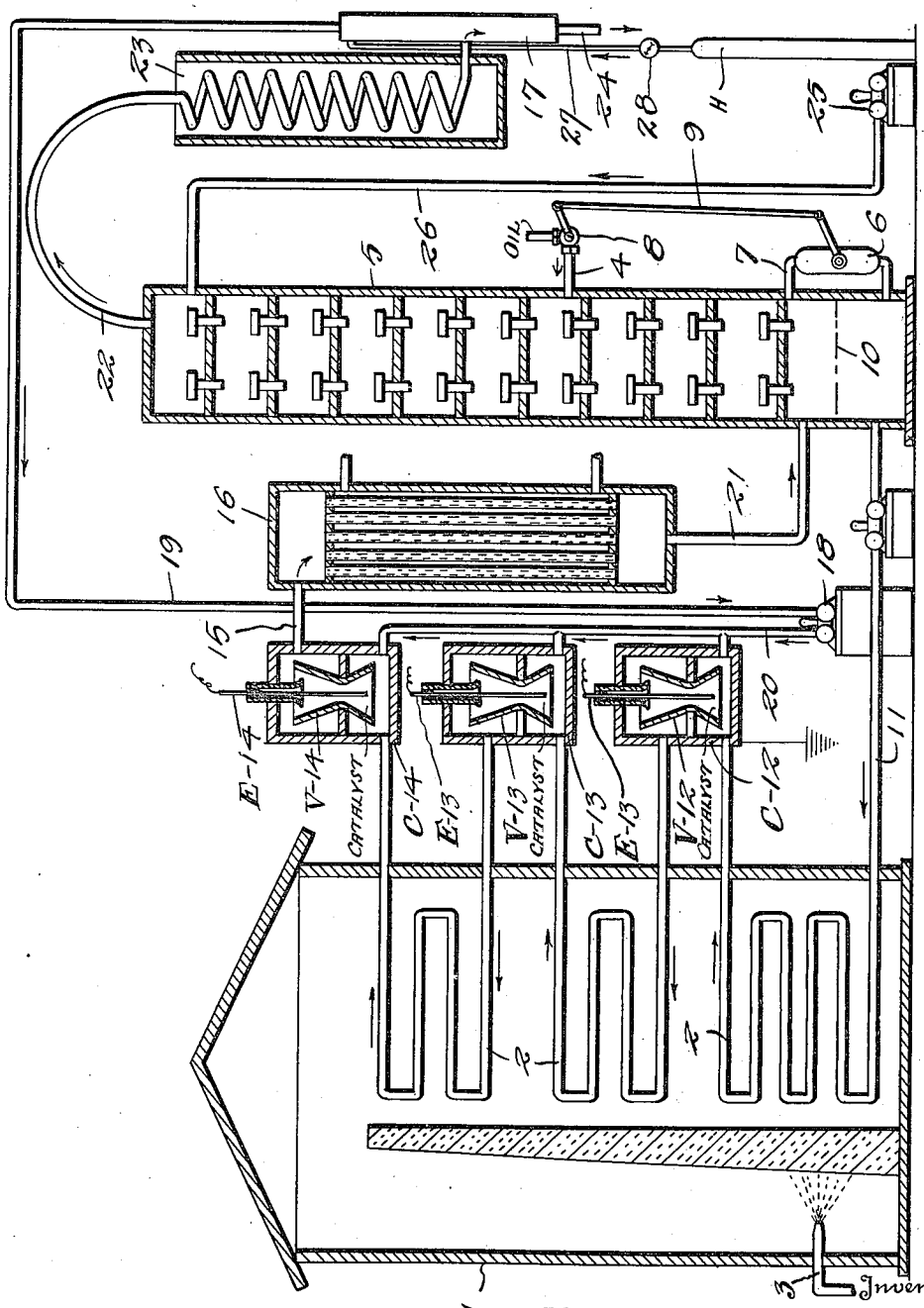
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PROCESS OF HYDROGENATING HYDROCARBON OILS

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PROCESS OF HYDROGENATING HYDROCARBON OILS

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7 Claims. (Cl. 196—53)

This invention relates to the conversion of heavy hydrocarbons into lighter hydrocarbons of the same or of a different series by the process of hydrogenation, and the present application constitutes a continuation in part of my application, Ser. No. 170,677, filed October 23, 1937.

More particularly the invention has for its principal object to effect such conversion by subjecting the vapors of the heavier or higher boiling petroleum oils with hydrogen, to catalytic action in the presence of or within an electrostatic field, with the catalysis material in the form of a Venturi-shaped tube or other mixing means, through which the vapors or gases pass so as to intimately contact the petroleum vapor and hydrogen, with simultaneous electric treatment to form a new permanent compound or compounds of the nature of lower boiling petroleum oils with higher octane rating.

Crude oils as it comes from the ground consists of liquid hydrocarbons of the C_nH_{2n+2} series, containing from ten to twenty percent of gasoline, a like percentage of kerosene, about five percent of gas oil and the remainder of from fifty to seventy percent fuel oil, suitable only for burning under steam boilers and for general heating purposes.

In recent years a process known as "cracking" has been practiced with these heavier hydrocarbon oils with the result that the production of approximately another twenty percent of gasoline is to be obtained from the original crude oil.

But while this treatment resulted in an additional yield of gasoline, the residue of these heavier oils so treated were rendered less marketable, large percentages of the heavy fractions being turned into non-condensable gas and carbon.

In the practical use of the present invention, there are made use of certain facts and practices which have not heretofore been recognized as essential to the accomplishment of the art, resulting in a degree of efficiency and of a higher yield of gasoline of a superior quality than has heretofore been possible.

As is well known, gasoline contains very little more hydrogen than does kerosene and the heavier oils. Below is given a table showing the chemical composition of the constituents of crude oil:

Name	Symbol	Percent carbon (by weight)	Percent hydrogen (by weight)
Methane	CH_4	75.00	25.00
Ethane	C_2H_6	80.00	20.00
Propane	C_3H_8	81.81	18.19
Butane	C_4H_{10}	82.76	17.24
Pentane	C_5H_{12}	83.33	16.67
Hexane	C_6H_{14}	83.72	16.28
Heptane	C_7H_{16}	84.20	16.20
Octane	C_8H_{18}	84.21	15.79
Nonane	C_9H_{20}	84.38	15.62
Decane	$C_{10}H_{22}$	84.51	15.49
Tridecane	$C_{11}H_{24}$	84.78	15.22
Undecane	$C_{12}H_{26}$	84.62	15.38
Dodecane	$C_{13}H_{28}$	84.71	15.29
Tetradecane	$C_{14}H_{30}$	84.85	15.15
Pentadecane	$C_{15}H_{32}$	84.91	15.09
Hexadecane	$C_{16}H_{34}$	84.96	15.04
Heptadecane	$C_{17}H_{36}$	85.20	15.20
Octodecane	$C_{18}H_{38}$	85.04	14.96
Nonodecane	$C_{19}H_{40}$	85.07	14.93

It is thus seen what a small amount of hydrogen is required to convert some of the heavier fractions of the crude oil into the lower boiling compounds. For example, heptane, which is considered the principal ingredient of gasoline, contains but 51/100 of one percent more hydrogen than does decane, the principal constituent of kerosene.

The accompanying drawing illustrates diagrammatically apparatus by means of which the present process may be carried out.

In the practice of the present invention and referring particularly to the apparatus illustrated in the drawing, there is employed a furnace 1 for heating the series of coils 2 of the pipe still. A suitable oil or gas burner 3 is made use of for heating the furnace. Crude oil or other liquid hydrocarbon is pumped from storage through pipe 4 and may enter the third or fourth tray of a dephlegmating bubble-cap type column 5. A float valve 6 of suitable form is coupled by the top and bottom pipes 7 with the lower part of the column 5 whereby the liquid level in the lower part of the column will effect movement of the float and actuate the valve 8 in pipe line 4 through the medium of the coupling 9, and when the level of the oil in the column falls below the line 10 in the chamber at the bottom of the column, the valve 6 will open the valve 8 in line 4 to admit crude oil so that the chamber at the bottom of the column will always be kept half

full. However, the reflux from the trays above will account for most of the contents of this chamber. This reflux, representing the heavier fractions of the oil which have not as yet been turned into gasoline, and the crude oil admitted by way of pipe 4, are pumped through pipe 11 to the heating coils 2, or the crude oil may be introduced into the system directly into this pipe 11 so as to pass directly to the first coil of the still.

When this oil has become vaporized by circulation through a sufficient number of turns of the first of the heating coils 2, the vapor first enters the lower chamber of one of a series of catalysis converters which are indicated by the characters C—12, C—13 and C—14 where the vapor receives a given amount of a mixture of hydrogen and hydrogen-rich gas, as will be more fully hereinafter described. The entrance of both the hydrocarbon vapor and the hydrogen and hydrogen-rich gas is made preferably tangentially so as to give to them as thorough a mixing one with the other as is possible.

In each of the converters the catalysis material is in a form which will bring about a close commingling of the molecules of the different gases and vapors passing from one heating coil to the other and from the top coil to the condenser. The object in having the material in this form is to bring the atoms of the different molecules into as close contact with one another as possible while at the same time having them in close proximity to or in contact with the catalytic material. In the diagrammatic illustration of the apparatus the catalysis material in each converter is in the form of a double conical tube or a tube generally similar to a venturi. These tubes are designated respectively for the converters V—12, V—13 and V—14. The outlet of the first of the coils of the series 2 in the furnace enters the first converter C—12 in the lower part thereof and the lower end of the second coil leads from the upper part of the first converter and into the lower part of the second converter. This procedure is repeated with respect to the coils and converters, as is clearly shown, and each converter is partioned in a plane passing through the constricted part of the tube therein so that the entering vapors will be compelled to pass through the tube before leaving the upper part of the converter.

Extending through the longitudinal center of each converter tube is an insulated high-tension electrode by means of which an electric field may be set up in each converter tube, however, the electric impulses impressed upon the mixed molecules of the vapors may also be impressed upon the mixture of hydrocarbon vapors and hydrogen by any other of the well known electrical devices generally used, with or without an insulated central electrode. These electrodes are designated respectively for the several converters E—12, E—13 and E—14.

The hydrocarbon vapor, having had the hydrogen and hydrogen-rich gas added and the mixed gases having received a high voltage, high-frequency charge of electric current of an accurately determined potential when passing through the catalysis tube V—12 and at a temperature just above vaporization or below a "cracking" temperature of the hydrocarbon oil, then passes from the first converter through the second one of the series of heating coils 2 which is maintained at a higher temperature so that the temperature of the mixed vapors will be increased but will still be kept below a "cracking" temperature. Here the combined hydrocarbon vapor and hydrogen-rich gas undergoes a "fixing" but not a disrupting of its molecular structure.

The vapor-hydrogen mixture then enters the second catalysis converter C—13, where it may or may not have additional hydrogen and hydrogen-rich gas added as before, and is subjected to another electrical charge of high-tension, high-frequency current and passes on to be "fixed" again in the next one of the furnace coils 2 and at a still higher temperature but below a "cracking" heat.

The vapor-hydrogen-rich gas finally receives the last electrical catalytic hydrogenation treatment in the converter C—14, from the top of which it passes by way of the pipe 15 into the upper part of the cooler 16 to be cooled for efficient dephlegmating-column action where the gasoline fractions that have been formed are removed and the dephlegmated reflux is then returned for recycling.

The numeral 17 designates a tank from the upper part of which the non-condensable gases are taken off for recirculation through the system, which non-condensable gases have heretofore been referred to as "hydrogen-rich gas". A suitable pump 18, connected with the tank 17 by the pipe line 19, accomplishes this function, transferring the hydrogen-rich gas through the distributor pipe 20 to the several converters.

The hydrocarbon oil fractions after being partly cooled in their passage through the cooler 16, enter the lower part of the dephlegmating column by way of the pipe 21 where the newly made gasoline is separated, the gasoline vapor leaving the top of the column through the pipe 22 to be condensed into liquid by a suitable water-cooled condenser 23, after having the non-condensable gases removed from the liquid gasoline in the separator tank 17, goes on to a suitable storage receptacle by way of the pipe 24. In the manner well known to the art, gasoline is pumped to the top tray of the column 5 by a suitable pump such as is indicated at 25, through the pipe 26 for the proper control of the reflux to regulate the end point of the gasoline produced. It is also well known that the reflux from the trays of the column finally reaches the chamber at the lower part of the column for recycling through the pipe still by way of the pipe line 11 and through the catalysis converters with which the still is connected.

The temperature of the hydrocarbon vapor as it passes into the first converter C—12, is about 575° F. It enters the second converter at about 600° F. and the third converter at about 675° F. These temperatures may be varied to suit different oils by regulating the furnace operation or by any other means which might be employed for vaporizing the hydrocarbon. Generally there is employed an electric potential of between 2000 and 3000 volts and having an oscillation period of between 20,000 and 40,000 cycles per second, producing a silent dark discharge which is impressed upon the vapor and hydrogen-rich gas as the same passes through the catalysis tubes in the converters. While the arrangement is such that with the electrical potential specified a silent dark discharge is most commonly or regularly employed, the character of the discharge may be varied to produce a corona or glow, when the central electrodes shown are employed, in accordance with the working or heat conditions of the converters.

Approximately one-tenth of one percent of hydrogen and from one to two percent of hy-

drogen-rich gas is admitted to each converter in proportion by weight of the hydrogen vapor treated.

I have found that hydrogenation of petroleum oil vapors takes place in two separate and distinct reactions. The expansive force of the heat on the vapors causes a loosening of the original hydrocarbon molecule. At this stage paraffines and olefines, of lower molecular weight are formed, and some hydrogen is released. For this reaction as little pressure as is possible should be employed in the vaporization of the oils in order that the molecules of the saturates and unsaturates can become loosened from each other as readily as possible, but immediately the additional hydrogen is introduced to form the desired lower boiling point fractions, slight pressure is desirable, as according to the law of mass action, reaction velocity is proportional to concentration and concentration is directly proportional to pressure. In the present invention, the vaporizing of the heavy hydrocarbon oils is accomplished with very low pressure, but immediately after the addition of hydrogen to the vapor, the mixture of the two receives a slightly increased velocity when passing through the double conical tube of the catalytic converter. The reaction desired is greatly assisted by the catalytic material of the tube.

In using the constricted tube to crowd together the atoms of the molecules of the mixed gases whereby there is effected a closer association thereof for the chemical addition of the hydrogen to the hydrocarbon vapors of high-boiling point fractions to those of lower boiling point fractions, such crowding action is not transmitted through the whole system. This allows the primary heat disruptive reaction, which slightly loosens the molecules from each other, to proceed under the most advantageous condition. This absence of high pressure allows the entire apparatus to be constructed of light and simple materials of relatively cheap construction and design.

I am aware of existing claims having been made in the existing patents of Robertson #1,238,339 and Cherry #1,229,886, likewise Schmidt and Wolcott #1,307,931, for the decomposing of liquid hydrocarbon vapors to form light from heavy hydrocarbons, and I, in a former patent, #1,347,119, used "a sparking electric discharge" to keep a catalysis clean and active, but I believe I am the first to use high-tension electric currents in which the frequencies employed are correlated with the particular catalysts used to assist such catalytic material to perform the act of saturating the unsaturated hydrocarbons present, in the closely confined space created by the shape of a constricted tube without raising such hydrocarbon vapors to "cracking" temperatures, and carrying out the treatment in separate steps, each at a higher heat than the previous one, to effect the final conversion, then separating the converted hydrocarbon vapors from the ones not sufficiently converted, and recycling them for further treatment until final conversion takes place and hydrogenation is accomplished without "cracking" having taken place at all, which results in the proper rearrangement of the molecules and gives to the gasoline so produced a very high octane number.

I have found by actual trial that with catalysis tubes containing chromium, a frequency in oscillation of the electric current should be from 20,000 to 25,000 per second to produce the most desirable results when converter C—12 operates at 575° F., C—13 at 600° F., and C—14 at 675° F., while if a nickel or molybdenum catalysis tube material is used, electric current oscillations of from 30,000 to 35,000 per second produce the best result. These temperatures are imparted by the heated vapors to the catalytic material tubes and the desired action of the catalytic materials is obtained at the vapor temperatures. When it is necessary to increase or lower the temperatures in the converters, that is, the temperatures of the catalytic material, such changes are accomplished by increasing or decreasing the furnace temperature. Thus if the furnace temperature is raised, the temperatures of the vapors in the coils 2 will be correspondingly raised, the highest vapor temperature being in the top coil and the lowest in the bottom coil and such vapor temperatures will be passed on to the tubes of catalytic material. I have found that it is only by correlating the electrical frequencies with certain catalysis materials and a certain degree of heat that good gasoline, and with high octane rating and without undesirable polymerized constituents, can be produced at the low temperatures used.

As an illustration of the foregoing, good results are obtained when operating the system while discharging current from the electrodes at the frequencies mentioned by having the temperatures of the converters C—12, C—13 and C—14 at 600° F., 640° F., and 680° F., when using catalyst tubes having the composition for the converter C—12, 80% aluminum, 15% iron and 5% zinc; for the converter C—13, 90% aluminum, 5% iron and 5% zinc, and for the converter C—14, 90% aluminum, 2½% iron and 7½% zinc. These temperatures referred to specifically in association with the above specifically defined catalysts may be varied to the temperatures previously referred to but it has been found that the three different percentages at the different temperatures given in association therewith for the converters seem to work best with the proportions stated for the catalyst materials. Nickel might be substituted for the aluminum but the iron and zinc proportions remain the same. With higher temperatures and higher frequency of electric current, less iron is required and more nickel or aluminum.

While the process described and illustrated diagrammatically sets forth the recycling of the non-condensable fractions with hydrogen gas, the process may be effectively carried out by the introduction of pure hydrogen gas into each converter without admixture with the uncondensed gases or fractions recovered from the separator 17.

Although the hydrogen gas may be introduced at any place in the system between the converters and the separating tank 17 or at the converters, as stated, it is preferably introduced as illustrated by coupling a high pressure cylinder H of the gas with the upper part of tank 17 by the pipe 27 in which a suitable metering valve 28 is interposed. Thus the flow of the hydrogen into the tank for mixture with the non-condensable gases may be accurately controlled, as is necessary for the most efficient operation of the process.

What is claimed is:

1. The process of converting heavy petroleum oil fractions to lighter fractions, which comprises vaporizing the heavy oil fractions, mixing the heated vapor with hydrogen gas, passing the vapor-gas mixture through a space encircled by a catalytic material, producing a high frequency silent dark discharge of electric current through

said space, raising the temperature of the vapor-gas mixture so treated above the original temperature of the vapor while maintaining the treated vapor-gas mixture below 680° F., and again passing the vapor gas mixture through a high frequency electric field forming a silent dark discharge in a space enclosed by a catalytic material.

2. The process of converting heavy hydro-carbon oils to lighter fractions, which comprises vaporizing such oils, passing such vapor at a temperature of less than 600° F., into a catalyst chamber, mixing the hydrogen gas with the vapor in said chamber, flowing the gas and vapor mixture in said chamber through a constricted space designed to produce agitation of the mixture, which space is circumscribed by a catalytic material, impressing on said mixture within the constricted space a non-sparking charge of high frequency electric current, and repeating the steps outlined in successive chambers with progressive increase in temperature in each chamber and constricted catalytic space, the final temperature being not higher than 680° F.

3. The process of converting heavy hydrocarbon oils to lighter fractions, which comprises vaporizing such oils, passing said vapor at a temperature of less than 600° F., through a catalyst encircled space, admitting hydrogen gas with the vapor just prior to its passage through such space, subjecting the mixture of vapor and gas within the catalytic space to a non-sparking high frequency electric field while maintaining the catalyst at a temperature at least as high as the temperature of the vapor passing through the space, passing the mixture through a second heated catalyst encircled space, mixing hydrogen gas with the mixture just prior to its passage through the second space, subjecting the mixture in the second space to a non-sparking high frequency electric field, and finally passing the mixture through a third catalyst encircled space after adding hydrogen gas to the mixture prior to its introduction into the third space and subjecting the mixture in the third space to a non-sparking high frequency electric field, the said spaces being composed of catalytic material of different compositions and the electrical frequency of said fields being regulated in accordance with the character of the catalytic materials, and the temperatures of the spaces, the final temperature being not greater than 680° F.

4. The process of converting heavy hydrocarbon oils to lighter fractions, which comprises the steps of vaporizing said oils, passing said vapor successively through a series of catalyst encircled spaces, the catalyst material of each of said spaces consisting of a mixture of aluminum, iron and zinc, the proportions of which are different for each catalyst space, introducing hydrogen gas for admixture with the said vapor prior to its passage through each of said catalyst encircled spaces, subjecting the hydrogen-vapor mixture to the action of a non-sparking high frequency discharge of electric current within each of said spaces, regulating the frequency of the electric discharge in each of said spaces in accordance with the composition of the adjacent catalytic material, and progressively increasing the temperature to which the hydrogen-vapor mixture is subjected in its passage through the successive spaces.

5. The process of converting heavy hydrocarbon oils to lighter fractions, which comprises the steps of vaporizing said oils, passing said vapor successively through a series of catalyst encircled spaces, the catalyst material of each of said spaces consisting of a mixture of aluminum, iron and zinc, the proportions of which are different for each catalyst space, introducing hydrogen gas for admixture with the said vapor prior to its passage through each of said catalyst encircled spaces, subjecting the hydrogen-vapor mixture to the action of a non-sparking high frequency discharge of electric current within each of said spaces, regulating the frequency of the electric discharge in each of said spaces in accordance with the composition of the adjacent catalytic material, and progressively increasing the temperature to which the hydrogen-vapor mixture is subjected in its passage through the successive spaces, the temperatures employed in the process being within the range of from 575° F. to 680° F.

6. The process of converting heavy hydrocarbon oils to lighter fractions, which comprises converting the heavy oil to a vapor, maintaining the temperature of the vapor under 680° F., mixing hydrogen gas with the vapor, passing the vapor gas through a passage of catalytic material having the form of a venturi, and discharging non-sparking high frequency current within the passage from a central electrode to the catalytic material while the mixed gas and vapor is passing through the passage.

7. The process of converting heavy hydrocarbon oils to lighter fractions, which comprises heating the heavy oil to convert the same to a vapor, maintaining said vapor temperature at not more than 680° F., mixing hydrogen gas with the vapor, and immediately passing the vapor gas mixture through a passage of catalytic material having a constriction therein, and simultaneously with the passing of the vapor gas mixture through said passage discharging non-sparking high frequency current from the central part of the space in the constricted portion thereof to the wall of the passage.

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