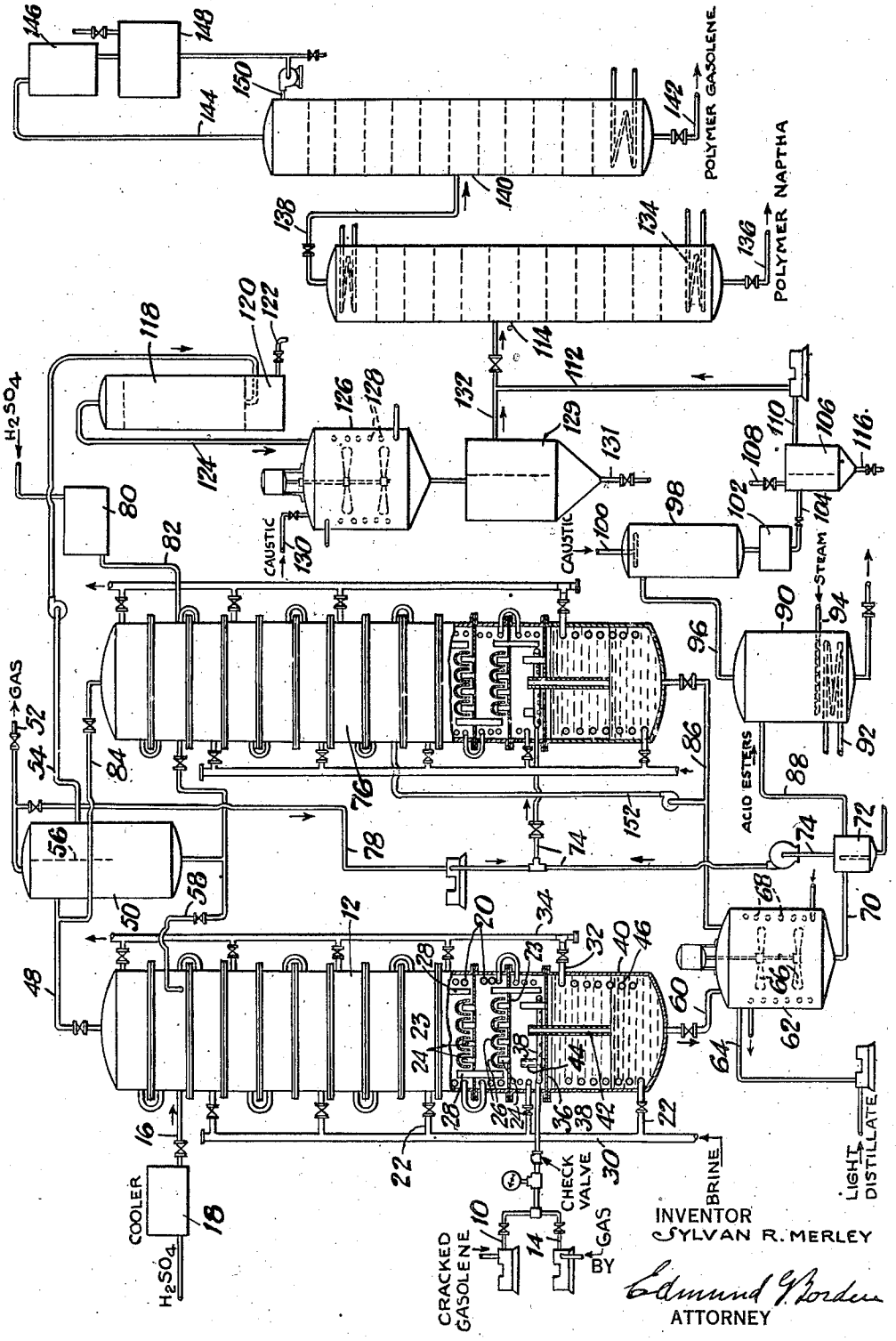
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MANUFACTURE OF HIGH ANTIKNOCK MOTOR FUELS

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MANUFACTURE OF HIGH ANTIKNOCK MOTOR FUELS

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2 Claims. (Cl. 196—10)

This invention relates to the production of an improved high anti-knock motor fuel.

The production of cracked gasoline as heretofore practiced has involved a step of chemical refining of the cracked gasoline distillate with sulfuric acid followed by redistillation, to obtain a suitable product substantially free of undesirable gum-forming constituents. The refining of cracked gasoline by sulfuric acid contact as heretofore practiced results in a product of lower anti-knock value by reason of the loss of desirable anti-knock constituents originally present in the untreated gasoline. When other methods of refining cracked gasoline are substituted for the sulfuric acid method with a view of improving its anti-knock characteristics, the resulting product will be found to have a lower end point and a lower calorific value by reason of loss of higher boiling paraffin hydrocarbon constituents eliminated because of their lower octane ratings.

The primary object of the present method is to provide a method of treating cracked gasolines in order to improve their anti-knock value without adversely affecting their calorific value.

A particular feature of the invention is a novel process of treating crude cracked gasolines with concentrated sulfuric acid under carefully regulated temperature conditions whereby a motor fuel product results having a higher calorific value and a higher octane rating than the crude gasoline as received from the cracking unit.

A further feature of the invention involves treatment of a mixture of crude cracked gasoline and unsaturated hydrocarbon gases with concentrated sulfuric acid and refining of the resulting products under carefully controlled conditions to produce a good yield of high anti-knock motor fuel.

Cracked gasoline distillates as now produced comprise a mixture of paraffinic hydrocarbons together with substantial proportions of mono, di, tertiary and more highly unsaturated olefins of different molecular weights. Treatment of such distillates with concentrated sulfuric acid presents difficulties which are not encountered in treating individual olefins, particularly straight chain olefins of low molecular weight, both because of the diluting effect of the paraffin hydrocarbons and because of the highly reactive character of the heavier mono-olefins and the di, tertiary and more highly unsaturated and unstable olefins present. Particular attention has to be paid to such reaction conditions as acid concentration and temperature control in order to insure a commercially practicable yield of useful anti-knock motor fuel. The process of the present invention rests largely on the discovery that an operative process requires the use of sulfuric acid of 90%–96% concentration and contact temperatures of not to exceed 70° F. when treating crude cracked distillates in liquid phase in accordance with the method herein described, whereby continuous stage by stage polymerization of highly reactive and less reactive constituents is effected in the presence of unreactive hydrocarbons, without substantial production of undesirable sulfur containing products or waste sludges.

Another important object of the invention is to provide a method of treating cracked gasoline with concentrated sulfuric acid so as to effect polymerization of unsaturated constituents while avoiding formation of undesirable sulfur-bearing constituents and large sludge losses.

With the above and other objects and features in view, the invention resides in the improved method which is hereinafter described and more particularly defined by the accompanying claims.

In the accompanying drawing a diagrammatic flow sheet illustrates a desirable apparatus layout for carrying out the process of the present invention.

Referring to the drawing, the crude cracked distillate to be treated is pumped in liquid phase, at a temperature of not to exceed 70° F. through a valved line 10 into the bottom of a contact tower 12 and thence upwardly therethrough in intimate contact with concentrated (90–96%) sulfuric acid in amount slightly in excess of that required to react with the olefins in the distillate. At the same time a stream of cracking still tail gas is pumped into the bottom of tower 12 through a valved line 14 at a temperature not to exceed 70° F., and the gas is also passed upwardly through the tower in contact with the concentrated sulfuric acid. The tail gas which is introduced at the base of tower 12 is preferably taken from the condenser equipment of the cracking unit and carries in vapor form two to five gallons of normally liquid hydrocarbons (higher than propane) which under the usual practice are recovered from the gas in an oil absorption plant. Experience has shown that the tail gas introduced through line 14 should carry sufficient reactive (olefinic) hydrocarbons to make up between 25% and 50% of the total reactive hydrocarbons which are introduced to the base of the tower 12 for treatment. Experience has also shown the advisability of limiting the hydrocarbon charge to the tower 12 to

those having a boiling point not substantially exceeding 275° F., in order to hold the resulting polymerized product within a boiling point range not substantially exceeding 410° F. end point.

Cracking still tail gases have been heretofore treated with concentrated sulfuric acid at low temperature for conversion of the olefinic hydrocarbon constituents to alkyl sulfates, followed by hydrolysis of the acid alkyl sulfates to produce alcohols. According to the present invention the unsaturated gaseous and liquid hydrocarbons are first contacted with the sulfuric acid at a time when such acid is diluted with a large amount of alkyl sulfates and liquid hydrocarbons, at a carefully regulated temperature in the close neighborhood of 70° F., at which temperature, with the acid concentration employed, a substantial proportion of the olefins are polymerized moderately without production of heavy polymers (tar) and avoiding formation of undesirable stable high sulfur compounds including disulfides.

To accomplish strict temperature and acid concentration control the concentrated (93%) sulfuric acid is introduced on the second tray below the top of tower 12 through a valved line 16 after passage through a cooler 18 in which the temperature of the acid is adjusted to approximately 35° F. The tower 12 is designed similarly to the usual bubble cap tower or absorber, and as the concentrated acid passes downwardly from the top of the tower it first reacts with olefins of the type of propylene and butylene to form acid alkyl sulfates. By the time the acid liquid reaches a tray above the mid-section of the tower 12, it consists of a mixture of concentrated sulfuric acid and alkyl sulfates in which the acid alkyl sulfates predominate. As the acid alkyl sulfates pass downwardly through the absorber, they react with additional olefins to form normal or dialkyl sulfates; and as the concentrated sulfuric acid passes downwardly into the lower portion of the tower, it reacts with the alkyl sulfates and also with the more reactive unsaturated hydrocarbons to form aliphatic, naphthenic and aromatic polymers most of which have boiling points within the gasoline range.

In order to regulate the temperature maintained on each tray of the tower 12 within narrow limits, the tower is equipped throughout its length for artificial cooling by cooling coils 20 which are mounted above each tray and through which brine or other cooling liquid is circulated at controlled rates from valved supply pipes 22. The olefinic hydrocarbons react strongly with sulfuric acid and acid alkyl sulfates, and the reactions are strongly exothermic, so that it is necessary to circulate cooling liquid through coils 20 in order to control the temperatures within the reaction tower at each part thereof to allow moderate, but not excessive, polymerization to take place.

As previously indicated, the tower 12 is substantially full of liquids during operation. The liquid and gaseous hydrocarbons entering the base of the tower flow upwardly and countercurrently to the saturated acid and alkyl sulfates which flow downwardly. To allow for this countercurrent flow, the bubble plates 23 have short upstanding pipes 24 fixed therein through which the gaseous and liquid hydrocarbons pass upwardly. Pipes 24 are covered by bubble caps 26 having slotted bottom edges under which the upwardly moving hydrocarbons are forced to pass into the heavier acid liquids on the upper surfaces of plates 23. The heavy liquids pass downwardly through the tower by means of pipes 28 so arranged on the plates 23 that their upper ends serve as overflow weirs at the level at which it is desired to keep the heavy liquid on the trays. The lower ends of pipes 28 dip into the body of heavy liquid held on plates below the plates to which the pipes are attached. A manifold 30 at one side of the tower is used to supply cooling liquid to each of the cooling coils 20 through the valved pipes 22, and the cooling liquid is discharged from coils 20 through valved discharge pipes 32 into a manifold 34.

A partition 36 forms the bottom of the absorption tower 12, and the crude distillate and tail gases are introduced into the tower by a perforated ring 38 located immediately above partition 36. A separating chamber 40 is attached to the base of the tower below partition 36 within which takes place quiet settling and separation of acid and alkyl sulfates from liquid hydrocarbons. A pipe 42 extends through partition plate 36 and its upper end forms an overflow weir for the heavy liquid on plate 36, such overflow liquid passing downwardly through pipe 42 into the lower portion of chamber 40. Upflow pipes 44 are also provided in plate 36 with their lower ends extending into chamber 40 and their upper ends located above the level of pipe 42. Pipes 44 afford the means for returning liquid hydrocarbons to the absorption zone after they have separated from the heavier acid liquids in chamber 40. Chamber 40 is provided with cooling coils 46 whereby to maintain a temperature therein corresponding to that obtaining on the lower plates of tower 12.

The mixture of gaseous and liquid hydrocarbons which is introduced to the tower 12 from ring 38 comes immediately into contact with the heavier mixture of sulfuric acid and alkyl sulfates on plate 36. The acid liquid on plate 36 comprises largely acid alkyl sulfates and dialkyl sulfates, together with a smaller proportion (say 20%–25%) of unreacted concentrated sulfuric acid. At the temperature of approximately 70° F. obtaining at the foot of the tower the more reactive olefins such as diolefins and tertiary olefins which are present in the entering crude distillate and tail gas, are immediately polymerized to higher boiling and more stable hydrocarbon products on contacting the concentrated acid at this temperature. Some of the unsaturated hydrocarbons (particularly straight chain olefins) entering the tower combine with the sulfuric acid to produce the corresponding acid alkyl sulfate. Some more of the unsaturated hydrocarbons react with acid alkyl sulfates to produce dialkyl sulfates. Also at this temperature some of the mono and dialkyl sulfates are decomposed by heat and by contact with concentrated sulfuric acid, and the olefins thus liberated are polymerized to higher boiling stable hydrocarbons. Careful regulation of the temperatures in all zones of the tower is necessary in order to inhibit oxidation reactions between the reactive hydrocarbons and sulfuric acid, with resultant liberation of SO_2 and metallic sulfur and formation of hydrocarbon compounds containing sulfur in chemical combination.

The dialkyl sulfates are oil soluble as well as acid soluble. The monoalkyl sulfates are not oil soluble but they are soluble in dialkyl sulfates as well as in sulfuric acid. During operation of the tower the liquid and gaseous hydrocarbons, including polymer products and both saturated

and unsaturated hydrocarbons, pass upwardly through the tower, while, owing to the difference in gravity, the sulfuric acid passes downwardly. Some of the dialkyl sulfates are carried upwardly through a portion of the tower, but do not reach the top before they become separated from the oil because of the fact that the alkyl sulfates are more soluble in the acid than in oil. Acid alkyl sulfates such as propyl and butyl acid sulfates are formed high up in the tower by reaction between the freshly charged sulfuric acid and the lighter straight chain olefins. As the acid sulfates flow downwardly into zones of gradually increasing temperature they absorb olefins to form normal sulfates such as propyl-amyl and butyl-hexyl sulfates. As these normal sulfates flow downwardly through the tower they in turn contact sulfuric acid and higher temperatures and are decomposed to produce acid sulfates, with liberation of nascent olefin and formation of polymers. Likewise the acid sulfates are in turn decomposed and polymerization of the liberated olefin takes place at the temperatures obtaining in the lower portion of the tower.

The importance of maintaining a careful regulation of temperature gradient between about 30° F.–35° F. at the top of the tower to approximately 70° F. at the foot of the tower when treating a mixture of crude light cracked distillate and tail gas with concentrated acid, cannot be over-emphasized. Some variation in temperature and acid concentration might be permissible in treating a single hydrocarbon, as for example, isobutylene, but in treating a mixture of hydrocarbon such as present in cracked distillate any material variation in temperature at any point in the tower may inhibit conversion of isobutylene to tri-butylene, for example, and in place thereof produce a mixed polymer with a highly reactive triple bond unsaturated hydrocarbon of so unstable a nature as to reduce any concentrated acid with which it contacts to form stable and undesirable sulfides and sulfur compounds.

The light liquid paraffinic and polymer hydrocarbons together with unabsorbed and uncondensed gases, including ethylene, leave the top of the tower 12 through the vapor line 48 and enter separator 50, where the fixed gas is separated from the liquid hydrocarbon and removed through the gas offtake 52. The liquid hydrocarbons are removed from the separator through a line 54, ported out on the opposite side of partition wall 56. Acid which is entrained in the liquid hydrocarbon leaving the top of the tower 12 collects in the bottom of separator 50 from whence it may be withdrawn through a line 58 and conducted back into the tower on a tray adjacent the top thereof.

The partially spent sulfuric acid and alkyl sulfates are removed from the separator 40 at the base of the tower through a valved connection 60 into a mixer 62. At the same time a cracked distillate preferably of approximately 400° F. end point, is pumped into the mixer through line 64. By means of the mixing paddles 66 the charge of mixer 62 is intimately mixed while holding the temperature therein at a point approximating that maintained in separator 40, by means of cooling coils 68. The distillate which is added to the spent acid-alkyl sulfate mixture in mixer 62 serves the purpose of promoting rapid separation and extraction of any liquid hydrocarbons, including polymers, which are entrained with the spent acid removed from separator 40. The temperature in the mixer is controlled to prevent any substantial polymerization. In some cases the distillate which is added to mixer 62 through line 64 may have to be of higher boiling point than gasoline in order to promote separation of heavy hydrocarbons entrained in the spent acid. From mixer 62 the charge is conducted through a line 70 to a centrifugal separator 72 where the hydrocarbons are separated from the heavier acid-alkyl sulfate mixture, the hydrocarbons being removed from the separator through a line 74 from whence they are pumped into the foot of a second acid contact tower 76 which duplicates in its design the contact tower 12. While feeding liquid hydrocarbons from the centrifugal separator 72 to the foot of the secondary contactor 76 through line 74, gaseous hydrocarbons are simultaneously pumped into line 74 through line 78, which receives the gases from the line 52 leading off from the top of separator 50. Concentrated sulfuric acid is supplied to the second from the top tray of contactor 76 through cooler 80 and line 82. The liquid and gaseous hydrocarbons which leave the top of contactor 76 are conducted through line 84 into separator 50, while the spent acid-alkyl sulfate mixture which is removed from the separator at the foot of tower 76 is conducted to mixer 62 through a valved line 86. Secondary contactor 76 is substantially identical in design with contactor 12, and its operation is substantially identical with the previously described operation of contactor 12 when practicing the process of the present invention.

The mixture of spent acid and mono and di-alkyl sulfates which is discharged from the centrifugal separator 72 is conducted by a line 88 to a desulfating still 90. In this still the centrifuged acid is heated to a temperature of 250° F.–350° F. by means of superheated steam supplied through heating coil 92, and also by direct steam distillation by means of steam introduced through perforated steam inlet 94. In some cases tail gas from the process may be introduced into still 90 along with the saturated steam through inlet 94. The distillation of the acid-alkyl sulfate mixture which takes place in still 90 effects decomposition of the alkyl sulfates and liberation of the olefins in a nascent state in which they polymerize quickly to higher boiling hydrocarbon polymers. The vapors of the hydrocarbon polymers are removed from the still through a vapor line 96 and are conducted into a scrubber 98 wherein the vapors are washed with caustic solution introduced through caustic supply inlet 100. The hydrocarbon vapors are condensed as well as being neutralized in passing through scrubber 98 and condenser 102, from whence they pass through valved line 104 into a separator 106. Any fixed gas which is not condensed is removed from the separator through gas outlet 108, and the washed oil leaves through 110, from which it is pumped through line 112 into the mid-zone of a fractionating column 114. Condensed water and caustic is removed from the separator 106 through valve drawoff 116.

The liquid hydrocarbons which are recovered in separator 50 comprise saturated paraffins which have been highly refined in towers 12 and 76 by washing with sulfuric acid and alkyl sulfates, in admixture with a large proportion of crude liquid polymers produced within the towers by the polymerizing reactions previously described. This mixture, which will be hereinafter

referred to as crude polymer oil, is conducted by pipe 54 into and upwardly through a sand filter 118. Any sulfuric acid sludge which is cleaned therefrom by passing through the filter, collects at the bottom 120 of the filter, and is removed through draw-off 122. The thus cleaned polymer oil is conducted by line 124 into an autoclave mixer 126 which preferably operates under pressure and is provided with heating coils 128 and a caustic supply inlet 130 for subjecting the oil to a strong caustic treatment for the removal of sulfur containing compounds including oil soluble sulfuric acids. The caustic treated oil is withdrawn from the autoclave 126 into a separator 129 wherein gravity separation takes place, the caustic sludge being removed from the separator through drawoff 131, while the treated light oil is conducted through offtake line 132 onto one of the middle trays of fractionating column 114.

Fractionation and stabilization of the polymer oil taken off from the tops of contact towers 12 and 76 and from the desulfator 90 is effected in tower 114 by heat supplied through the steam coil 134. The heavy fraction is removed from the base of tower 114 to storage through drawoff 136, and the light oil vapors are removed from the top of the tower through vapor line 138 into the central zone of a rectifying column 140. The stabilized and rectified polymer oil is withdrawn from the bottom of column 140 to storage through a valved drawoff line 142, and any light gas and vapors removed from the top of the column through vapor line 144 are passed through condenser 146 and separator 148, with return of reflux through connection 150.

Certain crude cracked distillates may contain a large proportion of highly unsaturated hydrocarbons or for some reason require a milder or more drastic treatment than others. It is preferred that the operating temperatures for the contact towers 12 and 76 which have been specified shall not vary substantially from the range 70°–30° to 35° F., and that the sulfuric acid concentration at the top of the towers lies within the range 90%–96% acid. Therefore any variation in the strength of treatment is preferably effected by modifying the acid concentration in the middle and lower portions of the towers by recirculation of spent acid and alkyl sulfates from the separators 40 at the base of each tower, as through connection 152 on tower 76.

Tests on the refined light polymer oil which is removed through line 142 show it to contain a substantial proportion of aromatic hydrocarbons and that it has a high octane value. In one particular instance when charging the apparatus through line 10 with a low end point cracked distillate having an A. P. I. gravity of 79.2, an initial B. P. of 73° F., and a distillation curve with 10% over at 95° F., 90% over at 204° F., and an end point of 285° F., a polymerized oil product was recovered having a boiling range of from 85° F. to 485° F. with 90% over at 410° F., a gravity of 65.0° A. P. I., and a volume about 60% that of the liquid distillate charged to the apparatus. This light polymer product had an octane number of between 80 and 90, and a solubility in concentrated sulfuric acid of 28% as compared to 19% acid soluble components in the cracked distillate originally charged, showing a large increase in the content of aromatic hydrocarbons. The treatment normally results in an increase in aromatic hydrocarbon content of about 33% as between the recovered light polymer oil and the original crude cracked distillate treated, with a corresponding drop of about 50% in the olefin content.

The heavy polymer fraction which is removed from the apparatus through drawoff 136 also has a high content of naphthenic and aromatic hydrocarbons, as well as branched chain aliphatics. This product has value both as a heavy motor fuel and as a blending stock for improving the octane rating of low end point straight run gasolines.

The invention having been thus described, what is claimed as new is:

1. In the process of manufacturing a high antiknock motor fuel by contacting unsaturated olefinic hydrocarbons with concentrated sulfuric acid, the improvement which comprises continuously introducing a stream composed of a mixture of liquid hydrocarbons produced by cracking petroleum oil and containing paraffinic and primary, secondary, and tertiary olefinic hydrocarbons having a boiling range up to approximately 275° F. into the first of a series of interconnected contact zones, introducing a stream of relatively cool concentrated sulfuric acid into the last of said series of zones, continuously passing said hydrocarbons and said sulfuric acid through said zones counter-current to each other and in intimate contact with each other in each zone, maintaining the first zone of the series at a temperature of about 70° F. and the last zone of the series at a temperature of about 30° F. whereby reaction products formed between said hydrocarbons and said sulfuric acid in the last zone of the series are carried with the acid toward the first zone of the series and subjected to gradually increasing temperatures thereby converting portions of said olefinic hydrocarbons into higher boiling products of relatively high octane number, and removing an improved high antiknock motor fuel product from the last zone of the series.

2. In the process of manufacturing a high antiknock motor fuel in which a continuous stream of cracked gasoline material and gaseous olefinic hydrocarbons are subjected to the polymerizing action of concentrated sulfuric acid, the improvement which comprises passing said stream of cracked gasoline and olefinic hydrocarbon gases upwardly through a contact zone in countercurrent intimate contact with a stream of concentrated sulfuric acid introduced into the upper part of said zone and acid reaction products resulting from said contact, maintaining a temperature of about 70° F. at the lower end of said zone and about 30° F. at the upper end of said zone, whereby acid reaction products are formed in the upper part of said zone and carried downwardly therethrough to react with the unsaturated hydrocarbons introduced into the lower part of said zone, removing the sulfuric acid residue material from the lower part of said zone and a liquid hydrocarbon product containing polymerized hydrocarbons from the upper part of said zone, extracting the sulfuric acid residue removed from said zone to recover polymerized hydrocarbons therefrom by continuously mixing therewith a stream of cracked gasoline and mixing said stream of cracked gasoline containing the extracted polymerized hydrocarbons removed from said sulfuric acid residue with the liquid hydrocarbon product removed from the upper part of said zone to produce said high anti-knock motor fuel.

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