Patented Aug. 31, 1926. 1,597,798

UNITED STATES PATENT OFFICE.

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METHOD OF TREATING LIQUID HYDROCARBONS.

No Drawing. Application filed July 21, 1922. Serial No. 576,638.

In connection with my copending applications, Serial No. 272,567, filed January 22, 1919, and Serial No. 435,355, filed January 6, 1921, I have found that by distilling or separating the lighter hydrocarbons of the first run from the original product and then returning the remainder of this product and repeating the process under certain conditions, I can obtain a considerable yield of lighter hydrocarbons suitable for use in internal combustion engines and of a new and better type than ordinary motor spirit. I have also discovered that by introducing a basic oxide, preferably an oxide whose carbonate decomposes at a relatively low temperature, such as magnesium oxide, I can break up the high molecular weight acids formed in connection with the process and obtain a cyclic method.

In carrying out the process, I first subject the hydrocarbon, which may be any fraction of mineral oil, such as a kerosene fraction or a product known in the art as "pressure tar", or heavier fractions, to the catalytic partial combustion or partial oxidation method, fully described in the above recited applications. In this method, the liquid hyrdocarbon is fed in measured quantities to a vaporizer where it is vaporized by heat, mixed with air which is admitted in regulated quantities, and the mixture is passed through a catalytic layer containing, for example, the complex oxides of molybdenum, vanadium, uranium, etc. In this method, I prefer to use a plurality of layers, introducing part of the total air used in the vaporizer, and a part between the screens, as in my copending application Serial No. 435,355. The partially oxidized product is then condensed and consists of oxidized compounds running from alcohols through aldehydes to aldehyde acids. I then distill the lighter molecular weight portions of this product, up to, say, 200° C., which forms a desirable engine fuel. If the heavier portions of the product which remain are then re-run through the apparatus, with an added portion of fresh oil fraction, a further decomposition occurs and further motor spirit product is obtained. However, if these operations are repeated, I have found that the proportion of lighter hydrocarbons is reduced, the heavier molecular weight bodies building up as the process is repeated. But I have also discovered that if, in re-running the material, I decompose the organic acids by certain basic oxides, I can provide a continuous process in which there is a substantially constant production of lighter molecular weight portions and the proportion of heavier compounds does not increase.

As an example of the process, I have employed the same apparatus as described in my copending application Serial No. 435,355, except that in the vaporizer, I provide a layer of a basic oxide, preferably an oxide whose carbonate decomposes at a relatively low temperature. For this purpose, I prefer lumps of magnesium oxide. In practice, I have supported a screen about four inches above the bottom of the vaporizer, on which is provided an eight-inch layer of lumps of magnesium oxide. Otherwise, the apparatus is the same as shown in my copending application, Serial No. 435,355.

In the first run, the process was carried out the same as in the said application, and I employed commercial Pennsylvania kerosene boiling between 200° C. and 300° C. After the first run, the condensed product was distilled up to 200° C., to obtain the lighter molecular weight bodies, and the remaining heavier material was re-run through the apparatus, using about 56% of the oxidized oil from the previous run, from which the light products had been distilled, and 44% of the fresh oil.

The temperatures during the run were as follows: Above the magnesium oxide layer and the vaporizer before entering the screen, the temperature was about 380° C. At the successive screens in the triple-screen apparatus, the successive temperatures were 340° C. at the first screen; 350° C. at the second screen, and 350° C. at the third screen.

The oil mixture above described was introduced at the rate of 250 c. c. per minute, and the air was fed into the vaporizer at the rate of one cubic foot per minute. The air at screen No. 2 entered at the rate of .5 cubic feet per minute, and at No. 3 screen at the rate of .5 cubic feet per minute. The carbon dioxide in the exit gas averaged 3.7% and the oxygen .8%, the latter showing almost complete utilization of the oxygen introduced.

In this run, 59.6 liters of the oil mixture were introduced, and the liquid product re-

covered was about 83% of this amount. The product collected from the condenser gave an initial distilling point of 125° C., 23% of it distilling under 200° C. A rotary liquid pump was used in the circuit, this also serving as an agitating and scrubbing device, and the product collected therefrom, which represented one-fourth of the total product, gave an initial distilling point of 100° C., and 28.5% distilled under 200° C.

The product was again distilled up to 200° C. to remove the light material, the residual distilled product was mixed with the fresh oil in the same ratio as before and another run was made with all conditions the same, except that the vaporized temperature was lowered to about 340° C. and the oil feed cut down to 200 c. c. per minute. A small amount of water, equal to 5% of the oil feed, was introduced into the vaporizer.

This second run gave results practically the same as the first run. The yield was 83.9%, the condenser product showed an initial distilling point of 92° C., 23% distilling under 200° C.; while the product collecting in the rotary water pump showed an initial distilling point at 82° C., 27% of it distilling under 200° C.

A series of these tests have shown that this affords a practical process for preparing a low boiling point liquid fuel from heavier hydrocarbons.

In several runs, the percentage of light product obtained, based on the original oil fed in, gave an average between 50% and 55%.

The fuel prepared in the above manner contains alcohols, aldehyde alcohols, aldehydes, ketones, ethers, aldehyde acids and hydrocarbons. The acids should be removed before the product is used in engines, and I also prefer to remove the more pungent aldehyde bodies present.

I have found that this purification can be effected by adding about 5% of dry caustic soda to the lighter distilled portions, heating to a gentle boiling under an invert condenser, for about three hours, and then slowly distilling. The distilled product has an agreeable odor, and may be made practically water-white in color, if the caustic treatment be carried out for a considerable period. I prefer to treat in this manner, removing the unpleasant aldehydic odors and leaving a product of a slightly yellow color, as the refining loss is less under these conditions and only amounts to about 10%. The material taken out is substantially a soap.

Extensive automobile engine tests with this fuel have shown that such fuel possesses many advantages. The presence of oxidized bodies give the fuel the property of carrying full loads without detonation or knocking, or with this action greatly reduced or practically eliminated. Furthermore, the presence of the oxidized bodies which give more easy combustibility make it possible to use a mixture of wider range in boiler points than is possible with a straight hydrocarbon mixture. In other words, the "end point" of the mixture may be and preferably is carried further than with ordinary motor spirit.

While I do not limit myself to any specific action or reaction which occurs during this process, I believe that the low molecular weight hydrocarbons result from decomposition of the oxidation products. The temperatures which I employ are below the ordinary cracking range for hydrocarbons, and a study of the low boiling point fractions shows that a considerable proportion consists of oxidized bodies. Probably the decomposition of these oxidation products proceeds in two directions—one leading to the elimination of carbon monoxide and carbon dioxide with the formation of new hydrocarbons of lower carbon content, and the other consisting in the breaking of the chains of oxidized bodies, giving rise to bodies of lower carbon content, which contain combined oxygen.

The fact that the percentage of light products formed grew less in re-running in the ordinary manner apparently shows that the oxidized bodies, particularly the acids, formed faster than they were decomposed in the re-run material, and the presence of the oxides makes the product substantially constant in re-running as to the yield of lighter products. With the use of this oxide, the percentage of total recovery of light products is practically the same in each re-run where the same percentage of re-run material is used in connection with a certain percentage of fresh material.

My process therefore affords a new commercial method by which heavier hydrocarbons may be converted into lighter hydrocarbons with percentages of recovery which make the same commercially practicable.

The operations as carried on by me thus far have been at atmospheric pressure, although the pressure may be either below atmosphere or above atmosphere, if desired. The apparatus may be varied widely, a catalyst may or may not be used, although I prefer to employ the same, a single layer of catalytic material or multiple layers may be employed, and many other changes may be made without departing from my invention.

I claim:

1. In the treatment of partially oxidized liquid hydrocarbons, the steps consisting of adding fresh hydrocarbon to at least a portion of the same, and subjecting the mixture to a step of partial oxidation.

2. In the treatment of hydrocarbons, the steps consisting of partially oxidizing the same while in finely divided condition, sepa-

rating the lighter portion of the product, adding fresh hydrocarbon to the heavier portion, and again subjecting the same to the step of partial oxidation.

3. In the treatment of hyrocarbons, the steps consisting of partially oxidizing a hydrocarbon while in finely divided condition, fractioning out a lighter portion of the products, mixing fresh oil with the heavier portion, subjecting said heavier portion mixture while in finely divided condition to partial oxidation, and decomposing a portion of the resultant product.

4. In the treatment of liquid hydrocarbons, the steps consisting of subjecting the same in finely divided condition to a step of partial oxidation, separating out a lighter portion, mixing the heavier portion with a fresh portion of oil, subjecting the heavier portion mixture while in finely divided condition to a step of partial oxidation, and again separating out a lighter portion of the product.

5. In the treatment of hydrocarbons which already contain artificially-introduced chemically-combined oxygen, the steps consisting of adding fresh hydrocarbon thereto, thermally decomposing the same, and subjecting it to a partial oxidation step.

6. In the treatment of hydrocarbons which already contain artificially-introduced chemically-combined oxygen, the steps consisting of adding a fresh portion of liquid hydrocarbon thereto, and subjecting the same in the vapor phase to thermal decomposition in the presence of contact material.

7. In the treatment of liquid hydrocarbons, the steps consisting of subjecting the same in finely divided condition to a step of partial oxidation, separating out a lighter portion, mixing the heavier portion with a fresh portion of oil, subjecting the heavier portion mixture while in finely divided condition to a step of partial oxidation, again separating out a lighter portion of the product, and decomposing a portion of the product.

8. In the treatment of liquid hydrocarbons, the steps consisting of partially oxidizing the same while in finely divided condition, separating out a lighter portion of the product, adding fresh hydrocarbon to the heavier portion, again partially oxidizing the same, and mixing the lighter portions thus obtained.

9. In the treatment of hydrocarbons which already contain artificially introduced chemically combined oxygen, the steps consisting of adding fresh hydrocarbon thereto, and subjecting the mixture to a step of partial oxidation.

10. In the treatment of hydrocarbons which already contain artificially-introduced chemically-combined oxygen, the steps consisting of adding fresh hydrocarbon to the same and then thermally decomposing the mixture.

In testimony whereof I have hereunto set my hand.

JOSEPH HIDY JAMES.