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PROCESS FOR REFINING HYDROCARBON OILS AND DERIVATIVES

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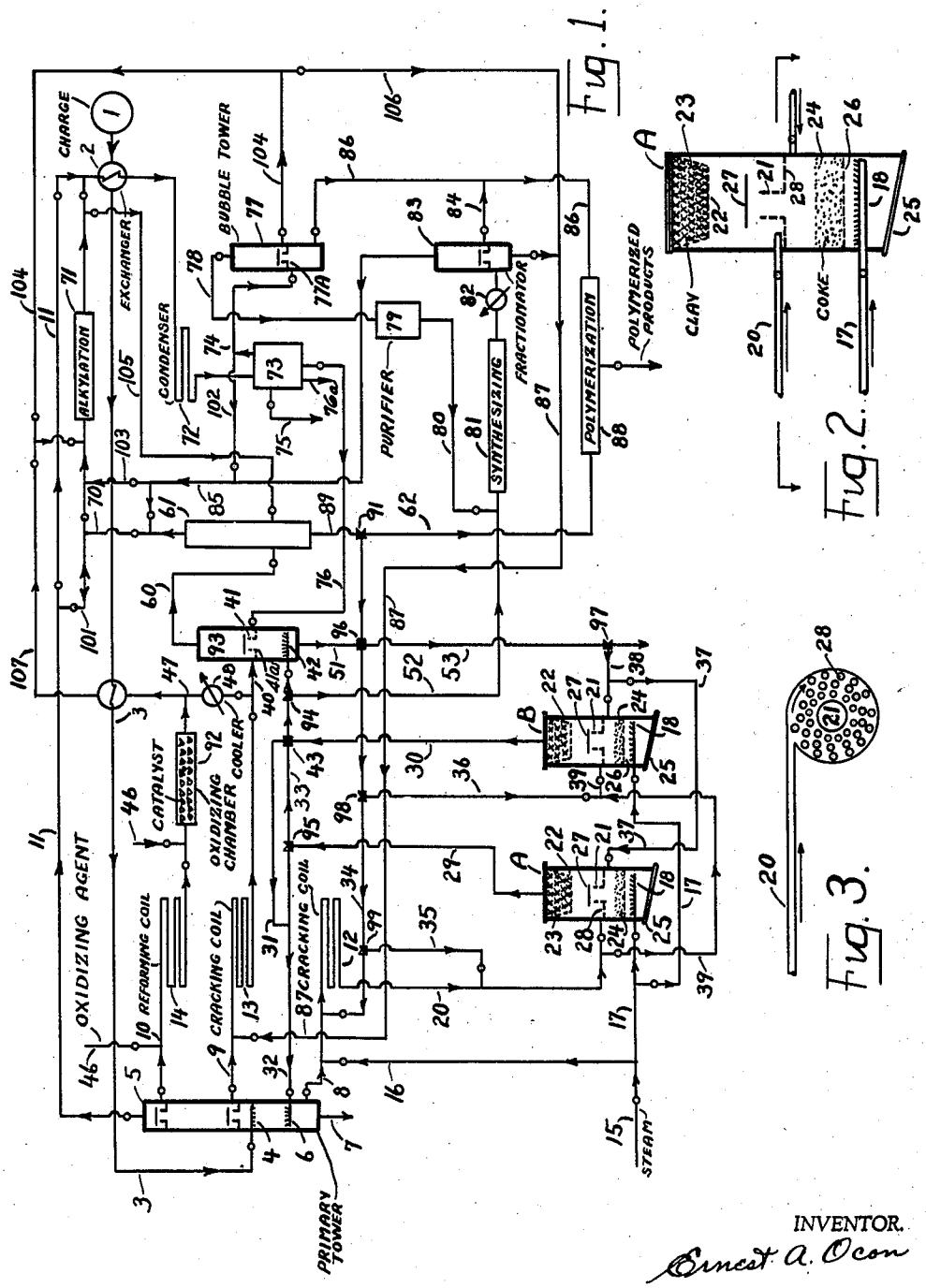


Fig. 1.

Fig. 2.

Fig. 3.

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PROCESS FOR REFINING HYDROCARBON OILS AND DERIVATIVES

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6 Claims. (Cl. 196—50)

This invention relates to heat treatments of bituminous liquids and gaseous hydrocarbons, such as mineral oils, natural gas, and their decomposition products. It is particularly concerned with the recovery of valuable commercial products useful in automotive engines, such as anti-knock motor fuels and lubricants from oxygenated and reactive derivatives of less useful portions and conversion products obtained from the natural materials, with economy in materials, fuel and apparatus.

It is now known that thermal cracking of high boiling hydrocarbons to produce anti-knock motor fuels is inefficient by itself. This is due to the fact that upon undergoing cracking to produce a maximum of high quality gasoline, the high boiling hydrocarbons are decomposed to a substantial extent into normally gaseous products and liquid products boiling above the gasoline range which are degraded for utilization as heating oils. Diesel fuel, cracking stock, and lubricants. Partially successful attempts have been made in the past to recover liquid products from the normally gaseous hydrocarbon materials by subjecting them to polymerization in the presence of certain well known acidic catalysts such as phosphoric acid and sulphuric acid which are highly sensitive and useful only apart from cracking treatments.

To avoid restrictions encountered with the use of acidic polymerization catalysts a different approach to the problem of recovering larger amounts of useful products from natural hydrocarbon materials has been found in the utilization of basic catalysts which operate efficiently in isomerizing the gaseous hydrocarbons when they are in a partially oxidized condition. More specifically, normally gaseous hydrocarbons can be readily activated by controlled oxidation into unsaturated and partially oxidized hydrocarbons, which in turn are susceptible of being readily rearranged into more highly active branched compounds by proper catalysts, as will be explained; and these more highly active organic compounds are thus made available for polymerization, alkylation and other reactions, such as dehydration, and/or hydrogenation if desired, for obtaining final commercial products having properties which are advantageous for automotive and similar purposes.

An object of this invention is to make possible an efficient cracking of a large proportion of bituminous liquids as clean or tar free distillates, which can be subjected to cracking conditions without undue coke formation either with or without the use of a catalytic contact mass. More specifically, it is intended to make use of mild oxidizing reactions and suitable catalysts to recover a larger proportion of useful vaporous products from the initial materials and to treat the normally gaseous products by an efficient method for increasing and improving the final liquid products of the entire process.

Later it will be explained how a recovery is made of the additional useful liquid products by the use of synthesis reactions involving oxidized hydrocarbon products. The process will be described by reference to the accompanying drawing, which illustrates diagrammatically a suitable apparatus for carrying out the process in a preferred manner.

In Figure 1 is shown means for performing combined operations of cracking, reforming, oxidizing, alkylating, synthesizing, polymerizing, etc.

In Figure 2 is shown more specifically the internal arrangement of chambers in which the residual products of the bituminous liquids are treated to release additional vapors and to form gaseous products.

In Figure 3 is shown a cross sectional view of Figure 2.

Consider that a charging stock of bituminous liquids, e. g., crude petroleum or topped crude, is passed from storage vessel 1 through a heat exchanger 2 by line 3 into a primary flash tower 5. This initial oil or charging stock in passage may be preheated to an incipient cracking temperature in heat exchanger 2 and in other heat exchange units.

When injected into tower 5, e. g. by spray device 4, the charging stock may be subjected to a blast of heated vapors from spray device 6 for promoting vaporization. Arising from the vaporized charge oil, the vapors may then be fractionated to form one or more distillates, e. g., a gas oil distillate for cracking, and a naphtha distillate for reforming, each of which may be withdrawn by valved lines 9 and 10. If desired, an intermediate distillate for Diesel fuel, also heavier distillates for lubricants may be withdrawn. A portion of the unvaporized oils collected in tower 5 may be withdrawn through valved line 8 to be passed in heated condition to a flash chamber, such as A or B, preferably through a mild heating or cracking coil 12. Difficultly distillable liquids passed to the flash chambers are preferably made to vaporize under subatmospheric pressure. Distillation and flashing of the heavy liquids may also be aided by heated gases introduced through

line 15 and valved line 17, e. g., hydrogen, steam, gaseous hydrocarbons, water gas, etc., may be introduced.

As shown with more detail in Figure 2 and Figure 3, a plurality of flash vaporization chambers, represented by A and B, are provided for the distillation of residual oils so that while one chamber is being used for distillation, another may be subjected to regeneration by removal of tarry materials. During distillation superheated steam may be injected into heating coil 12 through line 16. Another amount of steam may be added to the bottom of the distilling flash chamber by means of spray device 18. Residual oil passed through line 51 from separator 93 and/or reflux passed through line 89 from fractionator 61 may be added through line 34 to the residuals from tower 5 as they pass to coil 12 through line 8, or be injected into the lower part of the flash distillation chamber, A or B, from lines 53, 38 and 37. For simplication, three-way valves are shown at 99, 98, 97, 96, 95, 94, 91, and 43 for directing the materials into their desired courses, as will be hereinafter explained.

It is to be understood that the contact mass shown to be located in a basket 22 at the upper part of each distillation flash chamber, A and B, may be located in separate chambers interconnected between these chambers and tower 5, and that each of said contact masses may be provided with means for effecting regeneration.

The heavy oils from tower 5 are flashed alternately into the flash chambers by means of line 20 or valved line 39, preferably in a manner which permits the injected fluid to pass tangentially into a pool of liquid on either tray 21. Trays 21 have perforations 28 for passage of liquids. Above tray 21 is baffle plate 27 for knocking out tar particles. Below may be provided a grate 26 supporting coke bed 24. Underneath grate 26 may be located a steam jet 18 receiving from line 15 through junction 17. The flash chambers may be provided with moveable parts 25 to enable removal of coke. At the upper parts of chambers A and B may be provided contact masses 23 for eliminating tar and coke forming substances from the vapors passed therethrough. Materials useful as contact masses in this respect are activated clay, charcoal, fire brick, unglazed clay rings, bauxite, pumice, coke, ash or similar adsorbing masses which may also be used as cracking catalysts to promote additional cracking of vaporized hydrocarbons leaving the upper part of chamber A and B. With either chamber A or B in use to receive the heated residual oil from coil 12, purified vapors may be passed from line 29 or 30 to line 32 or 33 for introduction into the primary flash tower 5 through spray device 6 as the blast for aiding vaporization of the charge oil or for aiding vaporization in tower 93.

An intermediate condensate of the nature of gas oil withdrawn from tower 5 by valved line 9 may be heated for cracking in coil 13 to a temperature above 800° F. under suitable conditions with temperature, pressure, and time controlled, dependent upon the use of cracking catalysts disposed in the path of the gas oil compounds undergoing cracking in coil 13 for producing optical amounts of gasoline hydrocarbons. A lighter distillate, e. g., a heavy naphtha withdrawn by valved line 10 from tower 5, may be subjected to reforming conditions in heating tube 14. The conditions imposed in the reforming, of course, are somewhat dependent upon the further treatment in catalytic chamber 92 which may be used as an auxiliary reforming zone to supplement the pyrolytic reforming in coil 14.

In heating tube 14 the naphtha distillate hydrocarbons are properly activated for reforming at temperatures and pressures which are not excessive if they are treated with a mild oxidizing agent as, for example, by steam or air diluted with carbon dioxide, etc., for example at temperatures in the range of 900 to 1150° F., particularly, if they are brought into contact under substantially the same conditions with a mild oxidizing catalyst in chamber 92. The mild oxidizing agent, e. g. steam, oxygen diluted with inert gas, etc. may be introduced by lines 46.

Chamber 92 may be provided with a mild oxidizing catalyst, such as oxide of a divalent metal or element capable of combining with oxygen in an atomic ratio of 1 to 2. For example, oxides of copper, titanium, chromium, tungsten, vanadium, germanium, silica, cerium, etc., zeolites containing such metals or other siliceous materials with such metal oxides incorporated may be used. The space velocity is controlled to allow any degree of oxidation desired. Space velocities as high as 600 to 10,000 cu. ft. per hour per cu. ft. of catalyst may be used. Suitable temperatures for the reaction are in the range of 400 to 1100° F. with time of contact varying from about 5 minutes to 1 second. Partial oxidation products from chamber 92 may be passed through line 47 to cooler 48 under pressure, thence jointly with products from the cracking coil 13 by line 40 to separation zone 93, passing into a midsection where a pool of oil is collected on tray 41 with holes 41a, preferably in a manner to maintain the pool of oil in a turbulent motion for increasing vaporization of volatile products. Beneath tray 41 spray device 42 may be used for injecting gaseous products from flash chamber A or B, led thereto by lines 29, 30, and 33, especially when either of these chambers is undergoing regeneration to produce water gas. Vapors may be led from separator 93 by line 60 to fractionator 61 where vapors higher boiling than gasoline are collected as a condensate.

Fractionated vapors from 61 may be passed by line 70 through catalytic alkylation zone 71, thence be joined by overhead vapors and gases led by line 11 from tower 5 to pass through heat exchanger 2 to coil 72 for condensation. Products of condensation from 72 received in 73 can be separated into motor fuel liquids decanted by line 75. Valved by-pass line 101 permits introduction of overhead vapors and gases from line 11 also into alkylation zone 71, and also permits, by proper adjustment of valves on lines 101 and 11, for by-passing of the alkylation zone by fractionated vapors withdrawn from fractionator 61 by line 70 so that only lower boiling compounds with respect to gasoline such as normally gaseous compounds are delivered to the alkylation zone as by lines 85, 102, 103 and 104.

Vapor products issuing from the alkylation treatment in zone 71 may be re-run for removing high boiling ends by diverting these products through line 105 to a fractionator, e. g., 61 with overhead vapors from 61 at least partly bypassing the alkylation zone through line 101 to line 11.

Uncondensed gaseous products from receiver 73 may pass through line 74 to bubble tower 77 for recovery and separation of uncondensed gases by partial liquefaction under pressure using conventional means (not shown) for compress-

ing and cooling the gases as they pass to the tower 77. In bubble tower 77 gaseous hydrocarbons may be fractionated to obtain one or more cuts composed mainly of one or several aliphatic compounds having 2 to 6 carbon atoms per molecule including the various isomeric and unsaturated compounds. One or more of these cuts may be led from tray 77A by line 104 to zone 71 to take part in the alkylation reaction. A portion of the cuts may be sent by line 106 to cracking coil 13.

Gases passed overhead from 77 should comprise generally carbon monoxide, hydrogen, methane, ethane, ethylene, etc. withdrawn by line 78 for passage through purifier 79 containing a reagent for removing any undesired substances, such as sulphurous components, carbon dioxide and moisture. Calcium oxide is an example of such reagent, but others may be employed. Purified gases may be led from 79 by line 80 to synthesizing zone 81, provided with a catalyst fostering the formation of alcohols and/or higher hydrocarbons. Gases for the synthesis may be supplied directly from other sources as by line 52. The type of catalyst used in this treatment is exemplified by iron or cobalt activated by a weak alkaline oxide, e. g. zinc oxide, chromium oxide or alkaline carbonate. Various mixed catalysts, such as cobalt-copper-manganese, cobalt-thorium, cobalt-thorium-copper, cobalt-manganese, and the like may be employed. Temperatures of the order of 450 to 600° F., and pressures of about 5 atmospheres and above may be used. The duration of time is controlled to produce the desired types of products.

In the synthesis of hydrocarbons and alcohols from carbon monoxide and hydrogen, suitable adsorbent carriers may be used, such as magnesia, pumice, diatomaceous earth, bauxite and alike. At temperatures as low as 400° F., pressures of about 10 atmospheres or more and a rate of flow of about 10 or more cu. ft. per hour per cu. ft. of catalyst may be used. In place of iron, nickel gauze etched by alkaline zinc oxide may be used.

Products from the synthesizing zone are preferably fractionated in fractionator 83 with previous cooling in heat exchanger 82, if desired. Vapors passed into tower 83 may be fractionated into an overhead vapor comprising mainly lower alcohols removed by line 85, heavy unvaporized synthetic hydrocarbons to be withdrawn by line 87 to cracking coil 13, or recovered as Diesel fuel, lubricating oil, and cracking stock, and an intermediate motor fuel distillate to be withdrawn by line 84, these various fractions being removed from the system, if desired, by providing withdrawal lines (not shown) in lines 84 and 87. Overhead vapors and gases from tower 83 may be passed to alkylation zone 71 by lines 85 and 103.

In alkylation zone 71 it is desirable to use a catalyst which brings about formation of free radicals or which has dehydrating power. Various organo-metallic compounds, particularly quarternary compounds, may be used and also various types of alkylated metal compounds, e. g., tetraethyl lead. Also, catalysts which aid in forming unsaturated hydrocarbons from partially oxidized hydrocarbons by dehydration are employed, e. g. alumina, thoria, silica, etc. These reactions increase and enhance the desired motor fuel hydrocarbons as will be described.

An intermediate reflux passed through line 84 from tower 83 may be joined with bottoms of tower 77 withdrawn through line 86 to be used in catalytic polymerization performed in vessel 88. Reflux containing cyclic hydrocarbons passed through line 62 from fractionator 61 also may be used in the polymerization to obtain synthesized lubricants, improved cracking stock, and Diesel fuel materials, which may be fractionated in the usual manner.

In separator 73 a lower layer of aqueous solution containing alcohols or other dissolved partially oxidized hydrocarbons may be removed through valved outlet 76a for recovery by further treatment or be passed by line 76 to mix with cracked products entering separator 93.

Residuals from separator 93 and/or reflux from fractionator 61 may be joined by lines 51, 89, and 34 with residuals from the primary tower 5 entering coil 12 or be by-passed through lines 35 and 36 to the flash chambers A or B on stream for vaporization. Residual oil from separator 93 may be passed to the lower part of chamber A or B by lines 51, 53, 37, or 38 to the chamber on stream.

Alternately, after either tower A or B has been used in vaporizing residual oil, contact material in these towers is subjected to regeneration by steam or other oxidizing agent injected through jets 18 under conditions to produce substantial quantities of carbon monoxide and hydrogen. Temperatures in the range of about 1400 to 2000° F., more or less, may be attained in the coke within these towers for this purpose.

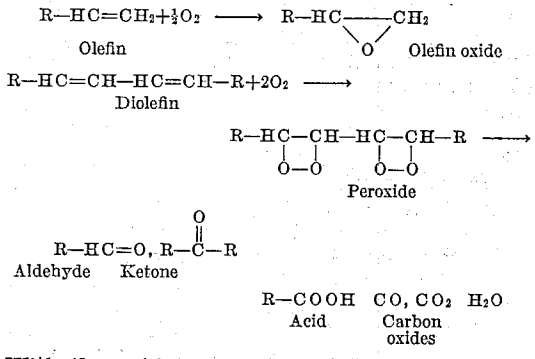
It has been found useful to supply coal or pyrobituminous material to towers A and B for replenishing the coke bed after each regeneration. Air or oxygen may be led into the solid fuel beds located in these chambers to obtain the temperatures needed during regeneration for producing water gas.

An important embodiment of this invention involves the production of gasoline boiling range branched chain aliphatic compounds and complex hydrocarbon compounds some of which contain ring structures from various lower boiling aliphatic hydrocarbons and their oxygenated derivatives. As indicated previously, carbon monoxide and hydrogen may be obtained in the oxidation of tarry residual oils such as those remaining on contact masses. Partially oxidized hydrocarbons, including alcohols, aldehydes, ketones and fatty acids may be developed in the partial oxidation of the reformed naphtha fraction. It has been described how hot products issuing from the naphtha reforming coil are advantageously subjected to mild oxidation which may be promoted by a mild oxidation catalyst. With this mild oxidation treatment carefully controlled a particular advantage is gained in lowering the extent of pyrolytic treatment to reform the naphtha hydrocarbons and in minimizing gas loss and loss by gum forming materials. The restricted oxidation converts gum forming diolefins readily into oxygen-containing aliphatic compounds while simultaneously activating paraffin hydrocarbons by dehydrogenation into olefins to a small extent.

With the formation of the olefins and oxygen-containing aliphatic compounds susceptible to efficient alkylation through a basic catalyst in the subsequent cooperating stage of the process the reforming treatment can be considerably moderated as explained.

By controlled mild oxidation of cracked or reformed naphtha hydrocarbons complete oxidation is avoided, molecular oxygen being mainly absorbed by diolefins which are most oxidizable. Olefins are oxidized to some extent. Some satu-

rated hydrocarbons may be converted to olefins by dehydrogenating the action of the oxidation. Oxidation reactions occurring are illustrated by:



With the oxidation controlled, the peroxides are checked from autoxidizing by chain reactions into undesired tarry polymers and gums.

One of the methods for arresting the oxidation of the partial oxidation products issuing from oxidizing chamber **92**, is to rapidly cool these products and to mix the cooled products with additional unsaturated hydrocarbons; a preferred method, as illustrated in Fig. 1, is to pass the oxidation products by line **107** more directly to the alkylation zone **71** wherein the basic catalysts react with the oxygen containing compounds to form compounds which are more stable to oxidation, also compounds which hinder oxidation by acting as inhibitors or antioxygens, such as the fatty acid soaps formed by the basic compounds. Additionally, the dehydration catalyst functions to prevent overoxidation by splitting out oxygen with hydrogen as water molecules while it aids in the isomerizing and alkylating reaction and removes energy of reaction.

The reactants for the alkylation can also be augmented by oxygen-containing aliphatic compounds obtained by oxidation of natural gas, processing of olefins with sulphuric acid to form alcohols, alcohols from fermentation of plant carbohydrates or synthesized from hydrogen and carbon monoxide, as described.

The method of isomerizing and alkylating oxygen-containing aliphatic compounds alone or together with olefins can be varied to produce lighter anti-knock motor fuels or safety fuels which are important for aviation motors. To obtain the higher boiling safety fuels the alkylation treatment may be applied to the total vapors of partially oxidized naphtha from zone **92**, admixed with carbon monoxide, hydrogen, additional oxygenated aliphatics and olefins, as from any or all of the lines **104**, **102**, and **85**. To obtain chiefly more volatile anti-knock fuels the alkylation is applied to reactants which are predominantly normally gaseous, e. g. fluids from lines **103** and **104**.

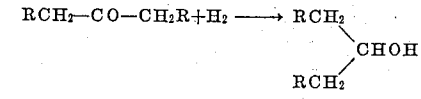
A principal feature of the isomerization and alkylation consists in treating the oxygen-containing aliphatic compounds with an alkali metal base or an alkaline base in order to convert at least a portion of these compounds into alkaline metal salts or soaps. For example, the alcohols and acids are reacted with a base as illustrated in the following equations:

$$RCH_2OH+KOH \rightarrow RCH_2OK+H_2O$$
$$RCOOH+KOH \rightarrow RCOOK+H_2O$$

Instead of KOH, other alkaline compounds or basic agents which are capable of easily forming the organic salts and soaps may be supplied, e. g. NaOH, metallic sodium of potassium dissolved in anhydrous alcohols, oxides or carbonates of alkali metals, or other highly reactive alkaline compounds. Alkaline metal salts of the oxygen containing compounds may also be preformed before being added to the alkylation zone **71** in which the dehydrating catalyst or alkylating agent is disposed.

The alkaline metal soaps and alkoxides undergo further reaction in the presence of a dehydrating catalyst or agent with carbon monoxide and hydrogen in the following manner:

$$RCH_2OK+CO \rightarrow RCH_2COOK$$
$$RCOOK+2H_2 \rightarrow RCH_2OH+KOH$$
$$2RCH_2COOK+H_2 \rightarrow RCH_2—CO—CH_2R+KOH$$



Thus, can be seen the reason for using hydrogen and carbon monoxide, the former somewhat in excess, together with the various oxygen containing compounds and alkaline material for obtaining the desirable branched motor fuel ingredients. It will be noted that the alkaline agent acts catalytically in being reformed, although some may react with sulphurous compounds present in the reactants. However, the sulfurized alkaline agent may be replaced by fresh agent and may be regenerated for reuse in a well known manner. By this method, a reduction of sulphur content is simultaneously accomplished.

While reactions illustrated above are occurring between the reducing gases and the salts of alcohols and acids in the presence of the dehydration catalyst, similar and additional reactions involving aldehydes, ketones, olefin oxides, reactive hydrocarbons, and the reaction products take place to build up branched complex compounds of high anti-knock value.

The dehydrating catalyst employed is preferably a difficulty reducible oxide, for example, an oxide of a divalent metal, such as zinc oxide. Other oxides may be used such as thoria, alumina, silica, and magnesia. Various anhydrous salts which are substantially neutral in character may be used such as sulphates or phosphates of Mg, Al, Ca, Cu, e. g., $AlPO_4$, $Mg_2P_2O_7$, $Mg_3(PO_4)_2$, $Ca_3(PO_4)_2$ copper-uranium-phosphate, and the like.

A desideratum in the selection of a catalyst for the alkylation is chiefly an agent having strong dehydrating action with little reducing or hydrogenating activity. For this reason it is desirable to omit such metals as nickel or iron. Nevertheless, the alkylation catalyst may have a limited amount of hydrogenating activity which is supplied generally by hexavalent metal oxides, e. g. chromic oxide, tungstic oxide, etc. A mixture of a divalent metal oxide, e. g., zinc oxide together with a tervalent metal oxide, e. g., chromic oxide may be used, preferably with the catalyst favoring hydrogenation present in minor proportions. Avoidance of more than a minor amount of hydrogenation is apparently necessary to prevent the active olefinic and oxygen-containing compounds from becoming converted into more inert saturated hydrocarbons before a desired amount of alkylation and isomerization is obtained. Thus, by controlling the catalytic tendencies among other factors any desired amount of alkylation and isomerization with limited hydrogenation of the aliphatic reactants is accomplished. Of course, if further saturation

of the alkylated and isomerized products is wanted for reducing residual combined oxygen or saturating remaining double bonds in the alkylation products, these products may be subsequently hydrogenated using any known method, hydrogenation catalysts, and suitable conditions.

Generally, the conditions for satisfactory dehydration in the alkylation zone are temperatures of the order of 400 to 1000° F., and moderately low pressures in the range of 1 to 10 atmospheres. The time of contact may amount to a fraction of a minute to 5 or 10 minutes depending upon the extent of alkylation desired, the activity of the catalyst and the temperature and pressure used.

The following examples will further illustrate how the invention may be carried out in practice, but the invention is not restricted to these examples.

Example 1

A paraffinic naphtha fraction boiling below 500° F. is heated in a coil to a temperature of above 950° F., under a pressure of about 50 atmospheres for a period of about one minute to obtain a reformed product comprising 80% gasoline distillate (end point, 437, octane number 75) and normally gaseous hydrocarbons, including olefins, and diolefins. These reformed products are passed continuously in vapor phase with their temperature at about 700 to 800° F. into an oxidation zone with proportioned amounts of air (.5 to 5% by volume of hydrocarbons) to contact with a chromium oxide catalyst for a period of about 2 to 30 seconds. The resulting partially oxidized hydrocarbons leaving the oxidation zone are substantially free from diolefines and contain a mixture comprising reformed gasoline hydrocarbon products unaffected by the oxidation, olefins, methanol, formaldehyde, acetone, acetic acid, their higher homologues and several per cent of undetermined oxygenated compounds, carbon monoxide, hydrogen, water vapor. The stream of oxidation products next is treated with added reducing gas comprising hydrogen and carbon monoxide to the action of ZnO mixed with 15 to 25% by weight of KOH for a period 1 to 2 minutes, under a pressure of 10 atmospheres and at a temperature of 500 to 550° F. A final condensate from the thus treated material amounts to a yield of about 90% based on the initial naphtha treated. The final gasoline distillate containing about 2 to 5% of oxygen containing compounds has an octane number of about 95 to 110, less than .1% sulphur and is substantially free from gum forming substances.

Example 2

A propane and butane cut (including isomers and olefins) is passed from a bubble tower stabilizer together with uncondensed carbon monoxide and hydrogen synthesis products (including about 10% methanol, 5% ethanol, with some aldehydes and about 1.5 mols of hydrogen to 1 mol of carbon monoxide) in to an alkylation zone maintained at about 600° to 800° F. The reaction mixture under a pressure of 5 atmospheres is contacted therein with an alkaline de hydrating agent composed of 10% alumina, 20% silica gel, 50% zinc oxide and 20% of K_2O, K_2CO_3. Products formed by reaction after 20 to 80 seconds of contact wtih the catalyst are subjected to fractional condensation to obtain about 4 gallons of motor fuel distillate (end point 300° F., octane number 90 to 95) per 1000 cubic feet of initial gas.

The motor fuels obtained by the described process of alkylating the partially oxidized hydrocarbons are eminently suitable as fuels for aircraft motors. They are obtained with any desired degree of volatility, have anti-knock ratings close to and above 100 octane, are substantially free from gum forming and sulphurous compounds. They give marked improvements with additional agents, such as tetraethyl lead. The process has many advantages over all known methods in that it eliminates the need for clay degumming or acid treatments and the losses incurred by these extra refining operations. It makes for a more complete utilization of all gaseous refining products.

It is to be understood that many modifications come within the scope of this invention and that said invention is not to be restricted by any of the examples or theory which have been given for the purpose of illustration.

This application is a continuation in part of my application Serial No. 130,227, filed March 11, 1937, now Patent No. 2,154,820.

I claim:

1. A method of treating a petroleum naphtha fraction which comprises heating said fraction under reforming conditions to produce higher anti-knock motor fuel hydrocarbons, reacting the reformed naphtha with an oxidizing agent limited in amount under mild oxidation conditions to principally oxidize unsaturated compounds, arresting said oxidizing reaction thereafter by reducing the temperature of the thus treated reformed naphtha products, and reacting said products in the presence of an alkaline metal base and a metal oxide dehydration catalyst, and with an added reducing gas containing hydrogen and carbon monoxide.

2. A method in accordance with claim 1, in which the reformed naphtha is subjected to mild oxidation in the presence of a mild oxidation catalyst.

3. A process for producing high anti-knock motor fuel which comprises cracking petroleum hydrocarbons to produce normally gaseous hydrocarbons and gasoline vapors including unsaturated hydrocarbons, separating said gasoline vapors and gases from higher boiling products of the cracking, admixing at least a portion of said gasoline vapors and gases with partially-oxidized unsaturated hydrocarbons boiling mainly below the gasoline boiling range, said partially-oxidized unsaturated hydrocarbons being oxygen-containing aliphatic compounds, and reacting the resulting mixture with reducing gas composed predominantly of hydrogen and partly of carbon monoxide under dehydrating conditions in the presence of an alkaline metal base and a metal oxide dehydration catalyst.

4. A process for producing high anti-knock motor fuel which comprises mixing normally gaseous hydrocarbons including olefines and oxygen-containing aliphatic compounds boiling mainly below the gasoline boiling range with reducing gas comprising predominantly hydrogen and a minor proportion of carbon monoxide, contacting said mixture with an alkaline metal base and a metal oxide dehydration catalyst at a temperature ranging from about 400° to 1000° F., under superatmospheric pressure, and for a period of about one to ten minutes.

5. A process for producing high anti-knock motor fuel, which comprises distilling and fractionating a crude petroleum to form a naphtha distillate fraction, a higher boiling cracking stock

distillate, and a residue, partially vaporizing said residue, passing vapors from said residue through an adsorbent contact mass, partially condensing the vapors passed through said adsorbent contact mass, commingling condensate from the thus treated vapors of the residue with distillates of the crude petroleum, cracking said cracking stock distillate, reforming said naphtha distillate in the presence of a small amount of an oxidizing agent and an oxidation catalyst to produce oxygen-containing aliphatic compounds boiling in the gasoline boiling range, arresting oxidation of the reformed naphtha distillate before substantial autoxidation into undesired tarry polymers and gums occurs, and combining products of the reformed naphtha boiling in the gasoline boiling range with gasoline products of the cracking.

6. A process for producing high anti-knock motor fuel which comprises distilling and fractionating a crude petroleum to form a naphtha distillate fraction, a higher boiling cracking stock distillate, and a residue, partially vaporizing said residue, passing vapors of said residue through an adsorbent contact mass, partially condensing vapors of the residue passed through said contact mass, commingling condensate from the thus treated vapors of the residue with the distillates of the crude petroleum, cracking said cracking stock distillate, reforming said naphtha distillate, partially oxidizing said naphtha distillate on being reformed to produce oxygen-containing aliphatic compounds boiling in the gasoline range, cooling the partially oxidized reformed naphtha, reacting the cooled partially oxidized reformed naphtha with a reducing gas containing principally hydrogen and carbon in the presence of a basic dehydrating metal oxide catalyst, and combining gasoline boiling range products from the thus treated naphtha with gasoline products of the cracking.

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