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2 Sheets-Sheet 1

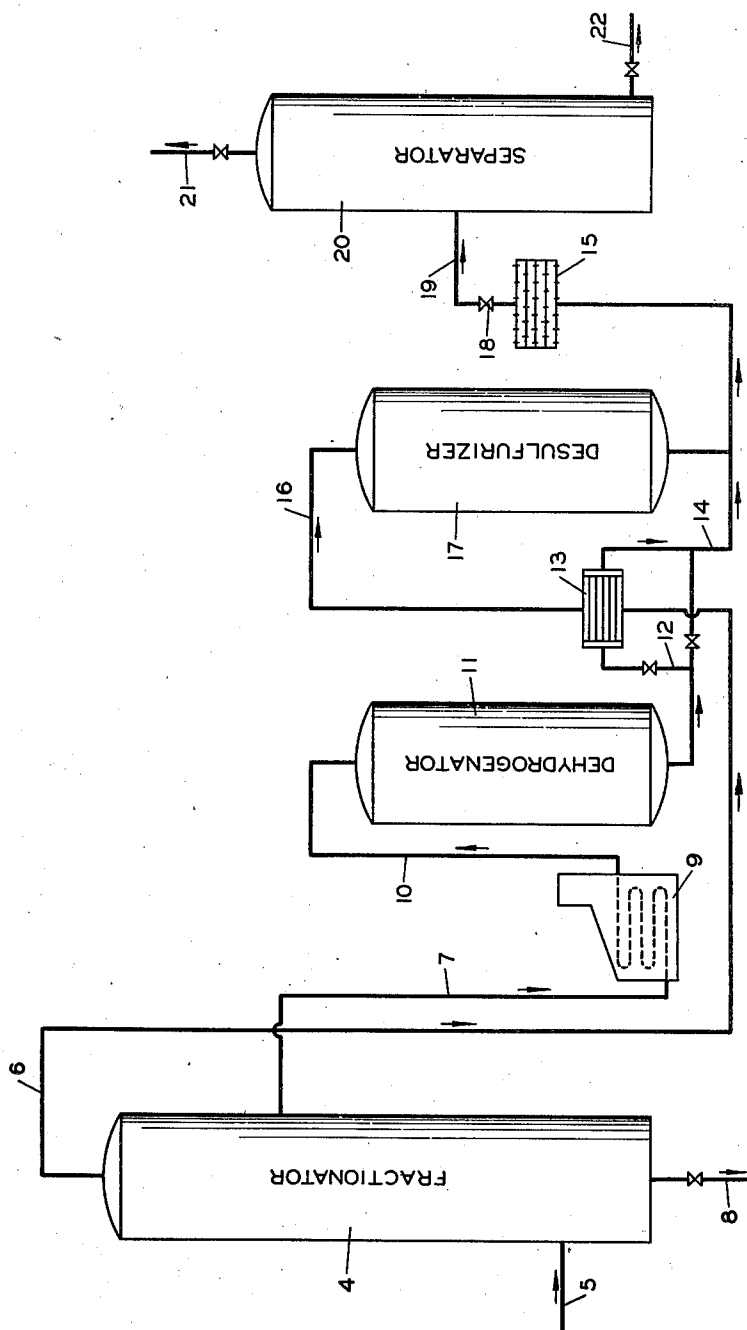


FIG. 1

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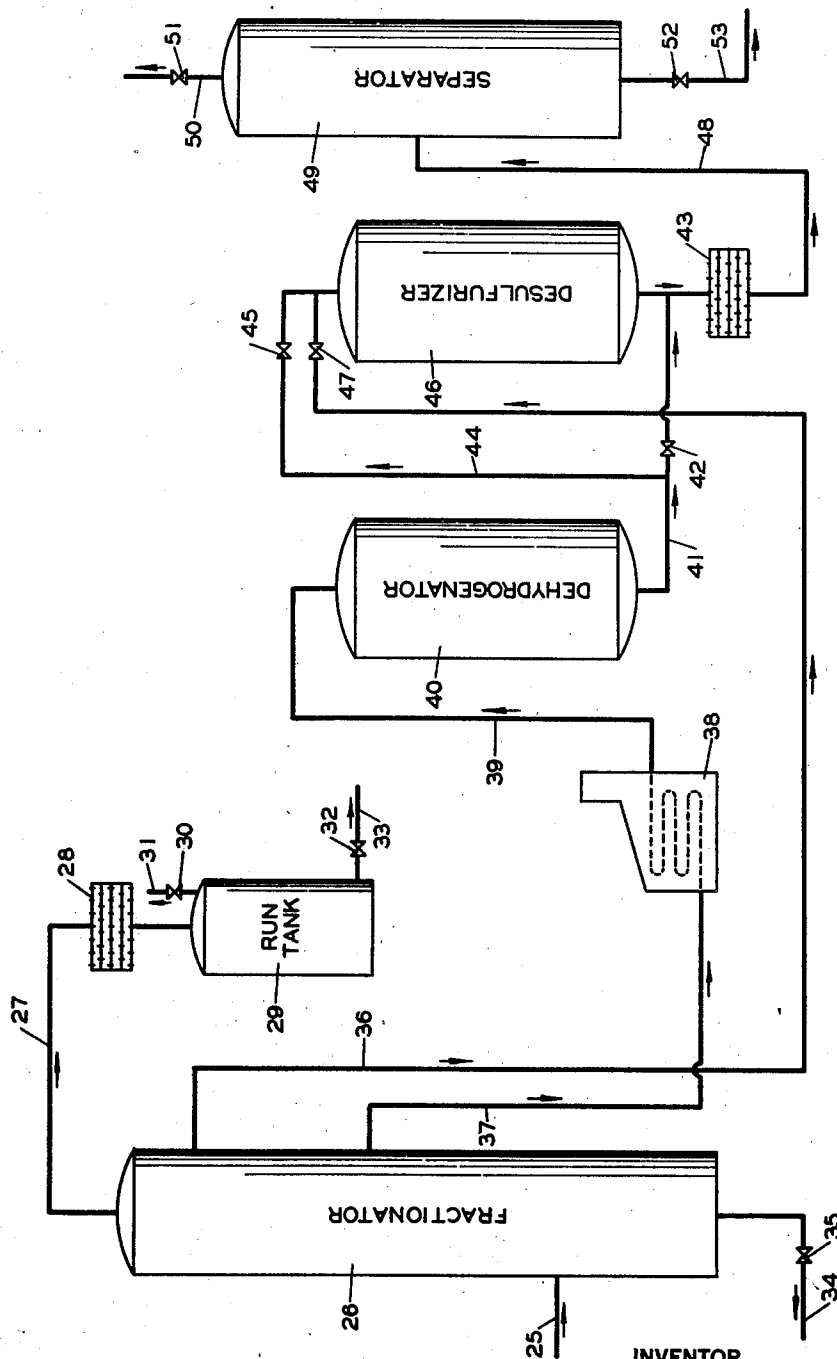
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TREATMENT OF HYDROCARBON OILS

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1 Claim. (Cl. 196—28)

This invention relates to the treatment of hydrocarbon oils and particularly to the treatment of petroleum distillates.

This invention is particularly concerned with the treating of hydrocarbons to produce an improved motor fuel. Hydrocarbon distillates, naphthas, gasoline, kerosene, and gas oils may be desulfurized in accordance with this invention. The desulfurization of the hydrocarbons in the manner disclosed herein results in improved octane number and lead susceptibility, characteristics which are particularly desirable in motor fuels.

It is well known that a hydrocarbon oil mixture may be treated as a whole by dehydrogenation or desulfurization to improve the quality of the oil and increase its market value. Catalytic dehydrogenation, widely used today, improves the octane number of the hydrocarbon oil and reduces its sulfur content. Catalytic desulfurization serves to remove undesirable sulfur compounds from hydrocarbons and may be carried out at much lower temperatures than those required for catalytic dehydrogenation. Caustic washing and clay treating are well known means of removing undesirable impurities from the hydrocarbons. The sulfur content of the petroleum distillates varies with the boiling point of the material. The total sulfur content in the distillates from most crudes and in most gasolines is generally higher in the higher boiling fractions than in the lower boiling fractions. Hydrogen sulfide and other very volatile sulfur compounds present in the distillates will, because of their volatility, be included in the low boiling hydrocarbons but these are readily removed by stabilization or by caustic wash and present no serious problem to the refiner. Other sulfur compounds in the petroleum are usually distributed in accordance with the boiling point, being present in greater amounts in the higher boiling fractions.

Due to the wide variations in the crude oils from which the petroleum distillates are obtained, it is almost impossible to state rules that will be valid in every instance. Generally, however, the distillates from a given crude oil, comprising the gasolines, kerosenes, naphthas, gas oils, etc., if broken down into the different boiling range fractions will yield low octane heavier fractions and higher octane lighter fractions. All of the distillate obtained from the topping of a crude oil may be subjected to catalytic desulfurization or catalytic dehydrogenation as known in the art. Catalytic dehydrogenation using bauxite catalyst removes the sulfur impurities and improves the

octane number of the charge stock by reforming some of the components in the heavier fractions. While the octane number of the hydrocarbon distillates may be generally improved by subjecting the entire mixture to catalytic dehydrogenation, some of the lighter components of the mixture may actually lose some of their anti-knock value. For example, some of the iso-paraffins, having good anti-knock properties may be converted to normal paraffins of lower anti-knock properties. Sulfur impurities are effectively removed from hydrocarbon oils by catalytic desulfurization but, aside from an improvement in the lead susceptibility, very little if any improvement is made in the octane number of the oil. While the operating conditions for catalytic desulfurization are not as severe as the operating conditions for catalytic dehydrogenation, some damage to the octane numbers of the lighter fractions may be experienced.

The present process provides a method of and apparatus for treatment of the hydrocarbons to obtain the optimum improvement in desirable characteristics of the hydrocarbons with a minimum amount of treatment. This is accomplished by separating the distillate into fractions having different boiling ranges and treating each fraction in the manner which will result in maximum improvement in the charge stock. The low octane, high sulfur, high boiling fractions, are subjected to catalytic dehydrogenation to remove the sulfur and increase their octane numbers. Intermediate fractions containing sulfur are subjected to catalytic desulfurization to remove sulfur impurities. The high octane, low sulfur, low boiling fractions are given only a mild treatment or no treatment. Since the catalytic dehydrogenation is carried out at much higher temperatures than the catalytic desulfurization, the waste heat from the dehydrogenation operation is utilized to heat the charge stock to the desulfurization process. Novel apparatus is provided for effecting the utilization of the waste heat for this purpose. The various fractions after treatment are blended and stabilized. The gases, such as hydrogen, hydrogen sulfide, methane, and the like are separated from the liquid hydrocarbons. The treated hydrocarbons after separation from the gas may be further treated in any conventional manner that may be desirable.

An object of this invention is to provide an improved method and apparatus for treating hydrocarbon oils.

Another object of this invention is to utilize waste heat contained in the effluent of one reac-

tion to supply the necessary heat for carrying out another reaction.

Still another object of this invention is to provide a process for treating a hydrocarbon mixture wherein the mixture is separated into a plurality of fractions and each fraction so treated that the maximum improvements in octane number, lead susceptibility, and sulfur content of the treated hydrocarbon mixture, result.

A further object of this invention is to provide novel apparatus for carrying out catalytic dehydrogenation and catalytic desulfurization.

Figures 1 and 2 are diagrammatic elevation views of two specific embodiments of the present invention.

With reference to Figure 1, the numeral 4 designates a conventional fractionator. The hydrocarbon oil to be treated, for example, a naphtha of low octane number and high sulfur content enters the fractionator through the pipe 5, and is cut into at least three fractions of different boiling points. A fraction having an end point of about 300° F. is taken from the top of the fractionator as a vapor through the pipe 6. This fraction has a relatively high octane number and contains some sulfur. A higher boiling fraction, having an end point of about 450° F. is taken off the fractionator as a liquid sidestream through the pipe 7. The 450° F. end point fraction contains a higher percentage of sulfur than the overhead product and has a low octane number. The remainder of the original naphtha is withdrawn from the base of the fractionator through the pipe 8, from which it may be passed to other refinery processes for further treatment. The relatively high sulfur, low octane, 450° F. end point fraction, is passed through the pipe 7 to the furnace 9 where it is vaporized and heated to a temperature in the range 900°-1050° F. The heated vapors are passed at this temperature and at a pressure less than 150 pounds per square inch through the pipe 10 and over the bauxite catalyst in the dehydrogenator 11. The dehydrogenation step accomplishes reforming of some of the hydrocarbons into others of higher octane number and removal of sulfur. A small amount of cracking may accompany the desulfurization reaction. The effluent of the dehydrogenation is passed through the pipe 12, the heat exchanger 13 and the pipe 14 to the cooler 15.

The relatively high octane, 300° F. end point fraction taken from the top of fractionator 4 is passed through the pipe 6 to the heat exchanger 13. In the heat exchanger the temperature of this fraction is raised to the range of 600-800° F. by indirect heat exchange with effluent from the dehydrogenator. From the heat exchanger, the heated vapors pass through the pipe 16 to the desulfurizer 17 where it is passed over a bauxite catalyst. The desulfurization is carried out at less than 150 pounds per square inch pressure and removes the sulfur without changing the structure of the hydrocarbons to any appreciable extent. Effluent from the desulfurizer is mixed with effluent from the dehydrogenator in pipe 14 and passed to the cooler 15. The cooled mixture from the cooler flows through the valve 18 and pipe 19 into the separator 20. Hydrogen, hydrogen sulfide, and other gases pass off the top of the separator 20 through the pipe 21. The treated liquid hydrocarbons from the separator flow through the pipe 22 to any desirable conventional refining processes or to storage.

With reference to Figure 2, the hydrocarbons to be treated flow through the pipe 25 into the

fractionator 26. From the top of the fractionator a low boiling, low sulfur content, high octane fraction in vapor form is passed through the pipe 27 to a condenser 28. Condensate and uncondensed gases passing the condenser flow to the run tank 29. The gases separated from the liquid in the run tank pass out through the valve 30 and pipe 31. Condensate is withdrawn from the run tank through the valve 32 from which it may be passed through the pipe 33 to storage or to any desirable treating process, for example, the condensate may be given a caustic wash, such processes being well known in the art and forming no part of the present invention.

The high boiling heavy ends are withdrawn from the base of the fractionator through the pipe 34 containing the control valve 35, to be disposed of in any suitable manner. At points intermediate the top and bottom of the fractionator are drawn off fractions of different boiling ranges through the pipes 36 and 37. The fraction drawn off through the pipe 37 is low octane, high sulfur, high boiling fraction suitable for dehydrogenation. This fraction is passed to the furnace 38 where it is raised to dehydrogenation temperature and from which it passed through the pipe 39 to the dehydrogenator 40. The dehydrogenator 40 is a catalyst chamber containing a suitable dehydrogenation catalyst. Effluent from the dehydrogenator flows through the pipe 41 from which it may be passed through the valve 42 to the cooler 43 or through the pipe 44 and valve 45 to the desulfurizer 46.

The fraction withdrawn from the fractionator through the pipe 36 has a good octane number and an intermediate sulfur content. The boiling range is between that of the fraction drawn off through the pipe 37 and that of the fraction passing overhead through the pipe 27. The fraction flows through the pipe 36 to the desulfurizer where it is admitted through the control valve 47. A quantity of hot effluent from the dehydrogenator, sufficient to raise the temperature of the intermediate sulfur content fraction to the desulfurization temperature, is admitted to the desulfurizer through the control valve 45. The desulfurizer 46 is a catalyst chamber filled with a suitable desulfurization catalyst. Effluent from the desulfurizer is passed to the cooler 43 where it is cooled and mixed with that portion of the dehydrogenation effluent passing the valve 42.

From the cooler 43 the treated hydrocarbons are passed through the pipe 48 into the separator 49. Hydrogen and other gases leave the top of the separator through the pipe 50 containing a control valve 51. Treated liquid is drawn from the separator 49 through the control valve 52 into the pipe 53 from which it may be passed to storage or further refining.

The specific embodiments described herein are given by way of illustration only and are not to be construed as limiting the present invention. While a bauxite catalyst is described, it is evident that other dehydrogenation and desulfurization catalysts, either natural or synthetic materials, may be used in the process of the present invention. The temperatures and pressures cited are those which are considered good practice at the present time for use with bauxite catalysts. If other catalysts are used, the temperatures and pressures used will be those at which the best results are obtained.

We claim:

The method of treating hydrocarbon distillates comprising separating the hydrocarbons into a

plurality of fractions having different boiling ranges and sulfur contents, contacting a low-boiling fraction with bauxite at a temperature in the range of 600-800° F. to desulfurize the same without substantial change in octane number, 5 contacting a high-boiling fraction with bauxite at a temperature in the range of 900-1050° F. to

improve the octane number and reduce the sulfur content of the same, blending the hydrocarbon fractions, and stabilizing the treated hydrocarbons to obtain improved motor fuel.

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