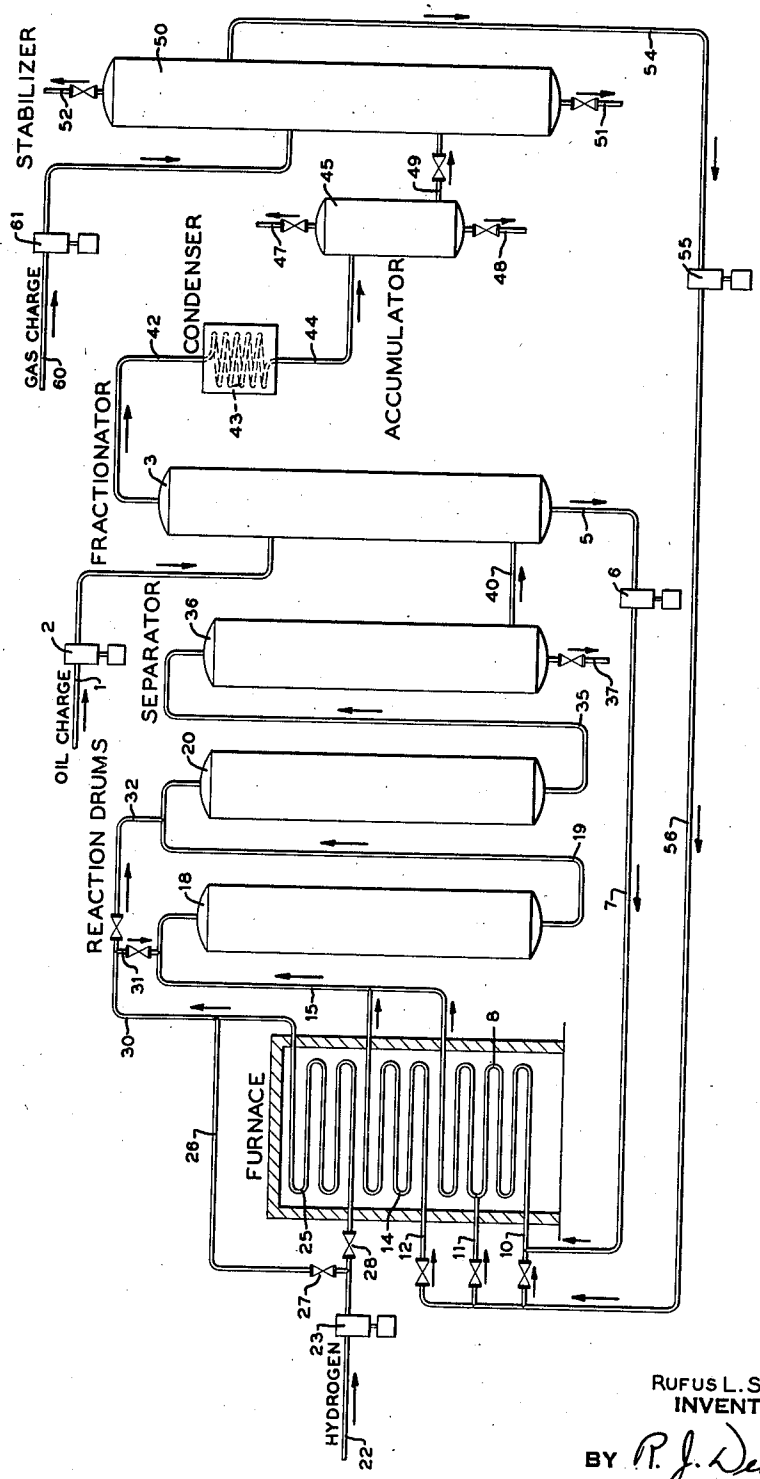
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CONVERSION OF HYDROCARBON OILS AND GASES

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RUFUS L. SAVAGE, JR.
INVENTOR

BY R. J. Dearborn

ATTORNEY

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CONVERSION OF HYDROCARBON OILS AND GASES

Rufus L. Savage, Jr., Port Arthur, Tex., assignor, by mesne assignments, to Texaco Development Corporation, New York, N. Y., a corporation of Delaware

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This invention relates to the manufacture of motor fuel by conversion of hydrocarbon oils and gases, outside the gasoline boiling point range, into products within the gasoline boiling point range. The invention has to do particularly with the conversion of higher boiling point oils into lower boiling point products in the presence of normally gaseous hydrocarbons and hydrogen, whereby combined cracking, polymerization and hydrogenation, as well as reactions of the nature of gas reversion, and inhibition of polymerization of higher boiling unsaturated products into tarry materials susceptible to coke formation, occur.

It has been proposed heretofore to crack hydrocarbon oils in the presence of added normally gaseous hydrocarbons to obtain gas reversion or produce the simultaneous and joint cracking and polymerization of the oil and gases, as well as interaction between the oil and gas to obtain intermediate boiling point products. In cracking hydrocarbon oils into lower boiling point products, such as gasoline, higher boiling unsaturated products are formed which tend to polymerize to tar or pitch and which are believed to be often responsible for coke difficulties. It has been found that by conducting the cracking operation in the presence of normally gaseous hydrocarbons, substantially less coke formation results, due to the inhibiting effect of normally gaseous hydrocarbons; or a combination of the gaseous hydrocarbons with the unsaturated higher boiling point oils to form intermediate boiling point products, which are less susceptible to coke formation, takes place.

In accordance with the present invention, it is intended to add the normally gaseous hydrocarbons and the hydrogen under conditions which will give the maximum conversion into high quality motor fuel products and to produce minimum formation of coke. In order to do this it is preferable to subject the oil and the normally gaseous hydrocarbons to conversion conditions whereby the maximum benefit from the gases is obtained prior to the reaction in the presence of the hydrogen; however, it is to be understood that the oil, hydrocarbon gases and hydrogen may be simultaneously subjected to a single conversion operation. According to one method of operation, the oil and hydrocarbon gases may be heated to conversion conditions of temperature and pressure and the mixture subjected to reaction, and then the hydrogen commingled with reaction products and the mixture subjected to further reaction. It is preferable, however, to heat the hydrocarbon oils to cracking or incipient cracking and, prior to substantial polymerization to coke forming materials, to incorporate with the hot products the normally gaseous hydrocarbons and then subject the mixture to reaction whereby the maximum benefits of the gaseous hydrocarbons are obtained. The hydrogen is then incorporated with the reaction products, whereby further conversion may be obtained under conditions to obtain the maximum benefit of the hydrogen.

It will be observed that a process is provided whereby combination cracking and gas polymerization, or gas reversion, is obtained, the gaseous hydrocarbons being added at the proper point to obtain maximum benefit, particularly with respect to inhibiting tar and coke formation and production of a maximum yield of motor fuel hydrocarbons. Reactions in the nature of hydrogenation will also be effected which will further prevent and retard undesirable polymerization reactions which result in the formation of fuel oils and often in the ultimate production of coke.

The process may be carried out with or without the aid of a hydrogenation catalyst, or one or more of the separate steps may be conducted in the presence of a hydrogenation catalyst. It is often desirable to at least carry out a portion of the reaction in the presence of a catalyst. A catalyst for this purpose may be any preferred or well known hydrogenation catalyst and preferably one of the type suitable for high temperature and pressure operations and which is not poisoned by sulfur.

Catalysts which may be used are heavy metals of the sixth group of the periodic system, especially molybdenum and tungsten, but also chromium and uranium and compounds thereof, or tin, lead, vanadium, rhenium, manganese, zinc, cadmium, aluminum or cobalt or compounds thereof. Suitable strongly hydrogenating catalysts are for example the sulfides of heavy metals, such as sulfides of metals of the sixth group of the periodic system, for example of molybdenum, tungsten or of nickel, cobalt, rhenium or a tungstate such as nickel tungstate. Catalysts having a less strongly hydrogenating action are, for example the oxides of the metals of groups 5 to 8, in particular group 6 of the periodic system.

The invention will be further understood from the following description read in connection with the accompanying drawing which shows a diagrammatic sketch of one type of apparatus for carrying out the process of the invention.

Referring to the drawing, a hydrocarbon oil

charging stock which may be crude residuum, gas oil, crude oil, heavy naphtha and the like, is charged through line 1 by means of pump 2 into a fractionating tower 3 which receives vapors from the conversion operation. In the fractionator 3 substantially all the vapors of higher boiling point than the desired motor fuel product are condensed and collected along with the unvaporized charging stock in the bottom of the fractionator which is withdrawn through the line 5. This material is forced by the pump 6 through the line 7 to a heating coil 8. In this heating coil the oil is subjected to conversion conditions which may be temperatures of about 700–1200° F. and pressures of about 200–5000 pounds or more. Provision is made for adding normally gaseous hydrocarbons, such as butane, propane, a mixture of butane and propane, or mixed C_4 cracked hydrocarbons, or a mixture of hydrocarbons of C_1 to C_4, such as natural gas or refinery gases, or cracking still gases. These gases may be added to the oil at the entrance of the coil through the valve controlled line 10 or at an intermediate point in the coil, such as at the point of incipient cracking, or at the point of incipient tar or fuel oil formation, through the line 11. It is also provided that the hydrocarbons gases may be introduced through the line 12 into the heating coil 14 and heated to an elevated temperature and pressure, such as about 800–1750° F. and pressures of 200–5000 pounds or more, then mixed with the hot products from the coil 8 in the line 15, leading to the reaction or soaking drum 18. In some cases it may be desirable to introduce the normally gaseous hydrocarbons through one or more or all of the lines 10, 11 and 12. The products from the soaking drum 18 are transferred through the line 19 to a second soaking drum 20, wherein further reaction is allowed to take place.

Hydrogen is introduced through the line 22 and forced under high pressure, which may be substantially the same or slightly above that maintained in the reaction drums 18 and 20, by means of the pump 23 to heating coil 25. The use of this heating coil is optional and the coil 25 may be by-passed by suitable manipulation of valve 27 in the line 26 and valve 28 in the line 22. It is preferable to heat the hydrogen to sufficient temperature, say about 500–1200° F. whereby there will be no excessive reduction in temperature when the hydrogen is introduced into the reaction products from the coils 8 and 14. The hydrogen is conducted through the line 30 which is provided with manifolds 31 and 32 for introducing the hydrogen either into the products entering the reaction drum 18 or the reaction drum 20. Reaction drums 18 and 20 may or may not be provided with a hydrogenation catalyst. It is preferable to provide at least the reaction drum 20 with a hydrogenation catalyst.

The reaction products from the drum 20 are transferred through the line 35 to a separator 36. This separator is preferably maintained under high pressure and a low level of liquid products is maintained by continuously or intermittently drawing off the fuel oil or tar from the bottom thereof through the valve controlled line 37. This tar draw-off line ordinarily leads to a reduced pressure tar stripper in which the tar may be flashed to produce a fuel oil bottoms and a distillate comprising gas oil and naphtha, a portion or all of which, preferably the gas oil at least, may be recycled to the system, for example to fractionator 3 or coil 8. Vapors evolved in the separator 36 are transferred through the vapor line 40 to the fractionator 3, referred to heretofore. Vapors including gasoline are removed from the top of the fractionator through the vapor line 42 and passed through a condenser 43 in which normally liquid hydrocarbons are condensed and passed through the run-down line 44 to accumulator 45, provided with a gas release line 47 and a liquid draw-off line 48. In the accumulator 45 a high pressure may be maintained and fixed gases, such as hydrogen, methane and ethane may be released through the line 47, if desired. The unstabilized motor fuel and gases are passed through the line 48 to a stabilizer 50 in which the motor fuel is stabilized by fractionating therefrom undesirable normally gaseous hydrocarbons. The resulting stabilized naphtha is withdrawn from the bottom of the stabilizer through the valve controlled line 51. A portion or all of the fixed gases, such as hydrogen, methane, ethane, may be released through the top of the stabilizer through the valve controlled line 52. A stabilizer side stream or reflux such as butane or propane or a mixture of butane and propane, or all or any desired portion of the normally gaseous hydrocarbons is withdrawn through the line 54 and forced by the pump 55 through the line 56 which communicates with lines 10, 11 and 12, referred to heretofore.

Extraneous gaseous hydrocarbons, such as natural gas, casinghead gasoline, refinery gases, etc., may be introduced through the line 60 and pump 61 into stabilizer 50.

As an example of the operation of the process of the invention, a reduced crude was heated to incipient cracking, for example to a temperature of around 750° F., and normally gaseous hydrocarbons amounting to about 25% by volume, were then commingled therewith and the mixture subjected to further heating to a temperature of around 900° F. and the reaction products introduced into a soaking drum maintained under a temperature of around 890° F. and a pressure of about 300 pounds. The reaction products from the soaker were mixed with about 10% hydrogen and the mixture subjected to further reaction at a temperature of about 875° F. in another soaking drum. The reaction products were then introduced into a separator from which a fuel oil was withdrawn to a tar stripper. A gas oil fraction was removed from the tar stripper and introduced as a reflux medium into a fractionator receiving vapors from the separator. The vapors comprising gasoline hydrocarbons were removed from the top of the fractionator, subjected to condensation and collected in a high pressure accumulator from which fixed gases were eliminated. The unstable condensate was introduced into a stabilizer in which a stable naphtha was withdrawn from the bottom and the remaining fixed gases were released from the top. About 10% of an extraneous product comprising mainly butane and propane was introduced into the stabilizer. A side stream, consisting principally of C_3 and C_4 hydrocarbons, was withdrawn from the stabilizer and recycled to the intermediate point of the heating coil, as described heretofore. An increased yield of about 7% of a stable, high grade motor fuel was obtained over that resulting from normal cracking of the hydrocarbon oil alone. Substantially less tar and fuel oil were produced. Also the tendency to coke formation in the reaction drums was substantially reduced.

While the process has been described in con-

nection with an operation involving clean circulation, it is to be understood that any well known or preferred type of cracking operation may be used in which suitable periods of reaction may be obtained, either by soaking drums or soaking coils. One type of operation which is specifically contemplated is one involving a super-clean circulation in which two fractionating towers are used instead of the one shown in the drawing. In such a type of operation a dirty recycle stock would be withdrawn from the bottom of the first tower and passed through a separate heating coil or directly to the reaction drum. From the bottom of the second tower a super-clean recycle stock would be withdrawn and passed through a separate coil into the reaction drum. The hydrocarbon gases in a super-clean type of operation might be injected into either or both of the clean oil or dirty oil coils, but it is preferable that the gases be introduced into the clean oil coil.

As another example of the operation of the invention, a crude residuum was heated to conversion temperatures and pressures, of about 900° F. and pressures of around 3000 pounds, in the presence of about 25% of normally gaseous hydrocarbons, such as butane and propane, and in the presence of a catalyst comprising molybdenum sulfide. About 10% hydrogen was then introduced into the reaction products and the mixture subjected to further reaction in the presence of the same catalyst. The final products of reaction were introduced into a separator in which a fuel oil was withdrawn, a major portion of which was recirculated to the reaction drums. The vapors were fractionated and the recycle stock recirculated to the heating coil. The remaining vapors were condensed to separate the gasoline and the gases recirculated to the system. A high yield of antiknock motor fuel was obtained and substantial reduction in the yield of fuel oil was observed.

Obviously many modifications and variations of the invention, as hereinbefore set forth, may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

I claim:

1. A process for the conversion of higher boiling hydrocarbon oils into lower boiling hydrocarbon oils which comprises raising the oil to temperatures of incipient cracking, then before substantial formation of coke forming materials adding normally gaseous hydrocarbons heavier than methane to the oil, further heating the mixture to cracking temperatures whereby coke formation is substantially retarded by said gaseous hydrocarbons, subjecting the mixture to reaction in the presence of a catalyst immune to sulfur poisoning to produce low boiling products from the oil and gaseous hydrocarbons and introducing hydrogen into the reaction zone to inhibit the formation of coke and tar and increase the yield of low boiling liquid products.

2. A process for the cracking of high boiling hydrocarbon oils to form gasoline boiling point hydrocarbons, which comprises heating the oil to cracking temperatures in a heating coil, introducing normally gaseous hydrocarbons heavier than methane into an intermediate point of said coil at about the temperature of incipient cracking to retard coke formation and to be converted into normally liquid hydrocarbons, subjecting the products from the cracking coil to reaction in the presence of a catalyst immune to sulfur poisoning in a reaction zone and introducing hydrogen into the reaction zone whereby the formation of coke forming materials is substantially reduced and the yield of gasoline materially increased.

3. A process for the cracking of high boiling hydrocarbon oils to form gasoline boiling point hydrocarbons, which comprises heating the oil to incipient cracking temperatures and prior to substantial formation of coke forming materials, commingling normally gaseous hydrocarbons heavier than methane with the oil to retard coke formation, further heating the mixture to cracking temperatures, subjecting the mixture to reaction to produce low boiling oil products from the oils and gaseous hydrocarbons, then contacting hydrogen with the reaction products and subjecting the mixture to further reaction at conversion temperatures in the presence of a catalyst immune to sulfur poisoning to further prevent coke and increase the yield of gasoline.

4. A process for the cracking of high boiling hydrocarbon oils to form gasoline boiling point hydrocarbons, which comprises heating the oil to cracking temperatures and, prior to substantial formation of coke forming materials, commingling normally gaseous hydrocarbons heavier than methane with oil, subjecting the mixture to reaction in the presence of a catalyst immune to sulfur poisoning in a primary reaction zone, commingling hydrogen with the reaction products and subjecting the mixture to further reaction in the presence of a catalyst immune to sulfur poisoning in a secondary reaction zone whereby coke formation is substantially retarded and said oil and gaseous hydrocarbons are converted into increased yields of low boiling products, including gasoline.

5. A process for the manufacture of gasoline, which comprises heating a high boiling hydrocarbon oil to cracking temperatures, commingling normally gaseous hydrocarbons between 2 and 5 carbon atoms with the hot oil prior to substantial formation of coke forming materials whereby coke formation is substantially retarded, subjecting the mixture to conversion in a reaction zone to convert oils and gaseous hydrocarbons to gasoline in the presence of a catalyst immune to sulfur poisoning, introducing hydrogen into the reaction zone to further reduce coke formation and increase the yield of gasoline, separating from the reaction products a gasoline fraction and a normally gaseous hydrocarbon fraction containing hydrocarbons between 2 and 5 carbon atoms, and recycling said gaseous hydrocarbon for commingling with said hot oil.

RUFUS L. SAVAGE, JR.