseous constituents comprising hydrogen, mildly hydrofining said petroleum oil boiling in the heating oil boiling range in a secondary hydrofining zone, the process being characterized in that the temperatures, pressures, feed rates, and catalyst activities in said hydrofining zones are such that the hydrogen consumption is below about 60 standard cubic feet per barrel of oil feed, removing the hydrofined

product from said secondary hydrofining zone and separating normally liquid hydrocarbons from normally gaseous constituents comprising hydrogen, combining said gaseous constituents comprising hydrogen from said initial and said secondary hydrofining zone, passing the combined stream to a purification zone, treating said combined stream in said purification zone under conditions to remove hydrogen sulfide therefrom, removing from said purification zone a stream comprising hydrogen and recycling said stream to said initial and said secondary hydrofining zones.

2. Process as defined by claim 1 wherein the feed to said initial hydrofining zone boils in the range from about 275° F. to 430° F. and wherein the feed to said secondary hydrofining zone boils in the range from about 400° F. to 650° F.

3. Improved integrated process for the production of high quality naphthas and high quality heating oil blends which comprises distilling a crude oil in an initial distillation zone to segregate a heavy naphtha fraction, reforming said heavy naphtha fraction at a pressure in the range from about 250 to 1000 lbs. and at a temperature in the range from about 850° F. to 1100° F., distilling the reformed fraction to segregate hydrocarbon constituents boiling in the motor fuel boiling range, passing said latter fraction to a product fractionator, segregating in said initial distillation zone hydrocarbon constituents boiling in the heating oil boiling range comprising a virgin heating oil, segregating in said initial distillation zone a gas oil fraction, cracking said gas oil fraction at a temperature in the range from 850° F. to 1100° F. and at a pressure in the range from atmospheric to 100 lbs. per square inch in the presence of a fluidized solid catalyst, distilling the cracked product in a secondary distillation operation to segregate a light catalytic heating oil and a heavy catalytic heating oil, passing said heavy catalytic heating oil to said product fractionator, segregating in said secondary distillation operation a heavy clarified oil, subjecting said clarified oil to a thermal cracking operation, distilling the thermally cracked products in a tertiary distillation operation to segregate a heavy heating oil, passing said heavy heating oil to said product fractionator, segregating in said initial distillation operation a residuum fraction, visbreaking said residuum fraction, distilling in a fourth distillation operation the visbroken fraction to segregate a visbroken naphtha, passing said visbroken naphtha to said product fractionator, maintaining the temperature and pressure conditions in said product fractionator to segregate hydrocarbon constituents boiling in the heavy naphtha boiling range, mildly hydrofining said heavy naphtha in an initial hydrofining zone, segregating in said product fractionator hydrocarbon constituents boiling in the heating oil boiling range, hydrofining said heating oil in a secondary hydrofining zone, the process being characterized in that the temperatures, pressures, feed rates, and catalyst activities in said hydrofining zones are such that the hydrogen consumption is below about 60 standard cubic feet per barrel of oil feed, removing the hydrofined product from said initial zone and separating gaseous constituents comprising hydrogen from normally liquid hydrofined hydrocarbons, removing the hydrofined product from said secondary hydrofining zone and separating gaseous constitutents comprising hydrogen from said normally liquid hydrofined hydrocarbons, combining said gaseous constituent streams, passing the combined stream to a treating unit, removing hydrogen sulfide from the combined stream in said treating unit, removing hydrogen from said treating unit and passing the same to said initial and said secondary hydrofiner, and combining bypassed heating oil constituents with said hydrofined normally liquid hydrocarbons from said secondary hydrofiner.

4. Process as defined by claim 3 wherein the feed to said initial hydrofining zone boils in the range from about 275° F. to 430° F. and wherein the feed to said secondary hydrofining zone boils in the range from about 400° F. to 650° F.

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