Aug. 17, 1937. K. G. MacKENZIE 2,090,007

MANUFACTURE OF MOTOR FUEL

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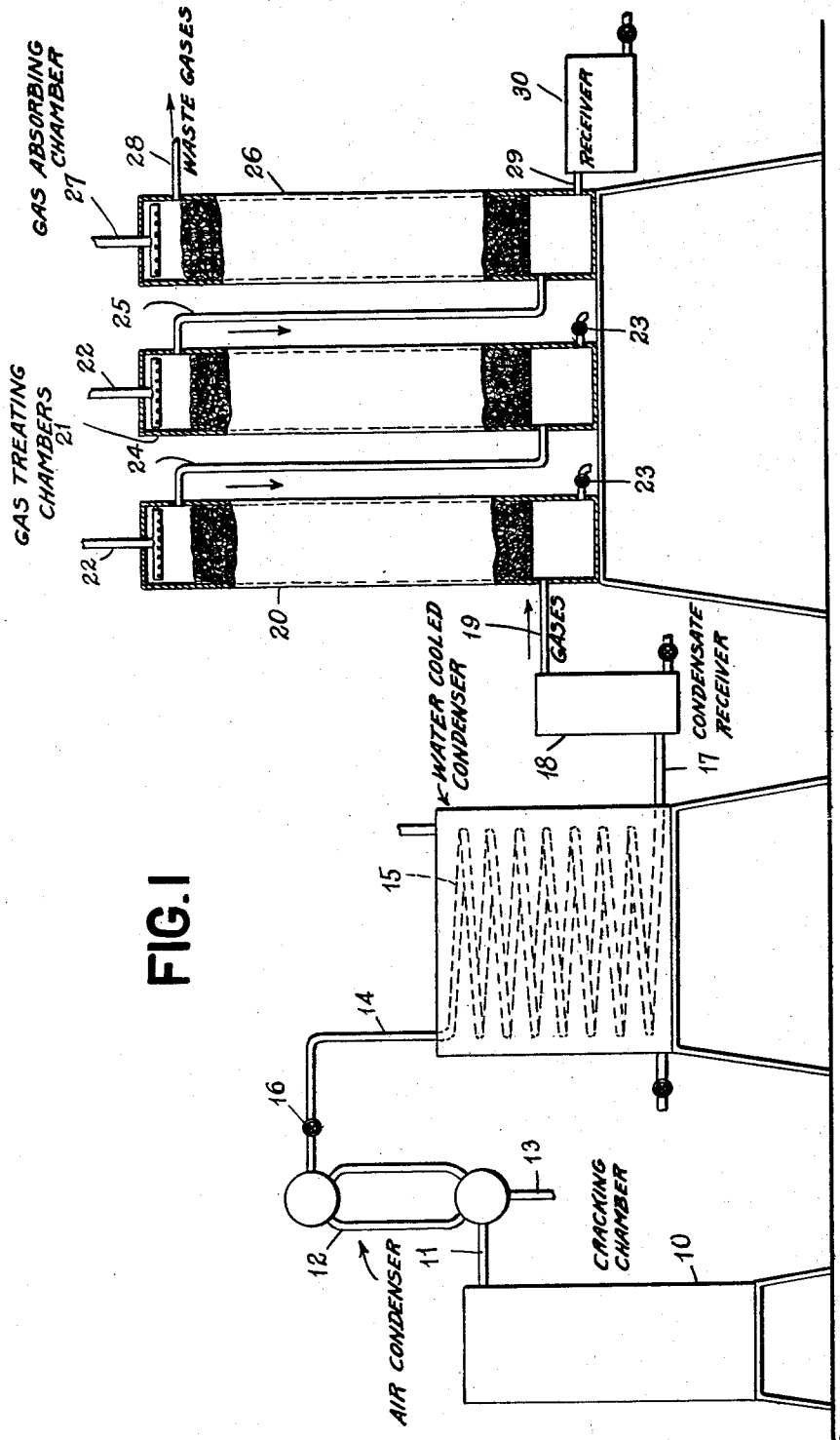


FIG. I

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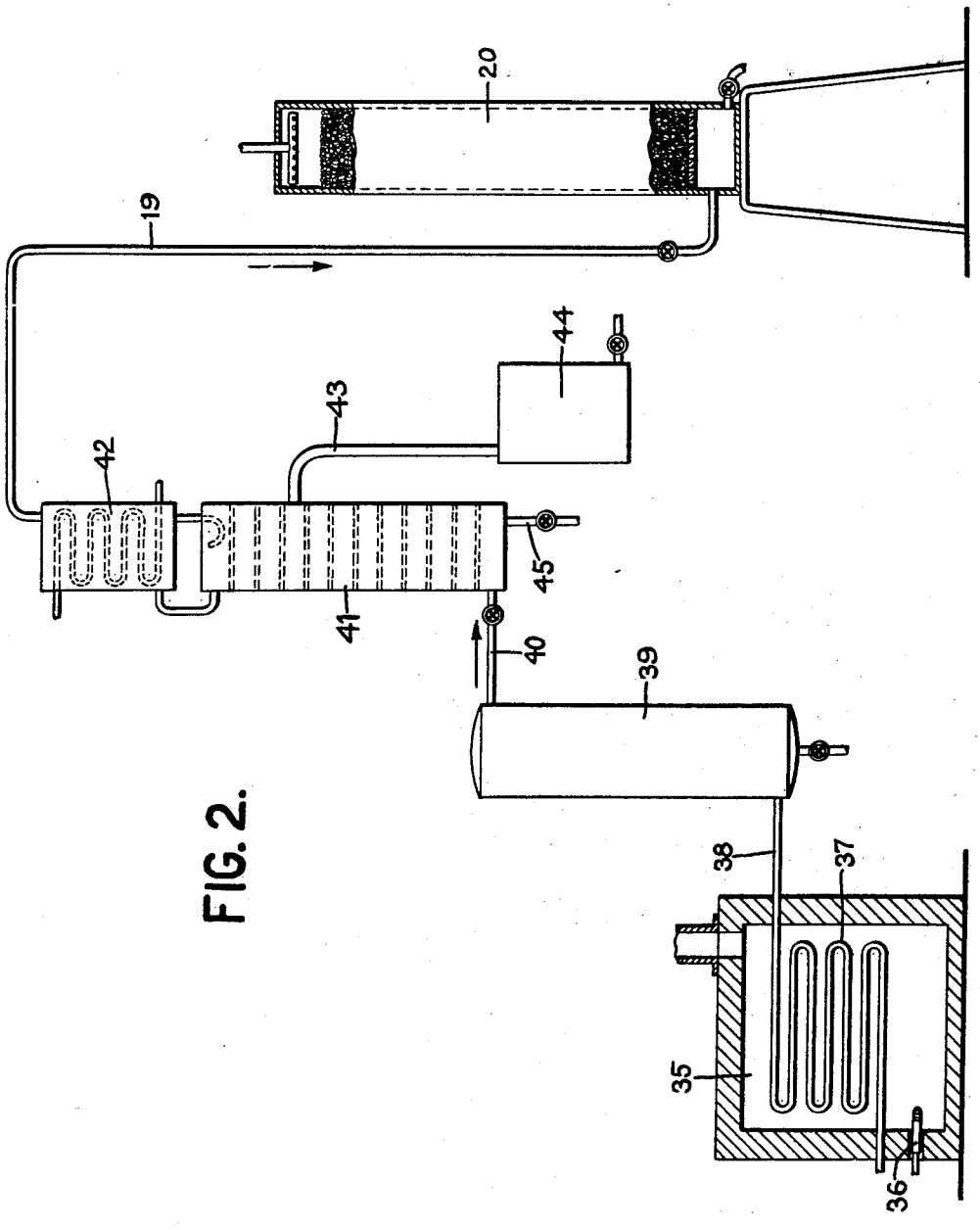


FIG. 2.

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# UNITED STATES PATENT OFFICE

2,090,007

## MANUFACTURE OF MOTOR FUEL

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Application September 26, 1928, Serial No. 308,535

4 Claims. (Cl. 196—23)

This invention relates to the production of light hydrocarbons, such as gasoline, and contemplates certain novel methods of treating and blending hydrocarbon vapors and distillates derived from the distillation of petroleum and other hydrocarbon oils with or without decomposition.

This application is a continuation in part of my co-pending application, Serial No. 565,626, filed June 3, 1922.

In cracking hydrocarbon oils for the production of gasoline there is usually formed a greater or less amount of so-called wild gases. These gaseous constituents generally consist of some permanent gases containing in solution quantities of condensable vapors. It is considered desirable to incorporate as large a proportion as possible of these light products in the liquid gasoline and consequently it has been sought to retain the wild constituents in the condensate derived from the cracking operation by condensing under superatmospheric pressure. Sometimes blending is resorted to and the wild gases are admixed, usually while under compression, with untreated petroleum distillates, the product thus obtained being subsequently distilled to yield fractions of desired boiling point.

Whatever may have been the precise method of obtaining the mixture containing the wild constituents it has been necessary to treat the product with acids or other chemicals in order to produce a marketable product adapted for use as a fuel for internal combustion engines or for other purposes. The cracked products derived from most of the cracking processes contain a comparatively large proportion of unsaturated compounds which react violently with reagents such as sulfuric acid and aluminum chlorid, with the evolution of considerable heat. The result is that great quantities of the lighter products which have been incorporated in the liquid are volatilized and lost. In addition to the losses resulting from chemical action and heat great losses also occur from the mechanical action of the agitation usually accompanying the treatment. Thus present methods of treatment are very wasteful and inefficient.

The primary object of my invention is to avoid the losses which characterize present methods of treating and handling cracked products and to so treat cracked constituents that marketable products are obtained. In accordance with my invention, therefore, the wild gaseous constituents derived from the cracking operation are segregated from the more easily condensable bodies which may then be purified by treatment with suitable reagents. The constituents thus segregated, either in the form of vapors or condensates, are then admixed with a liquid product that has been treated with a suitable acid or other purifying agent, the light constituents and the heavier treated liquid being blended in such proportions that the resultant liquid product will have the specifications required for the product desired. The desired boiling range of the heavy treated liquid or distillate is preferably secured prior to the blending by means either of condensers or by re-distillation, thereby avoiding unnecessary losses of the light constituents which would otherwise occur if distillation were resorted to subsequent to the blending operation. In some cases the wild constituents are filtered or treated to remove color bodies or material held in suspension or they are treated with alkalies or other suitable purifying agents prior to the blending with the liquid base.

One feature of the invention involves the blending of the wild cracked constituents or condensates therefrom with a hydrocarbon distillate having a boiling point range of that of the heavier constituents of gasoline. The lighter products entering into the mixture furnish the lower boiling point constituents of the motor fuel and the result is that a product having the low initial boiling point desired for easy starting in hydrocarbon motors and having also a sufficiently high boiling fraction to give the desired calorific power, is produced.

In order to more fully disclose my invention, I will now proceed to describe the methods of operation, reference being had to the accompanying drawings in which Fig. 1 is a diagrammatic elevation of an apparatus adapted for carrying out the invention and Fig. 2 is a diagrammatic elevation of a modified form of apparatus.

10 designates an apparatus for cracking oil and may be of any desired character, it being understood that my invention has no reference to any particular method of carrying on the cracking operation per se. The apparatus may be equipped with a vapor line 11 leading to a suitable air condenser or separator 12 having a reflux pipe 13 adapted to return to the cracking zone the insufficiently cracked constituents. A vapor line 14 extends from the separator 12, or directly from the cracking apparatus, if desired, to the condensing coil 15 which is preferably water-cooled. Interposed between the still and condenser there is a pressure relief valve 16. When using an air condenser, such as the separator 12, it is generally desirable to place the pressure control valve

in the outlet from the separator rather than in the vapor line 11 and accordingly the valve 16 has been shown as being in the line 14. The valve 16 is used to hold the hydrocarbons in the still or converter 10 at the desired pressure and also serves to reduce the pressure in the condenser 15 so that condensing may be carried on at comparatively low pressure, for example at atmospheric pressure. It is to be understood that the practice of my invention is not confined to a method of operation in which condensing is carried on at atmospheric or low pressure but it is usually preferable when employing my process to condense at substantially atmospheric pressure.

The condenser is equipped with an outlet 17 which leads to the receiver 18 wherein the condensate is collected. A pipe 19 conducts the uncondensed constituents, including the wild gases, to a compressor or absorber or other blending apparatus wherein the vapors and gases are admixed with a treated hydrocarbon oil. It is sometimes desirable to treat the gases and vapors with certain chemical reagents in order to remove sulfur compounds and in order to remove color materials. The pipe 19 is therefore shown as extending to one or more treating chambers such as the vessels 20 and 21. The treating chambers are preferably provided with contact material, and with spray pipes, such as 22, by which chemicals may be sprayed over the contact material. In the drawings I have illustrated the treating vessels as consisting of the two towers 20 and 21 but it is to be understood that any convenient number may be used, the number employed being dependent upon the character of the impurities in the vapors and gases and upon the character of the chemical used. Each tower is equipped with an outlet pipe 23 by which the treating fluids may be withdrawn. One or more pipes, such as 24, are provided to conduct the vapors from one treating chamber to the next in succession and an outlet pipe 25 is provided for the last treating vessel, such as 21. If desired, the treating vessels may be enclosed in heating jackets or otherwise heated in order to prevent any material condensation of the gases and vapors while being treated as I have found that when treating with alkali solutions, for example, there is a greater tendency toward the formation of emulsions if the constituents being treated are in a liquid state than if they are in the form of vapor.

The pipe 25 extends to a suitable compression, absorption, or other blending apparatus. As shown in the drawings it terminates in the absorbing chamber 26 which preferably contains suitable contact material and is provided with a spray pipe 27 by which the liquid which is to be blended with the vapors and gases is admitted to the absorption chamber. It is to be understood that my invention is not limited to the use of absorption as a means of blending gases with liquids but that compression as well as other equivalent means may be used in the blending operation. I find it is generally desirable, however, to use absorption since the product obtained is generally more stable than one produced by compression. The absorbing chamber 26 is provided with the gas outlet 28, and with a liquid outlet 29 by which the blended product is conducted to a receiver 30.

In the preferred method of operation a suitable hydrocarbon oil is subjected to pyrogenic decomposition and the vaporous products of the reaction are allowed to pass to the condenser 15 wherein condensation is effected at substantially atmospheric pressure. In this method of operation there will be a much greater proportion of bodies uncondensed in the condenser coil than when condensation is carried on under superatmospheric pressure. The condensed fluids commingled with the vapors and gases, including the wild constituents, are passed into the receiver 18 wherein the condensate is collected. The liquid product thus collected in the receiver constitutes what is commonly known as cracked naphtha distillate and may be purified by treatment with suitable reagents such as aluminum chlorid, sulfuric acid, alkali solutions and other well known purifying materials, in order to produce a marketable product such as is adapted for fuel for an internal combustion engine. The uncondensed constituents are conducted by the vapor line 19 directly to a blending chamber or else to such treating or filtering means as may be desired.

The purifying treatment given the gaseous constituents is dependent upon the character of the impurities, the extent to which the impurities are present and the proportion of gaseous products which it is desired to blend with a given liquid base. In some cases it is merely necessary to pass these light bodies through suitable separators or through filtering or adsorbing material, such as fuller's earth or charcoal, whereby color bodies are removed. In other cases chemical treatment is desirable. An alkali is ordinarily the best treating material for the gases and vapors obtained from the destructive distillation of hydrocarbons. It is sometimes well to employ a comparatively cheap material capable of removing the bulk of the impurities in one treating vessel, as the tower 20, and to use in a second tower, as 21, a more expensive material capable of removing impurities which were not attacked by the chemical in the first tower. Thus it has been found advantageous to pass the gaseous products first through a lime solution and then through a lead-soda solution. The chemical reagents used may be either in the form of solutions or in the form of dry material through which the vapors are permitted to pass. Various chemicals have been found advantageous, such as lime, lead-soda, soda ash, potassium carbonate, caustic soda, lye, iron oxid, and the like. It is often advantageous to treat the gases with a comparatively cheap reagent such as milk of lime and then to pass the treated gases through fuller's earth or charcoal to remove color bodies or other materials held in suspension in the gases. It is preferable to treat the gases with a reagent capable of attacking the impurities, such as sulfur compounds, but which does not combine with the hydrocarbons as losses are thereby reduced. It is sometimes unnecessary to treat the gases with any chemical in which case the gases may be passed directly to the blending chamber.

The gaseous constituents having received such treatment as may be necessary or desirable are then passed into the blending chamber 26 wherein they come in contact with a suitable liquid hydrocarbon oil which is admitted through the pipe 27 and are blended with this liquid to produce a blended liquid product having the characteristics desired. The product admitted through the pipe 27 comprises a treated product, such as a petroleum distillate which has been treated with sulfuric acid, aluminum chlorid or other reagent, and is of such nature that it will pass the standard tests for marketable products. The

treated liquid base is blended with the gaseous constituents including the so-called wild gases derived from the cracking of hydrocarbon oils. The liquid base may be a product derived from the decomposition of hydrocarbons or from the simple distillation thereof. Thus the liquid base may be either a cracked naphtha distillate which has been suitably purified or a naphtha distillate produced by mere fractionation and proper purifying treatment. I have found that certain of these gaseous products may be blended without treatment of any kind with a treated hydrocarbon distillate and if the proportion of untreated bodies and treated liquid is properly adjusted the resultant blended product will be found to be suitable for the market. As has been pointed out, with some of the gases a chemical treatment, such as an alkali treatment or the passing of the gases through filters or separators, may be necessary. This is especially true in the case of gases derived from Mexican crude and similar petroleums which have comparatively large proportions of sulfur compounds, and in which case chemical purification is usually required. In any case the practice of my invention avoids the treatment of the blended product by agitation with the resultant loss of the lighter bodies by mechanical action and also avoids treating the blended product with an acid, such as sulfuric acid, or with aluminum chlorid, or other reagent in which heat is generated during the reaction and in which substantial losses occur due to volatilization of the lighter products. By means of my invention the lighter vapors and gases, including the wild constituents, are so treated and blended with a finished stock that these losses are avoided.

The character of the purifying treatment accorded the light vaporous fractions, which include the wild gases, depends very largely upon the crude oil source from which these fractions may have been derived. In most cases, however, a treatment comprising the passing of the vapors through suitable adsorbent material or alkali solution has been found to be adequate. The vapors thus purified are then blended with the liquid base which has been properly purified. The treatment required for the liquid base is generally different from that given the lighter fractions; the heavier liquid base must generally be treated with more powerful reagents, such as sulfuric acid, aluminum chlorid and the like, in order that the ultimate blended product will meet the specifications desired. In blending the lighter fractions with the liquid base the lighter bodies may be in the vapor form or they may be cooled sufficiently or otherwise treated to produce a liquid or condensate which may then be admixed with the liquid base.

In one method of practicing my invention instead of following the usual procedure of blending the lighter gases with a comparatively heavy stock and then distilling the blended product in order to yield a distillate of desired tests I have found it generally more economical to blend the light constituents with a product, which when so blended will yield a product having the desired tests. Thus in the production of motor fuel I have used successfully a liquid base having an initial boiling point around 280° F.–300° F. and an end point of about 400° F.–425° F. by admixing this product, which it will be noted comprises largely the heavier fractions of gasoline (according to standard specifications now in use), with a light volatile product derived from the cracking of hydrocarbon oil and comprising (as it came from the condenser) a gas or a gaseous product containing condensable vapors in solution, the blended product having an initial boiling point of about 85° F.–100° F. and an end point of 400° F.–425° F. This type of product contains sufficiently heavy constituents to give a high calorific value to the gasoline and at the same time its low initial boiling point makes it susceptible of easy starting in hydrocarbon motors. This preliminary determination of the boiling range of the liquid base before the blending step may be accomplished by means of condensers or by redistillation and thus avoids losses of the lighter constituents otherwise incident to the usual fractional distillation subsequent to the blending operation.

In the practice of my invention various modifications may be made from that which has been described specifically in this specification. For instance, in one method of operation the wild gases may be subjected to compression to produce a liquid product which may subsequently be blended with a reagent-treated liquid. In another method of operation instead of holding the temperature in the final condenser, which receives the products derived from the distillation or cracking of hydrocarbon oils, at atmospheric temperature or thereabouts, such as is commonly done, a comparatively high temperature may be maintained in order to collect a liquid at such a temperature that it will not be possible for any material quantity of wild gases to be present therein. This liquid may be drawn off to a cooler and treated as may be desired. The vaporous product which contains the wild gases may then be removed from the high temperature receiver and treated by any of the methods which have been described herein for handling the gases and vapors.

In Fig. 2 a furnace 35 having a burner 36 surrounds a heating coil 37, in which oil may be raised to a cracking temperature, and is connected by pipe 38 to cracking still 39. The vapor space of the still 39 is connected by pipe 40 provided with a suitable valve to the lower part of a fractionating column 41 above which is provided an ordinary form of reflux condenser 42 connected by suitable vapor and liquid return lines. The reflux condenser 42 is connected by a pipe 19 to a treating chamber 20 similar to that shown in Fig. 1. The pipe 43 leads from the liquid level at an intermediate tray in the column 41 to a receiver 44 for liquid condensate. The fractionating column 41 may also be provided with a draw-off pipe 45 for withdrawing the heavier fractions which may collect at the bottom of the column. The operation of this modified form of apparatus may be similar to that illustrated in Fig. 1.

The oil in passage through the heating coil 37 is raised to a cracking temperature and passed by the pipe 38 to cracking still 39. This cracking still may receive external heat or it may be insulated and sufficient heat be derived from the hot oil entering through the pipe 38. Vapors of the cracked hydrocarbons pass by pipe 40 into the fractionating column 41 where they are separated into three fractions; the lightest fractions pass out at the top of the column and the reflux condenser 42 into pipe 19 and may be retained in vapor state and thus refined in chamber 20 as heretofore described. The intermediate fraction may be drawn off from an intermediate tray in the column 41 and flows through pipe 43 to receiver 44 from which it may be drawn off and

treated in any suitable manner. The heaviest fraction collects at the bottom of the column 41 and may be drawn off through the pipe 45 and may serve as a stock for further cracking.

The oil in heating coil 37 and in still 39 may be and preferably is under substantial pressure and this pressure may be carried through the fractionating column 41 and reflux condenser 42 by maintaining the valve in pipe 19 partially closed. In another method of operation the pressure may be reduced before the vapors reach the fractionating column 41 by the valve in pipe 40.

In the operation of this apparatus it may be desirable to allow vapors to pass out of the reflux condenser 42 which will produce a condensate having a relatively low end boiling point, as for example 250° to 300° F. These light vapors may receive a suitable treatment in column 20, which as previously pointed out may be less drastic than that necessary to suitably refine a heavier condensate; these vapors may be refined either while maintained in vaporous condition, or they may even be cooled and condensed and refined in liquid state. The intermediate fraction which may be drawn off through the pipe 43 may suitably have an end boiling point of 400° to 425° F. After the vapors in chamber 20 have been refined they may be blended, as previously pointed out, with heavier refined oil to produce a suitable motor fuel. This heavier oil may suitably be the refined condensate from the receiver 44.

It is well known that as a result of cracking reactions a mixture of hydrocarbons is produced. Some of these hydrocarbons are gases at normal atmospheric pressures and temperatures; these are the most volatile. Next in order of volatility are the hydrocarbons having relatively low boiling points, but which are normally liquids. Both these classes of hydrocarbons are present in the commercial motor fuel which is a mixture of these hydrocarbons with still heavier hydrocarbons having higher boiling points, and therefore of lower volatility. The gaseous and low boiling hydrocarbon constituents of motor fuel, on account of their great volatility, have a tendency to escape from the liquid mixture and are those generally termed in the industry "wild" constituents. The terms "wild gases" and/or "lighter constituents" are used throughout the specification to designate those gaseous and light liquid constituents of motor fuel which have a strong tendency to volatilize and escape, especially upon increases in temperature, such as may readily be encountered in treating.

Obviously, various modifications of the invention may be effected without departing from the spirit and scope of the invention. The true scope of the invention is defined in the appended claims.

What I claim is:

1. The process of making motor fuel from cracked hydrocarbon vapors which comprises separating by fractional condensation a cracked naphtha distillate as liquid and a lighter fraction comprising substantial amounts of motor fuel constituents, subjecting the lighter fraction to a relatively mild refining treatment, and blending the refined lighter fraction with cracked naphtha distillate from which the lighter fractions have been separated and which has been refined by a more drastic refining treatment, whereby a marketable motor fuel is produced.

2. The process of making motor fuel from cracked hydrocarbon vapors which comprises separating by fractional condensation a cracked naphtha distillate as liquid and a lighter fraction comprising substantial amounts of motor fuel constituents, subjecting the lighter fraction to a relatively mild refining treatment with an alkaline reagent and blending the refined lighter fraction with cracked naphtha distillate from which the lighter fractions have been separated and which has been refined by a more drastic treatment including treatment with sulfuric acid, whereby a marketable motor fuel is produced.

3. The process of making motor fuel from cracked hyrocarbon vapors which comprises separating by fractional condensation a cracked naphtha distillate as liquid and a lighter fraction comprising substantial amounts of motor fuel constituents, subjecting the lighter fraction to a relatively mild refining treatment such as to effect no substantial loss of valuable unsaturated hydrocarbons, and blending the refined lighter fraction with cracked naphtha distillate from which the lighter fractions have been separated and which has been refined by a more drastic treatment including treatment with sulfuric acid, whereby a marketable motor fuel is produced.

4. The process of making motor fuel from cracked hydrocarbon vapors which comprises separating by fractional condensation a cracked naphtha distillate as liquid and a lighter fraction comprising substantial amounts of motor fuel constituents, subjecting the lighter fraction to a relatively mild refining treatment comprising contact with fuller's earth, and blending the refined lighter fraction with cracked naphtha distillate from which the lighter fractions have been separated and which has been refined by a more drastic treatment incdluding treatment with sulfuric acid, whereby a marketable motor fuel is produced.

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