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TREATMENT OF HYDROCARBON OILS

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This application is a continuation-in-part of my application Serial No. 667,674 filed April 34, 1933.

This invention refers more particularly to the treatment of hydrocarbon motor fuels of low antiknock value, such as straight run gasolines produced from paraffinic crudes though the process is also applicable for improving the knock rating of gasoline fractions from other sources, e. g. those from naphthenic base crudes and from cracking processes.

In a more specific sense the invention has reference to a catalytic process which constitutes an improvement over the usual high pressure reforming operations on gasolines in that a minimum of cracking occurs in the ordinarily accepted sense of the term and the yields of desired product are higher under special conditions in regard to temperature, pressure and time. Further objects and advantages will become apparent in the following description of the nature of the process.

The present process is readily distinguishable from pyrolytic or cracking processes used to reform gasolines in the employment of higher temperatures, lower pressures, much shorter time factors and particular catalysts. In ordinary cracking processes conducted upon petroleum fractions of a distillate character for the production of high yields of gasoline of improved anti-knock value, it is current practice to employ temperatures within the approximate range of 850° to 1000° F., pressures of from 100 to 500 pounds per square inch above atmospheric and a long time factor, the last being obtained by the employment of large vaporizing or reaction chambers following the heating elements. Under these ordinary conditions of operation an equilibrium is approached due to the use of the long time factor, and a certain amount of secondary reactions of polymerization and condensation takes place following the primary reactions of decomposition. In contra-distinction to these conditions of operation the present process may be employed to limit the decomposition reactions to the primary reactions of decompositions so that equilibria corresponding to the temperatures and pressures as ordinarily employed are not reached and the secondary polymerization reactions are obviated.

As a general rule the antiknock value of a hydrocarbon motor fuel mixture increases with its content of olefinic and cyclic (particularly aromatic) compounds. This rule cannot be stated as absolute since experiments on pure com-

pounds have shown that the knock rating is also a function of such factors as the length of the straight chain in the paraffin hydrocarbons, the position of the double bond in the corresponding olefins, the degree of partial or complete saturation of the cyclic hydrocarbons and the presence of minor amounts of substances which may exert an accelerating or a retarding influence upon the rate of combustion of the fuel. While it may be stated generally that the antiknock value of a hydrocarbon fuel mixture is increased by loss of hydrogen in decomposition reactions of various types, other reactions may also take place such as isomerization involving the formation of branched chain saturated and unsaturated hydrocarbons and the formation of hydrocarbons of a mixed straight chain and cyclic character. The reactions involved in the treatments of the present process are apparently distinct from those which occur in ordinary cracking operations.

In one specific embodiment the invention comprises vaporizing gasoline without substantial decomposition thereof and subjecting the vapors to pyrolysis at temperatures of from approximately 1200 to 1500° F., under sub-atmospheric pressures for times not in excess of 0.04 second in the presence of activated magnesite catalysts.

According to the present invention an activated magnesite catalyst is employed in the zone of intensive heating or in other words the main reaction zone. The term "activated magnesite" is hereby defined as including the residual material resulting from the calcination of magnesium carbonate either natural or artificial and comprising principally magnesium oxide of a more or less porous character. Thus the calcining of the original carbonate is essentially the activating step, although the porosity may be influenced by the presence of other gases which are passed in a stream through a mass of particles of the ground carbonate to carry off the carbon dioxide evolved. Magnesium carbonate begins to decompose to yield the oxide at temperatures of approximately 350° C. (662° F.) and if heated long enough at this temperature will be converted to the oxide. However, the use of higher temperatures permits the use of shorter times. When employing an incompletely converted magnesite at the start of a reforming process of the present character and under the temperature conditions which characterize it, any carbonate remaining is gradually decomposed so that the essential catalyst is finally a porous and active magnesium oxide, which may be designated as activated magnesite.

The carbonate of magnesium, MgCO_3 , is known as magnesite as it occurs in nature, and this is the cheapest and most readily available primary source of catalyst for the present process. It is most commonly encountered in a massive or earthy variety and rarely in crystal form, the crystals being usually rhombohedral. In many natural magnesites, the magnesium oxide may be replaced to the extent of several per cent by ferrous oxide. The mineral is of quite common occurrence and its use is economical. This mineral is related to dolomite, the mixed carbonate of calcium and magnesium. Dolomite, however, is not of as good service as the relatively pure magnesite in the present instance but under certain conditions depending on results desired it may be employed.

In the activation of this material it is preliminarily heated to a temperature and at a pressure in the neighborhood of that preferred for the cracking and reforming operations for a period of time sufficient to convert substantially all of the magnesite to magnesium oxide of high porosity. In the preliminary activating treatment a stream of gas may be conducted through the material to assist in flushing out the carbon dioxide evolved and produce other effects upon the structure and surface characteristics of the contact material. In some cases air may be used, in other cases hydrogen, carbon dioxide or even hydrocarbon gas mixtures such as natural gas or the vapors of the oil to be treated. When using oil vapors the process of treatment for increasing antiknock value may be started after the magnesite has attained a proper degree of activation as evidenced by the results obtained in the direction of increased antiknock rating without high losses.

Precipitated magnesium carbonate may be employed alternatively with the natural mineral as a source of catalytic material. While catalysts of varying activity may be prepared from either magnesite or the precipitated carbonate their influence upon the reactions of decomposition will vary with the starting material and the exact manner of its preparation so that alternative but not exactly equivalent catalysts may be prepared.

It has been observed that, when activation by the hydrocarbon vapors is practiced, increase in activity seems to follow the deposition of a certain amount of carbon on the surface of the catalyst though it is not known at the present time whether the increase in activity of the mass is definitely related to this deposit of carbon. The general steps thus briefly enumerated for the activation of contact masses may be employed in many cases also to effect its regeneration after it has become coated with tarry polymers after a certain period of use, e. g. the use of air to burn or oxidize the carbonaceous and tarry matter deposited on the catalyst to cleanse its surface.

The exact course of the chemical reactions involved in the decomposition by heat of hydrocarbon oil mixtures having the complex composition of gasoline is difficult to follow, on account of the extremely large number of hydrocarbon compounds present. In the case of normal straight-chain paraffin hydrocarbons there is some evidence to support the view that scission of the chains occurs between the central carbon atoms so that, for example, a molecule each of hexane and hexene are produced when duodecane is cracked. Apparently the primary re-

actions of decomposition are followed by secondary reactions involving polymerization of olefins from the primary decompositions and with increased pressure and long time factor some ring-closures occur to form naphthenic and aromatic compounds. Obviously the exact nature of the decompositions is much more complicated but from a practical standpoint in the cracking of hydrocarbon oil mixtures such as gasolines, it seems probable that the formation of coke and gas which constitute undesirable by-products of the cracking reactions is a phenomenon accompanying the secondary reactions, so that if conditions are properly controlled to prevent polymerization, coke formation will also be prevented. The ratio of coke to gas in the cracked products will depend, to a considerable extent to the ratio of carbon to hydrogen by weight in the stock cracked and to a lesser extent by the form of their combination.

In applying the process of the invention to the treatment of gasolines for the improvement of their antiknock characteristics they are vaporized in any convenient manner, for example, during passage through tubular heating elements and are then passed through a highly heated zone containing granular activated magnesite and maintained at some optimum temperature within the range previously specified for a very short time period corresponding usually to less than 0.04 second and sometimes as low as 0.001 second. When under these high temperatures sub-atmospheric pressures are preferably maintained by withdrawing the gaseous products of the reactions from the receiver of the process at a suitable rate, the preferred pressures in the high temperature zone being of the order of 50 mm. of mercury absolute. The catalyst may be distributed throughout the zone of intensive heating and in a state of subdivision which presents sufficient contact surface without causing too great resistance to flow.

The present invention is especially characterized by the fact that extensive decomposition of gasolines may be brought about without the formation of heavy hydrocarbon polymers of a high boiling or tarry character and without separation or decomposition of any material amounts of carbon in the reaction zone or in succeeding portions of the equipment. Owing to the avoidance of polymer formation the yields of desired products are higher and runs in commercial equipment are lengthened on account of the lack of coke deposition which ordinarily causes hazards, due to over-heating of tubes and clogging of equipment. It is to be specifically pointed out that the present process of making high antiknock hydrocarbons from those present in gasolines produces substantially no coke and/or pitchy or tarry substances especially in comparison with the well known reforming processes of the prior art. Apparently the character of the reactions induced by the use of the catalysts mentioned is in the direction of splitting off of hydrogen and rearrangement of branched chains so that the content of unsaturated, isomeric straight chain and cyclic hydrocarbons, is increased, without extensive cracking in the ordinary sense of the word since cracking reactions are characterized by the formation of more heavy polymers and tar as well as gas.

While the invention is particularly directed to the pyrolysis of straight-run or uncracked distillates, it is further comprised within its scope to employ corresponding liquid products from crack-

ing processes as the term is ordinarily used in the trade and to crack oil vapors if necessary or desirable prior to their passage through the main reaction zone in which the reactions of gas and liquid formation are brought about.

Obviously the proportioning of relative sizes of parts of different types of equipment which may be used to carry out the process will depend upon many factors such as the character of the oil which it is desired to treat, the increase in knock rating desired, the heats of vaporization and decomposition of the vapors involved and other factors. The matter of design of commercial units may be based to some extent on the operation of small scale experimental units, as is done in many other commercial development projects.

The materials entering into the construction of the reaction zone of the process will require some consideration since temperatures above those to which the ordinary materials of construction are ordinarily subjected are employed in many instances at this point. Thus temperatures in the neighborhood of 1200 to 1300° F are high enough so that the tensile and compressive strength of ordinary steels is definitely reduced and they possess greatly lessened resistance to deformation, which must be reckoned with in view of the fact that there is external pressure upon any tube or arrangement of tubes which may be employed corresponding to the degree of vacuum in use which may at times be that equivalent to 50 mm. of mercury absolute or lower. There is a further reason for avoiding the use of ferrous metals as materials for the main reaction zone in that many of these metals may exert not only an undesirable and difficultly controllable catalytic action but that they also tend to form carbides by direct combination with the carbon in the oils and further the tendency toward coke-formation, the avoidance of which constitutes one of the primary advantages of the present invention.

In place of metals such materials as silica, firebrick, carborundum, sillimanite, alundum, corundum and other high melting point refractory materials are preferred for materials to constitute the main reaction zone. The tube or tubes of the reaction zone may be heated by any convenient economical method, heat being supplied in some instances by electrical resistors which are wound around the tubes and protect them from unnecessary radiation loss by being embedded in suitable insulating materials surrounding the tubes. A somewhat cheaper method, although not always capable of effecting the same exact control of temperature, may consist in heating the reaction zone by the direct impingement of oil or gas flames thereon. Evidently the greatest overall heat efficiency of the process will be attained by preliminary heating of the vapors by ordinary means to the maximum temperature consistent with the decomposition reactions desired prior to their passage through the reaction zone which is thus relieved of excess burden.

The following example is illustrative of improvement of gasoline quality, while operating according to the process of the present invention. The data in the tabulation shows the principal characteristics of the stock charged to the process (which was the straight run

Pennsylvania gasoline) and shows also the corresponding properties of the product obtained by treating the vapors of this gasoline at 1300° F. and 50 mm. absolute pressure in the presence of a catalyst prepared by calcining granular magnesite at a temperature of about 1500° F., the time that the vapors were under these conditions being approximately 0.04 second.

Comparison of straight run and treated gasolines

Properties	Charge	Product
Gravity, °A. P. I.	64.9	62.6
I. B. P., °F.	94	100
10% over at.	148	148
50% over at.	236	228
90% over at.	324	320
E. B. P., °F.	375	379
Octane number.	52	68

The conversion indicated by the figures in the preceding table was accompanied by a loss in gas corresponding to approximately 10% of the charge and substantially no loss in heavy polymers or coke. The data shows that better results are obtainable by the present process than by ordinary re-forming operations, particularly in the relatively low loss incurred for the improvement in antiknock value shown and in the absence of heavy polymerized oils. The present process is operable also in more compact apparatus than that commonly employed in re-forming operations.

The invention is sufficiently disclosed and described in the foregoing specification and the single instance of results obtained but the invention is to be in no way limited to the exact details of the description or the particular numerical data introduced.

I claim as my invention:

1. A process for the reforming of low antiknock hydrocarbon distillates containing straight chain paraffins within the boiling range of gasoline to improve the antiknock quality thereof without substantial decomposition, which comprises subjecting the distillate while in heated vaporous condition at a temperature between 1200° F. and 1500° F., and for the period of time not in excess of four one-hundredths of a second and under a subatmospheric pressure of less than 50 millimeters, to the action of a catalyst comprising essentially activated magnesite.

2. A process for the reforming of low antiknock hydrocarbon distillates containing straight chain paraffins within the boiling range of gasoline to improve the antiknock quality thereof without substantial decomposition, which comprises subjecting the distillate while in heated vaporous condition at a temperature in excess of 1200° F., and less than 1500° F. and for a time not in excess of four one-hundredths of a second and under subatmospheric pressure to the action of a catalyst comprising essentially activated magnesite.

3. A process for reforming straight chain paraffins boiling within the gasoline range which comprises subjecting the paraffins, in vapor phase and under subatmospheric pressure, to the action of activated magnesite at a temperature of from about 1200 to 1500° F. and for a time period not in excess of four one-hundredths of a second.

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