Patented Mar. 1, 1938 2,109,866

UNITED STATES PATENT OFFICE

2,109,866

TREATING OF MOTOR FUELS

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No Drawing. Application August 6, 1935, Serial No. 34,911. In the Netherlands September 21, 1934

1 Claim. (Cl. 196—52)

This invention relates to a process for improving the knock rating of motor gasolines.

Certain gasolines produced by distillation from crude petroleum oils, shale oils and/or hydrogenated oils possess low octane number. Octane number is a unit for measuring antiknock value and is defined in method D–357–34T of the American Society for Testing Materials. It is known that straight chain paraffinic as well as certain cyclic hydrocarbons are chiefly responsible for poor anti-knock properties of gasolines, and that by exposing gasolines containing badly detonating hydrocarbons to temperatures normally of the order of 600° C. to 800° C. for a predetermined length of time, a change in the structure of some of the components takes place, which results in an improvement of the octane number of said gasoline. This process is called reforming. Reforming, however, has the disadvantage of producing a comparatively high percentage of fixed gas, which is usually of the order of about 25% or higher. Superatmospheric pressure may reduce the formation of normally non-condensible gases, but frequently not to an extent to warrant the construction of high pressure reforming units capable of withstanding the high temperatures of reforming.

I have discovered that gasolines of low octane number, particularly straight run gasolines, can successfully be converted to gasolines of higher octane number without appreciable gas loss, if the vapors of the low octane number gasoline are conducted over suitable catalysts at moderate temperatures ranging from about 300° C. to about 525° C. The catalysts which I have found to be most effective are inorganic phosphates and certain silicates. The catalytic activity of the phosphates is somewhat dependent on the metal radical, the phosphates of metals of the first, second and third groups of the periodic system being most effective, although all inorganic phosphates which are stable at the temperatures of my process are capable of improving the knock rating of low octane number gasolines to some extent. Of the silicates, those which exhibit a large surface and which are not subject to sintering or decomposition with resulting decrease of surface are suitable. In particular asbestos and base exchanging silicates of the type of permutite are very effective.

In practice, hydrocarbon vapors which may contain normal paraffinic hydrocarbons of the type of gasoline and preferably produced by evaporation under substantially non-cracking conditions from a suitable mineral oil, are brought to the effective conversion temperature and are conducted over the catalyst at a temperature which lies between about 300° C. and 525° C. The catalyst is kept in a suitable vessel which may be unheated and protected from heat losses by insulation, or which may be heated in a suitable manner.

While the hydrocarbons make contact with the catalyst, they undergo a change, the nature of which is not clearly understood. It appears that some cracking occurs, as is evidenced by the formation of small quantities of fixed gas. However, normally the octane number improvement in my process is much larger for a given gas loss than is the case in ordinary reforming. As in cracking, in my process the rate of octane improvement and gas formation increases with increasing temperature, but contrary to cracking in which over a wide temperature range octane improvement and gas formation follow approximately parallel lines, I find that within an optimum temperature range of comparatively narrow limits of the order of about 25° C., a considerable octane improvement can be produced with practically no gas loss. The actual optimum operating temperature depends upon the catalyst and the material being treated and can be readily determined by experiment. The time of reaction must be carefully controlled because of its effects on the relation of gas formation to octane improvement under temperature and pressure conditions. The time should be so limited as to result in as high an octane number improvement as economical considerations with respect to gas losses will permit.

The improvement in octane number which can be achieved by my process usually ranges from about 5 to 15 points, a 10 point raise being considered a fair improvement. Gas losses are usually of the order of 10% or less, and can consistently be held below 15%. It has been found that substantial improvements can be obtained principally on relatively low octane number gasoline, since such gasolines contain components which can be most readily reformed by the method of this invention. Gasolines having octane numbers above 65 in some cases may not respond sufficiently to warrant the expense of their treatment by this method.

The process is preferably carried out at substantially atmospheric pressure, because this enables the use of relatively inexpensive equipment, although superatmospheric pressures can be applied up to the point of incipient liquefaction of the treating stock at the temperatures of the

treatment. Superatmospheric pressure, while comparatively little affecting the gain in octane number has a tendency further to reduce gas losses.

Catalysts which operate at a relatively low temperature generally permit an improvement in octane number accompanied by a smaller loss of gas than is the case with catalyst requiring higher temperatures. This does not mean however, that a catalyst requiring an operating temperature of, say, 500° C. will always produce a lower octane gasoline than a 400° C. catalyst, since the opposite may often be the case; the gas loss at the higher temperatures is usually found to be higher for equal octane improvement.

It is important that the catalyst be properly prepared to allow for maximum contact with the vapors passing over it. It should be granular, as in the case of permutite, or fibrous, as in the case of asbestos. If granular, it should preferably have a mesh size of 10 to 90 U. S. standard. Solid catalysts such as most phosphates may be prepared by simply disintegrating them and screening to the proper size, or by grinding and briquetting. Ground tertiary calcium phosphate, for example, was wetted with water, pressed into briquets and dried. The briquets were broken into sections of about 10 mesh.

The catalyst may also be deposited from solutions on a suitable carrier which itself may be inert or active. For instance, asbestos was wetted with a strong solution of sodium phosphate, and was dried at about 200° C.

The prepared catalyst is placed into any suitable tower or container to form a filter-like bed through which the vapors are conducted.

The catalyst can be used for many hours before it loses part or all of its conversion efficiency. Loss of efficiency is due to coke being gradually deposited on the catalyst, coke formation being the results of polymerization of olefines contained in the vapors. When the efficiency of the catalyst has dropped to a point of insufficient conversion, the reaction may be stopped or the hydrocarbon vapors may be diverted through another bed of catalytic material. Hot air is then passed over the spent catalyst to effect combustion of the carbonaceous deposits. The temperature and the amount of air are preferably so controlled to prevent the temperature in the bed of catalyst to rise above about 800° C. during the process of regeneration. At temperatures above 800° C. there is danger of permanently destroying the activity of some of the catalysts.

In the following illustrative examples the type of improvement which my process is capable of imparting to low octane number gasolines is clearly shown.

Example I

A Mexican straight run gasoline having an octane number of 55 was conducted at a temperature at 450° C. in the vapor phase over boron phosphate, prepared by heating on a steam bath orthophosphoric acid and boric acid in the ratio corresponding to the compound BPO_4. The time of contact of the gasoline vapors with the catalyst was of the order of 5 seconds. The gasoline which was recovered from the treatment had an octane number of 62.5, while practically no fixed gas was formed.

Example II

A Mexican straight run gasoline having an octane number of 56 was conducted in the vapor state at a temperature of 500° C. over tertiary calcium phosphate. The octane number rose to 66.5 while the gas loss was 12%.

Example III

Vapors from a straight run gasoline having an octane number of 54 were conducted through a bed of permutite at 475° C. The octane number of the resulting gasoline was 61.5 and gas losses were below 10%.

Example IV

A Mexican straight run gasoline with an octane number of 52 was conducted in vapor form at a temperature of 500° C. over asbestos of short fibre. The octane number was increased to 66.5 at a gas loss of about 12%.

I claim as my invention:

In the process of improving the antiknock rating of a gasoline distillate containing normal paraffinic hydrocarbons of a low antiknock rating, the steps comprising contacting the distillate in the vapor state with boron phosphate at a conversion temperature below normal reforming temperature for a time sufficient to effect a substantial increase in octane number but insufficient to cause a gas loss of a magnitude characteristic of reforming.

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