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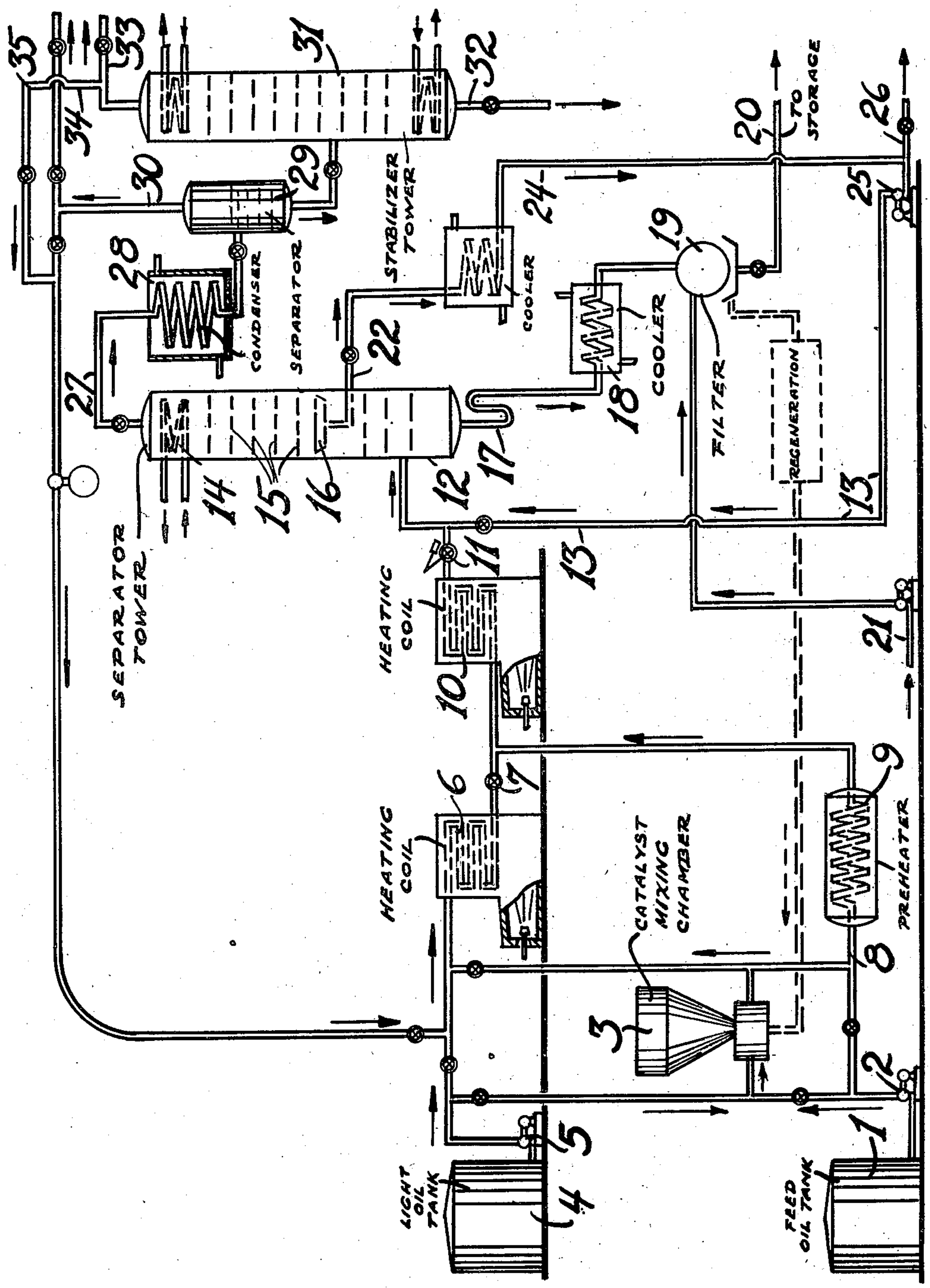

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METHOD FOR CONVERTING HYDROCARBON OILS

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2 Claims. (Cl. 196—52)

The present invention relates to the art of converting high boiling to low boiling hydrocarbons, and more particularly to a catalytic process for producing motor fuels of improved quality. The invention will be fully understood from the following description and drawing.

The drawing is a semi-diagrammatic view in sectional elevation showing the path of the oil through the equipment.

The present invention is a continuation-in-part of a prior application Serial No. 248,164, filed December 29, 1938.

Many cracking methods are known and a wide range of cracking conditions has been disclosed. It has been desirable to improve the quality of gasoline produced and it has been found necessary to carefully adapt cracking methods and conditions to particular feed stock available for cracking. In the present invention a further improvement is made by clearly specifying narrow ranges of temperature and pressure for certain feed stocks when employed in a particular cracking method with certain catalytic agents in a particular condition. It has been found that greatly improved results are obtained by a combination of all of these various factors which appear to be equally necessary in order to gain the results desired.

Referring to the drawing, numeral 1 denotes a feed tank from which the oil to be cracked is taken by pump 2. This feed stock is a type known as an overhead or distillate stock, preferably a gas oil, free from large quantities of asphaltic or tarry constituents and boiling above 400° F. Numeral 4 denotes a second tank from which a lighter oil is taken by a pump 5. This second stock is a heavy naphtha or kerosene distillate. The two stocks from the tanks 1 and 4 may be admixed prior to passage through a catalyst mixing chamber 3, or either the one or the other may be passed through the said mixer, but the preferred manner is to pass the heavy naphtha from tank 4 through the mixer 3 where the catalyst is added and this mixture is then passed through a heater coil 6 so as to reach a high temperature and to effect at least partial reforming of the said stock. The reformed oil vapor then passes through a reducing valve 7 and meets the gas oil stream which has preferably been preheated in the preheater 9.

The mixed oil along with the catalyst is then further heated and cracked in a coil 10 and is discharged into separator tower 12 through a release valve 11. It is preferred to add quenching oil by means of a pipe 13. The separator is fitted with refluxing coil 14 and fractionating plates 15 in the usual manner and a pan 16, or other equivalent means, is provided for withdrawing an intermediate cut. Heavy tarry oil containing the catalyst is taken from the base of the tower 12 by a pipe 17 which leads to a coil 18 and thence to a filter 19 which is employed for removing catalyst from the oil. Oil is taken by a pipe 20 to storage, not shown. The filter may be provided with a precoat of fresh catalyst in clean oil by a pipe 21 and the catalyst may be stripped from the filter and returned to the catalyst mixing chamber 3 preferably after regeneration, but the amount of catalyst is so small and cheap that it may be economically discarded. Intermediate oil from the pan 16 is drawn off by pipe 22, thru cooler 23, thence by pipe 24 and pump 25 it may be supplied as the quenching oil previously mentioned as being added at pipe 13. A portion may be drawn off by line 26 and used as a heating oil. The overhead from tower 12 containing naphtha, lighter easily liquefiable hydrocarbons and fixed gases, is passed by a vapor pipe 27 to a condenser 28 and separator 29 from which the fixed gas is taken off by a pipe 30. The liquid fraction passes to a stabilizer tower 31 of the usual construction. Stabilized gasoline is removed by a pipe 32 while the lighter, easily liquefiable hydrocarbons, mainly containing 3 and 4 carbon atoms, are taken overhead. These fractions may be withdrawn by a pipe 33 or returned by a pipe 35, either alone or together with the fixed gases for repassage through the reformer and cracking coils.

In the operation of the present process it is important that the gas oil be cracked under the influence of a stream of finely divided catalyst while completely in the vapor phase and for this purpose a substantial volume of lighter hydrocarbon fractions is added sufficient in quantity to completely bring the gas oil into the vapor phase. While such gas oils have been cracked in vapor phase previously, it has been done only at low pressures, for example, at atmospheric or at the most about 100 pounds per square inch, but in the present process pressures of at least 300 pounds per square inch are required and frequently the pressure may amount to 1000 pounds or more. Temperature is likewise higher than is usual say from 1000 to 1100° F. Such temperatures have been used commercially but only at low pressures and it has not been considered feasible at the high pressures specified above. It has been found possible, however, to operate the present process by the joint action of the catalytic agent and the presence of the relatively large volume of lighter easily volatile hydrocarbons.

From what has been said above, it will be seen that the presence of the lower boiling hydrocarbon is of great importance. If naphtha is used, the amount may vary from 10 to 35% of the heavier oil to be cracked depending on the temperature and the pressure used, that is to say, the naphtha content measured as fractions boiling below about 400° F. should amount to at least 10% of the gas oil to be cracked. Naturally if the gas oil contains an excessive or unusual amount of heavy fractions, the proportion of naphtha is greater than when a gas oil of the usual characteristics is used. With lower temperatures and pressures, the amount of the naphtha may be in the range from 10 to 15% only, but better results are obtained with higher pressures of 500 to 700 pounds per square inch and under these conditions it is necessary to use 15 to 30% of naphtha. The naphtha may be admixed directly with the gas oil if desired, but it is preferred to effect some naphtha reforming in the coil 6 in absence of the gas oil. This coil 6 is operated at a temperature from 950 to 1100° F. under pressure and the reaction is preferably conducted in the presence of the catalytic agent. The pressure should be sufficient so as to not only force the oil through this coil but likewise to maintain a pressure of 300 to 1000 pounds per square inch in coil 10, which is used for the cracking and is fed directly from coil 6 as shown.

Instead of naphtha, butane and propane or either the one or the other may be used as the vaporizing medium but it is generally desirable to return the propane and butane fractions produced in the operation and to add thereto some 15 to 25% of heavy naphtha based on the gas oil treated. In this way a balanced operation is obtained. Even the heaviest distillate gas oils can be brought into vapor phase in the coil and cracked satisfactorily while in the presence of the catalyst and in addition the heavy naphtha is reformed. By complete vaporization is meant the absence of a liquid phase however small.

Another factor which has been mentioned but not specifically disclosed above is the catalyst to be employed. The preferred catalysts are the natural earths, such as fuller's earth, bentonite, and preferably those which have been treated with sulfuric acid, hydrochloric or hydrofluoric acids, and which are therefore in the class of the activated natural earths. In addition to these, synthetic earths may also be employed, such as the gels of silica, activated alumina or mixtures or co-precipitated gels, hydro gels and the like, especially gels of silica and alumina or silica and magnesia. These gels may be used alone or they may be modified by the addition of metal agents containing, for example, nickel, iron, cobalt, manganese, vanadium, chromium, molybdenum, tungsten, their oxides, sulphides and the like.

The amount of the catalyst is quite small; for example, good results are obtained with $\frac{1}{10}$ to 10 pounds of the catalyst per barrel of the oil to be cracked. The catalyst, a finely divided powder or in granular form, together with the oil passes easily through the heating coils and other equipment without settling out or causing any difficulty. It may be removed by filtering or sedimentation and regenerated by burning off the carbon or by other means and may be reused.

The action of the catalytic agent is readily observed and permits the use of coil temperatures which are considerably higher than could be employed in its absence. Long runs are possible only by the use of the catalyst in conjunction with the higher pressure specified and the presence of the lighter oil which permits operation in the vapor phase. It has been found that if the catalyst is omitted the higher temperatures either cannot be reached at all or if reached, the operation must be discontinued after a short time because of coking difficulties. Even if the catalyst be present and the operation is not conducted completely in the vapor phase, coking difficulties will also make themselves felt within a relatively short time. If small amounts of the catalytic agent are present and sufficient of the light hydrocarbon is also present to maintain the heavy oil completely in a vapor phase, excellent results can be obtained for long periods of time without coking difficulties, giving rise to an excellent grade of naphtha.

It is somewhat difficult to specify definitely the specific temperatures, pressures and the amount of the lower boiling oil to be present at the same time. The above mentioned ranges are given approximately, but it will be understood that these several conditions must be mutually adjusted within the ranges given so as to bring about the reaction completely in the vapor phase. Experience has shown that this is the pre-requisite for excellent results.

With the above combination of cracking conditions, feed mixtures and catalysts, it is possible to obtain high grade naphthas with octane numbers from 72 to 75 without any coking difficulties and without dangerously over-heating the cracking coils.

As an example of the present operation, a feed stock consisting of 65% of heavy gas oil, 25% of lighter gas oil and 10% of heavy naphtha was admixed with 1.4 pounds of clay per barrel of the gas oil and this mixture was passed once through a heated coil wherein temperature was raised rapidly to 1060° F. while under a pressure of 350 pounds per square inch. The run was continued for several days without any difficulty in operation and the products were separated in the usual manner. The naphtha distillate produced amounted to 52 vol. per cent of the oil charged. A gas oil suitable as a domestic heating oil amounted to 13 vol. per cent, the gas was 12 wt. per cent and 4.5 vol. per cent excess butane and a tarry fuel oil of 20 vol. per cent was produced. No coke was produced and after removal of the clay catalyst from the tarry oil, it was found suitable for fuel oil. The naphtha had an octane number of 73.3.

In other runs it has been found that the temperature could not be reached without the catalyst because of overheated tubes and coking difficulties. Likewise coke difficulties rapidly developed if the naphtha was omitted from the feed. With lower pressures the yields of gasoline dropped off rapidly.

The present invention is not to be limited by any theory of the reaction or any particular types of feed oils or conditions except as specified in the claims.

We claim:

1. An improved cracking process which comprises passing heavy naphtha through a heating coil under pressure above 400 pounds per square

inch and at a temperature sufficient to reform the naphtha, then admixing the reformed naphtha while hot with a heavier distillate oil to be cracked, and passing this mixture through a second heating coil under pressure of at least 300 pounds per square inch and temperatures between 1000 and 1100° F., while in a completely vaporized condition and in the presence of a finely divided siliceous cracking catalyst whereby a substantial portion of the heavier distillate is cracked to gasoline, then separating the gasoline so produced.

2. An improved cracking process which comprises mixing a finely divided siliceous cracking catalyst with a heavy naphtha fraction, passing the resulting mixture through a heating coil under a pressure of about 400 pounds per square inch and at a temperature sufficient to reform the naphtha, then admixing the reformed naphtha while hot with a heavier distillate oil to be cracked, passing the last-named mixture through a second heating coil under a pressure of at least 300 pounds per square inch and at a temperature between 1000° F. and 1100° F. while in a completely vaporized condition whereby a substantial portion of said heavier distillate is cracked into gasoline in the presence of said finely divided siliceous cracking catalyst and heavy naphtha fraction, and thereafter separating the gasoline from the cracked products.

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