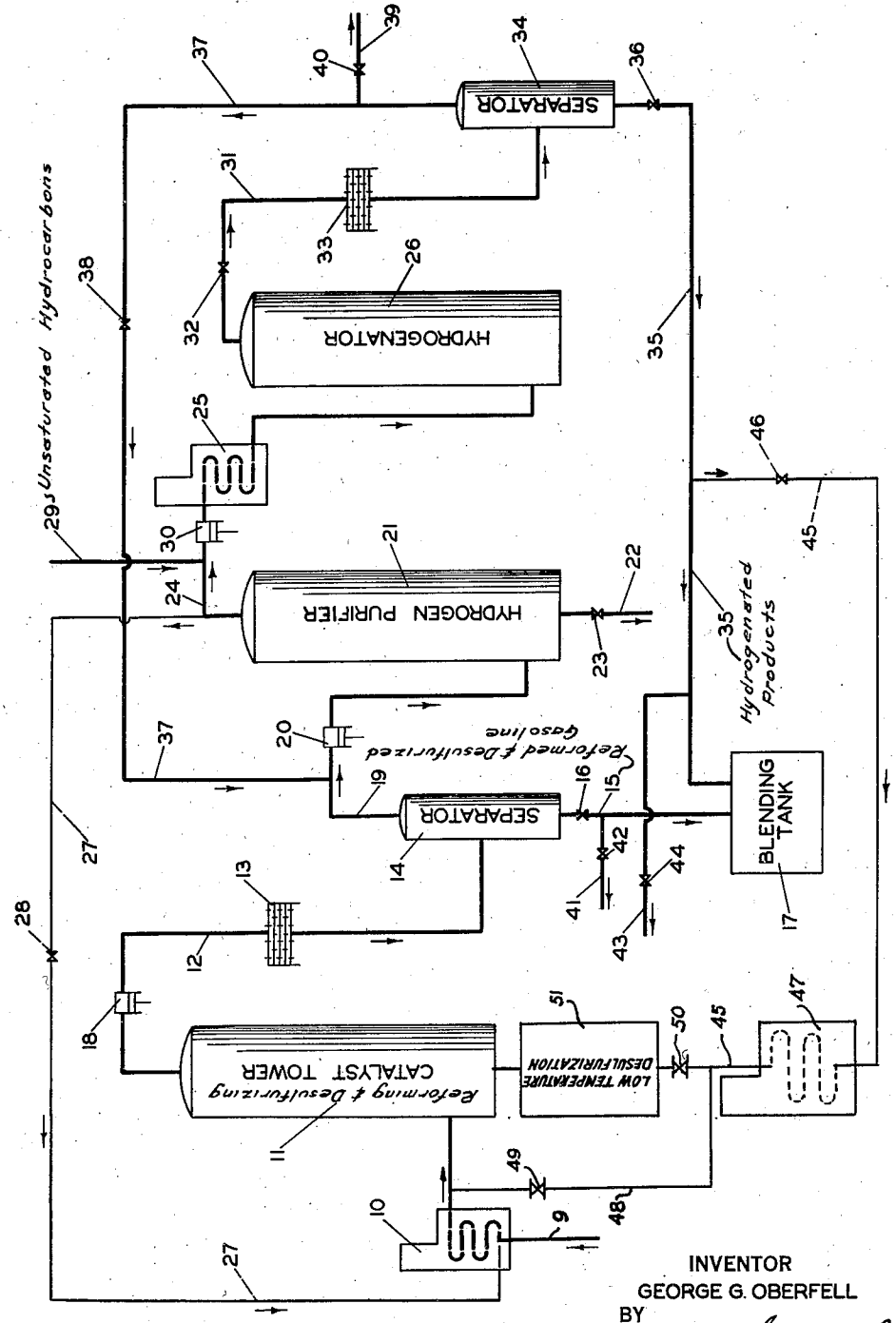
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PROCESS FOR DESULFURIZING AND REFORMING HYDROCARBONS

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PROCESS FOR DESULFURIZING AND REFORMING HYDROCARBONS

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This invention relates to the treatment of hydrocarbon oils and is directed more particularly to the treatment of lighter fractions of petroleum oils such as those produced by cracking of heavier petroleum oils, by straight run distillation of such oils or by extraction of liquid fractions from natural gas, as well as lighter hydrocarbon fractions obtained from shales, destructive hydrogenation of coal, and the like. The term "distillate" when used in this specification does not indicate any limitation as to the source of the material described.

More specifically, the present invention contemplates the treatment of relatively low boiling hydrocarbon fractions for the production of an improved motor fuel and for the removal of sulfur therefrom by a novel and efficient method hereinafter described. This method offers distinct advantages over other methods at present employed in that it is specifically directed toward the removal of all types of sulfur compounds, including those which are especially refractory or resistant to the action of the reagents and processes known to the prior art.

This invention contemplates further the production of an improved motor fuel having an increased octane number and tetraethyl lead susceptibility by blending the products of desulfurization and dehydrogenation treatments carried out in a manner hereinafter more fully described.

It has become general practice to improve the anti-knock value of motor fuels by adding lead alkyls thereto in small quantities. However, it has been found that motor fuels vary greatly in their response to this treatment. For example, of two motor fuels with equal anti-knock value before addition of tetraethyl lead, one may show an increase of ten octane numbers and the other only five, following addition of one cubic centimeter of tetraethyl lead per gallon of motor fuel. The increase in octane number obtained by adding a given quantity of tetraethyl lead to a gallon of motor fuel has been termed the "lead response" or "lead susceptibility" of the fuel.

The present invention is partially based upon the discovery that differences in lead response among motor fuels of substantially the same hydrocarbon composition are due to certain impurities present in most motor fuels which greatly

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reduce the effectiveness of tetraethyl lead in suppressing knocking in internal combustion engines. These impurities are of the sulfur, nitrogen and oxygen type, of which the sulfur compounds appear to be the most important. Thus, removal of these impurities and particularly the sulfur compounds results in an improved lead response.

In ordinary refining practice, the methods and reagents heretofore in use are effective for the removal of some of the types of sulfur compounds present in petroleum distillates. For example, elementary sulfur, mercaptans, sulfides and disulfides are relatively easily removed, while the heterocyclic sulfur compounds such as the thiophenes and thiophanes are quite refractory and difficult to remove by simple methods. The most difficult types of distillates to desulfurize are those which result from cracking of higher boiling hydrocarbons, especially those which contain a relatively high percentage of sulfur, thus resulting in the formation of distillates containing sulfur predominantly in the form of refractory heterocyclic or other compounds. Such distillates require severe treatment for the removal of the refractory sulfur compounds.

It is, therefore, one of the objects of this invention to improve the lead response of motor fuels by an improved method of reducing the sulfur content of such fuels.

It is another object of the present invention to provide a sequence of steps which will effectively remove refractory sulfur compounds from hydrocarbons containing the same, such as cracked distillates, and which will enable the production of a motor fuel having improved lead response and anti-knock characteristics.

It is a further object of this invention to treat different hydrocarbon materials so as to enable the production of an improved motor fuel blend of increased octane number and lead susceptibility in an economical manner.

Improved motor fuels may be produced in accordance with my invention by subjecting natural gasoline and/or low end point straight run gasoline, on the one hand, and cracked distillates or mixtures thereof with straight run gasoline, on the other, two separate and distinct forms of treatment, using by-products of one treatment in carrying out the other, and blending the resulting products of each treatment. Accordingly, the

natural and/or straight run gasoline is subjected to a combined desulfurization-reforming operation, preferably under mild conditions of temperature with the aid of certain catalysts. In this treatment a certain amount of dehydrogenation occurs and hydrogen is produced and recovered therefrom and utilized in another portion of the process. In this step of the process, the gasoline treated is improved by effecting changes in hydrocarbon structure such as isomerization, lowering of the sulfur content and the production of certain unsaturated hydrocarbons which are known to affect favorably the antiknock properties of the resultant fuel.

The second portion of my process includes a hydrogenation step and is applied to fuels comprising cracked distillates which contain the more refractory sulfur compounds referred to above. This hydrogenation may be either simple or destructive and with or without known hydrogenation catalysts and accomplishes desulfurization to a degree which depends upon the hydrogenation conditions. A further effect of this hydrogenation is that the distillate is stabilized against subsequent gum and color formation by the action of hydrogen on the sulfur compounds and on the highly unsaturated compounds which are found in cracked materials, especially conjugated diolefins, which tend to polymerize and oxidize very readily. The completeness of stabilization depends, of course, on the type of material treated and the hydrogenation conditions. Usually no further treatment for removing gum-forming substances is necessary, although sometimes a slight clay or other treatment is found advisable. The sulfur and highly unsaturated compounds are hydrogenated without a great deal of concomitant hydrogenation of mono-olefins to paraffins, which latter reaction of course would be undesirable and cause loss in octane number of the cracked stock.

The hydrogen produced in the reforming or dehydrogenation operation as described in connection with the first portion of my process is of considerable quantity, and may be as much as 50–90% of the off gases. This hydrogen may be readily separated from other constituents of the off gases such as methane and hydrogen sulfide, and then be utilized in the hydrogenation step in the second portion of the process. The hydrogen may be recycled in the hydrogenation step.

The products of the aforesaid reforming and hydrogenation operations may then be blended as desired to produce an improved motor fuel.

As referred to above, cracked distillates contain certain refractory sulfur compounds which are not completely removed by a single hydrogenation step as described above. Accordingly, as a modification of the above described method, I have found that the aforesaid refractory sulfur compounds can be removed in a simple, economical and effective manner by subjecting the hydrocarbons to be treated to a two-step treatment in place of the single hydrogenation step in the second portion of my process. In the first step the hydrocarbon is contacted in vapor form with hydrogen at elevated temperatures in a relatively high pressure zone of say, 500 to 1,000 pounds pressure, or even more. The conditions of temperature, pressure and reaction time are selected so as to avoid appreciable thermal decomposition or cracking of the hydrocarbons, and since no catalyst is present in this step, it is one in which purely thermal hydrogenation takes place. In the place of the aforesaid thermal treatment a mild catalytic hydrogenation step may be used under conditions which avoid cracking or decomposition of the hydrocarbons.

The effluent from this first step is then passed to the second step which is a low pressure catalytic desulfurization or a reforming operation, depending on the type of material initially treated and upon the nature of the desired product. This second operation may conveniently be that which is utilized in the first portion of my process for the treatment of natural and/or straight run gasolines, the second step in the treatment of cracked distillates being thereby combined with the first portion of the process, a blending of the fuels being obtained thereby and the dehydrogenation or reforming step having a dual function. The hydrogen produced in this step is conveniently and economically utilized in the hydrogenation operation as heretofore explained.

Referring to the drawing wherein there is diagrammatically illustrated one form of apparatus for carrying out my invention and its modifications, the low octane material such as straight run or natural gasoline is introduced through pipe 9, and preheating furnace 10 into reaction zone 11 at the proper temperature and pressure for reforming. The reaction zone 11 contains a catalyst, preferably bauxite, which is capable of bringing about desulfurization and reforming with isomerization and concomitant dehydrogenation. The said zone is maintained at a suitable reforming temperature, in the case of bauxite within the range of 900–1200° F., and at pressures of atmospheric or higher but generally below 100 pounds per square inch. Flow rates are so chosen that only a minimum of cracking occurs. The effluents from the reforming zone 11 pass through pipe 12 to condenser 13 wherein the improved motor fuel is condensed and then to separator 14 wherein the condensate is separated from the gaseous effluent of the reforming operation and may be withdrawn from the system through line 15 containing valve 16 to blending tank 17. A compressor is indicated at 18 which may be utilized if desired to aid in the condensation.

The gaseous fraction from the separator 14 will contain from about fifty to ninety per cent hydrogen, depending upon the reforming conditions, the remainder being largely hydrogen sulfide and methane with smaller amounts of other normally gaseous hydrocarbons. This fraction is passed through line 19 and compressor 20 to separator 21 wherein hydrogen of sufficient purity for use in hydrogenation operations is separated from the other constituents of the gaseous fraction. This separation may take the form of chemical or catalytic removal of hydrogen sulfide, fractionation or oil absorption, depending upon the economics of the installation and the composition of the hydrogen-bearing gas. The undesired gases are withdrawn from the system through one or more valved lines, represented in the drawing by line 22 containing valve 23, and the purified hydrogen is passed through line 24 to heater 25 and to hydrogenator 26.

If desired, a portion of hydrogen may be recycled to reaction zone 11 by passing it through line 27 controlled by valve 28 into heater 10, where it is mixed with the incoming charge stock in pipe 9. This recycling of hydrogen gives very desirable results. Presumably it may depress the dehydrogenation reaction somewhat but sufficient additional isomerization apparently

takes place under these conditions to more than make up for the lowered content of unsaturated material, so that an increased octane number is obtained.

Unsaturated hydrocarbons, such as cracked gasoline, or the like are introduced into the system through line 29 where they pass through line 24, in admixture with hydrogen from the separator, and through furnace 25 to the hydrogenator 26. A compressor 30 in line 24 may be used if necessary. The mixture of hydrogen and unsaturated hydrocarbons is maintained under known conditions of temperature, pressure and reaction time suitable for hydrogenation. The hydrogenation operation may be either thermal or catalytic, and either simple or destructive, depending upon the stock to be hydrogenated and the result desired, as will be well understood by those skilled in the art in the light of the present disclosure. The effluents from hydrogenator 26 pass through line 31 containing valve 32 to condenser 33 and then to separator 34, wherein the hydrogenated products liquefied in condenser 33 are separated and withdrawn from the system through line 35 containing valve 36 to blending tank 17. Of course, the operation of separator 34 will vary with the type of material treated and the type of hydrogenation carried out, in order to obtain a product of motor fuel boiling range.

Gases containing hydrogen not consumed in the hydrogenation operation are returned through line 37, controlled by valve 38, and line 19 to separator 21 wherein the hydrogen is again purified and then recycled. Line 39 controlled by valve 40 provides for withdrawal of suitable quantities of hydrogen and any other gases separated in separator 34 in the event that more hydrogen is produced than consumed, thus tending to pyramid in the system.

Line 41 containing valve 42 and line 43 containing valve 44 branch off from lines 15 and 35 respectively to allow the withdrawal of products in case there is an excess of one or the other over that required for blending in tank 17. The blending of products in tank 17 produces an improved motor fuel having the desirable properties referred to above.

This process is especially economical in the use of heat, and in the operation of the process a number of heat-exchanging steps are utilized which are not shown in the drawing, being obvious to those skilled in the art.

A modification of the process as hereinabove described is illustrated by line 45 controlled by valve 46, which conducts the hydrogen-treated cracked distillate through furnace 47, line 48 and valve 49, valve 50 being closed to the low pressure catalytic desulfurizing or reforming zone 11. There the refractory sulfur compounds which have been initially treated in the preliminary hydrogenation step 26 are finally converted to hydrogen sulfide, and thus removed. Also, the cracked distillate may be blended in catalyst tower 11 with the straight run material which may be introduced into the system through pipe 9. When this modification of the invention is used, it is desirable that the hydrogenation step 26 be one which is either thermal or a mild catalytic treatment under conditions which will avoid cracking or decomposition. Such a treatment has been found to modify the refractory sulfur compounds, possibly by reduction to sulfur compounds which can then be readily acted upon in the low pressure catalytic desulfurizing or reforming step 11. The thermal operation may be carried out at a pressure of 500 to 1,000 pounds and at a temperature of about 550 to 750° F. A mild catalytic step may be used in place of the thermal hydrogenation, using a mild hydrogenation catalyst such as molybdic oxide—nickelous oxide at temperatures below cracking or decomposition.

In using the modified method only for treating cracked distillates for the removal of refractory sulfur compounds therefrom, no straight run distillate is introduced into the apparatus at 9 and the desulfurizing and reforming operation at 11 becomes the second step in the process receiving the pre-treated cracked distillate from the hydrogenating operation 26. In this case, it is usually preferred to maintain the desulfurizing catalyst in tower 11 at a somewhat lower temperature than when natural gasoline or straight run distillate is concomitantly reformed.

Another useful modification is to maintain a temperature gradient or two temperature zones in catalyst tower 11, and to introduce the cracked distillate which has already been treated with hydrogen through line 45 and valve 50, valve 49 being closed into the low-temperature zone 51 of the catalyst, wherein further desulfurization takes place. The cracked stock may be blended with straight run or natural stock either before or after it has passed through the low-temperature zone, and either before or after said straight run or natural stock has been desulfurized and reformed in the high-temperature zone. Using bauxite, for example, as a catalyst, the high-temperature zone would be held at from about 900 to 1200° F. while the low-temperature zone would be maintained at from about 500 to 800° F.

I claim:

1. A process for producing an improved motor fuel which comprises contacting a first motor fuel of relatively low antiknock value and lead susceptibility and containing sulfur in substantially non-refractory form with a reforming catalyst in a reforming step under conditions of temperature, pressure and rate of flow such that substantially no cracking takes place but hydrogen is produced and desulfurization occurs, contacting a second motor fuel consisting of a cracked distillate containing refractory sulfur compounds and unsaturates, with hydrogen at elevated temperatures and pressures but below reforming temperatures in a separate step to effect hydrogenation and pre-treatment of said refractory sulfur compounds, introducing said hydrogenated and pre-treated cracked distillate into the reforming step to eliminate said sulfur compounds, whereby said cracked distillate and said first motor fuel are blended, and withdrawing the blended motor fuel obtained thereby.

2. A process according to claim 1 in which the reforming step comprises at least two zones, one of which is maintained at a lower temperature than the other, and in which the pre-treated cracked distillate is introduced into the lower temperature zone.

3. A process for producing an improved motor fuel which comprises contacting a first motor fuel of relatively low antiknock value and lead susceptibility and containing sulfur in substantially non-refractory form with a reforming catalyst in a reforming step at a temperature of about 900° to 1200° F., and a pressure and rate of flow such that substantially no cracking takes place but hydrogen is produced and desulfurization occurs, contacting a second motor fuel consisting

of a cracked distillate containing refractory sulfur compounds and unsaturates with hydrogen at a temperature of about 550 to 750° F., and a pressure of about 500 to 1000 pounds in a separate step to effect hydrogenation and pre-treatment of said refractory sulfur compounds, introducing said hydrogenated and pre-treated cracked distillate into the reforming step to eliminate said sulfur compounds, whereby said cracked distillate and said first motor fuel are blended, and withdrawing the blended motor fuel obtained thereby.

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