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HYDROCARBON CONVERSION

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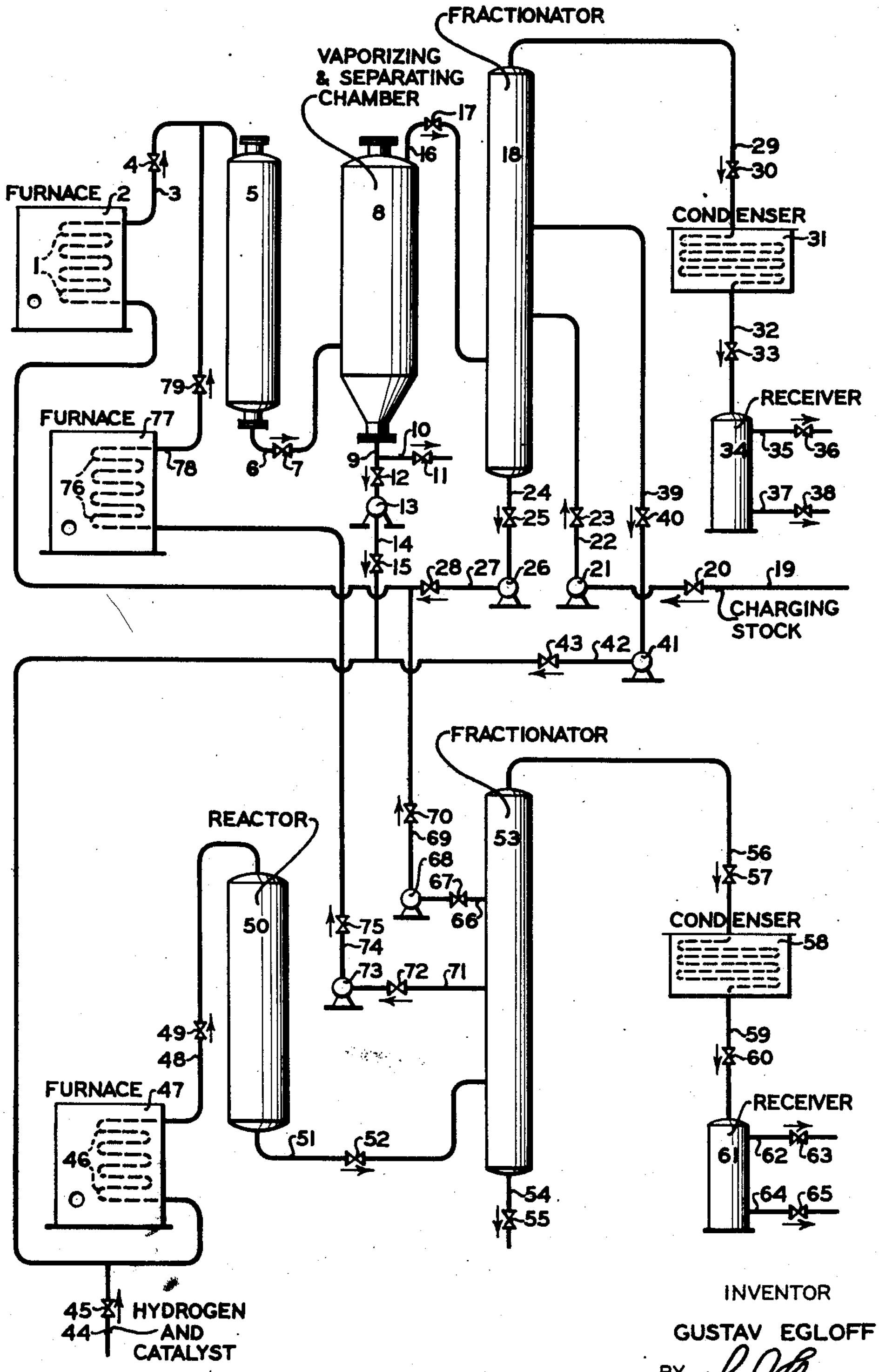

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# UNITED STATES PATENT OFFICE

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## HYDROCARBON CONVERSION

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5 Claims. (Cl. 196—49)

This invention relates to a process for the production of high yields of good antiknock gasoline from hydrocarbon oil heavier than gasoline and more specifically to a process in which the charging oil, together with heavy insufficiently converted hydrocarbons, is thermally cracked and light insufficiently converted hydrocarbons are non-destructively hydrogenated either in the presence of or out of the presence of cracked residue formed in the thermal cracking step, and the insufficiently converted hydrocarbons from the hydrogenation step returned to the thermal cracking step for further treatment.

Light insufficiently converted hydrocarbons and cracked residue formed in the thermal cracking process will ordinarily contain relatively high percentages of olefinic and aromatic hydrocarbons of relatively low hydrogen content, and when subjecting these hydrocarbons to further cracking (pyrolytic) relatively large amounts of carbonaceous substances and gas are formed, whereas the heavy insufficiently converted hydrocarbons and the charging oil will contain hydrocarbons of a relatively higher hydrogen content, since they are composed principally of paraffins and naphthenes, and these hydrocarbons may be successfully cracked pyrolytically without undue formation of gas and carbonaceous substances. If, on the other hand, the light insufficiently converted hydrocarbons and cracked residue are subjected to a non-destructive hydrogenation treatment during which only relatively small yields of gasoline are produced, such insufficiently converted hydrocarbons subjected to this treatment are converted into hydrocarbons of a higher hydrogen content and may be subjected to further thermal cracking, thereby considerably augmenting the yield of gasoline ordinarily produced in the absence of such treatment.

In one embodiment the invention comprises thermally cracking a hydrocarbon oil to form gasoline, insufficiently converted hydrocarbons, and liquid residue, separating said insufficiently converted hydrocarbons, together with the charging oil, into two fractions, a light fraction comprising relatively low boiling hydrocarbons, such as gas oil, and a heavy fraction containing the hydrocarbons boiling above said relatively low boiling hydrocarbons, supplying said heavy fraction to the cracking step as said hydrocarbon oil, commingling said light fraction with said liquid residue and reacting the mixture with hydrogen to increase the hydrogen content thereof, separately fractionating the products from the hydrogenation step to separate gasoline boiling range hydrocarbons from the heavier products, returning said heavier products to the thermal cracking step, and finally condensing the gasoline boiling range hydrocarbons separated in both steps.

In a more specific embodiment the invention comprises subjecting a hydrocarbon oil to thermal cracking in a heating coil and communicating reaction chamber, separating the conversion products into a non-vaporous liquid residue and vaporous conversion products, fractionating said vaporous conversion products, together with the charging oil, to substantially separate fractionated vapors boiling in the range of gasoline from the higher boiling hydrocarbons, including the higher boiling insufficiently converted hydrocarbons and charging oil, further separating said higher boiling hydrocarbons in the fractionating zone into a light oil fraction and a heavy oil fraction, supplying said heavy oil fraction to the thermal cracking step as said hydrocarbon oil, commingling said light oil fraction with said non-vaporous liquid residue and reacting the mixture with hydrogen to increase the hydrogen content thereof, fractionating the products from the hydrogenation step to separate gasoline boiling range hydrocarbons and normally gaseous products from the heavier products, further separating said heavier products into light reflux condensate and heavy reflux condensate, supplying said light reflux condensate to the thermal cracking step, subjecting said heavy reflux condensate to conversion in a separate heating coil and commingling the products from said separate heating coil with the conversion products leaving the first mentioned heating coil prior to the introduction of the latter to the reaction chamber.

The accompanying diagrammatic drawing illustrates in conventional side elevation one specific form of the apparatus which may be used to accomplish the objects of the invention. It should be understood, however, that the invention is not limited to the particular form of apparatus herein described but may be applied to other thermal cracking processes in which insufficiently converted hydrocarbons formed during conversion have a relatively low hydrogen content and where it is desirable to increase the hydrogen content in order to improve the yields of gasoline obtained from such processes.

Referring to the accompanying drawing, hydrocarbon oil of the type to be described later is supplied to heating coil 1 in the manner to be described, preferably under a superatmospheric pressure ranging, for example, from 100 to 500 pounds or more per square inch and is heated therein to a cracking temperature of the order of 850 to 1050° F., or thereabouts, by means of heat supplied from furnace 2. Reaction products leaving coil 1 are directed through line 3 containing valve 4, commingled with other reaction products formed in the manner to be described, and the mixture supplied to reaction chamber 5.

Reaction chamber 5, in the case here illustrated, is preferably maintained under a superatmospheric pressure of approximately the same order or slightly less than that employed on the outlet of the heating coil and is preferably insulated to reduce radiation losses and conserve heat in order that cracking reactions instigated in the heating coils may proceed to the desired degree of completion. Conversion products leaving reaction chamber 5 are directed through line 6 containing valve 7 into vaporizing and separating chamber 8 which, in the case here illustrated, is preferably operated at a substantially reduced pressure relative to that employed in chamber 5 which may range, for example, from 50 to 150 pounds or more per square inch. Vaporous conversion products supplied to chamber 8 are separated from the non-vaporous liquid conversion products and the latter substantially further vaporized to form a non-vaporous liquid residue. Non-vaporous liquid residue separated in chamber 8 is removed therefrom by way of line 9 and may be recovered as a product of the process by way of line 10 containing valve 11. Preferably, however, the non-vaporous liquid residue in line 9 is directed through valve 12 to pump 13 which discharges through line 14 containing valve 15 into line 42 and the non-vaporous liquid residue thereafter subjected to treatment in the manner to be described.

Vaporous conversion products, together with vapors evolved in chamber 8, are directed through line 16 containing valve 17 into fractionator 18. Preferably also, charging oil which may comprise a relatively heavy reduced crude oil or some similar hydrocarbon oil is supplied to fractionator 18 by way of line 19, valve 20, pump 21, line 22, and valve 23. Charging oil and vaporous conversion products are fractionated in fractionator 18 to separate fractionated vapors boiling substantially in the range of gasoline from the higher boiling hydrocarbon oils and the latter substantially further separated into a relatively light hydrocarbon oil fraction comprising, for example, hydrocarbons boiling substantially in the range of gas oil or the like and a heavier hydrocarbon oil fraction which contains a hydrocarbon oil boiling above said light oil fraction. The heavy oil fraction separated in fractionator 18 is directed through line 24 containing valve 25 to pump 26. Pump 26 discharges through line 27 containing valve 28 and the heavy oil fraction is commingled with a light reflux condensate fraction separated in a subsequent fractionation step in the manner to be described, and the resulting mixture supplied to heating coil 1 for treatment in the manner previously described.

Fractionated vapors separated in fractionator 18 are conducted through line 29 containing valve 30 to cooling and condensation in condenser 31. Distillate, together with undissolved and uncondensed gases from condenser 31, is directed through line 32 containing valve 33 into receiver 34 wherein the distillate and gases are collected and separated. Undissolved and uncondensed gases collected and separated in receiver 34 are directed through line 35 containing valve 36, recovered as a product of the process or subjected to any desired further treatment. A portion of the distillate collected and separated in receiver 34 is returned to the upper portion of fractionator 18, by well known means not shown, as a refluxing and cooling medium in cooling the end point of the fractionated vapors, while the residual portion thereof is removed from receiver 34 by way of line 37 containing valve 38, recovered as a product of the process or subjected to any desired further treatment.

The light oil fraction separated in fractionator 18 is directed through line 39 containing valve 40 to pump 41. Pump 41 discharges through line 42 containing valve 43, and this light oil fraction, in the case here illustrated, may be commingled with the non-vaporous liquid residue from chamber 8, the mixture commingled with hydrogen and a suitable powdered catalyst introduced by way of line 44 containing valve 45, and the mixture supplied to heating coil 46.

The catalytic material may comprise any suitable hydrogenation catalyst preferably of the type not readily poisoned by sulfur compounds and may include the oxides or sulfides of compounds, such as molybdenum, chromium, nickel, iron, and the like. The mixture of oil, catalyst, and hydrogen introduced to coil 46 is heated therein to a temperature of the order of 600 to 900° F. by means of heat supplied from furnace 47. The heated mixture leaving coil 46 at a superatmospheric pressure of the order of 100 to 300 pounds or more per square inch is directed through line 48 containing valve 49 into reactor 50. The conditions, including time of contact, amount of hydrogen, temperature and pressure, are normally adjusted so that comparatively little destructive hydrogenation to low boiling hydrocarbons occurs, for it is intended to increase the hydrogen content of oil subjected to treatment in this step, so that upon further cracking of this hydrogenated oil additional yields of valuable motor fuel may be obtained.

Reaction products, together with used catalyst, leaving reactor 50 are directed through line 51 containing valve 52 into fractionator 53. Unused catalyst is separated from the reaction products in fractionator 53 and is removed from the system along with heavy residual oils supplied to and formed in the hydrogenation treatment by way of line 54 containing valve 55. The catalyst may be recovered from the heavy residual oil, reactivated, and returned to the system for further treatment. Reaction products from which heavy residual materials have been removed are further fractionated in fractionator 53 to separate fractionated vapors boiling substantially in the range of gasoline from the higher boiling reaction products and the latter condensed and removed from the fractionator as light and heavy reflux condensate fractions.

Fractionated vapors separated in fractionator 53 are conducted through line 56 containing valve 57 to cooling and condensation in condenser 58. Distillate, together with undissolved and uncondensed gases from condenser 58, is directed through line 59 containing valve 60 into receiver 61 wherein the distillate and gases are collected and separated. Undissolved and uncondensed gases collected and separated in receiver 61 are removed therefrom by way of line 62 containing valve 63 and, when desired, unused hydrogen in the gas may be separated by well known means, not shown, and this unused hydrogen returned to the hydrogenation step for further use, or all of the gas removed from receiver 61 may be recovered as a product of the process. A portion of the distillate separated in receiver 61 may be returned to the upper portion of fractionator 63 by well known means, not shown, as a refluxing and cooling medium in cooling the end point of the fractionated vapors, while the residual portion thereof is removed from receiver 61 by way of line 64 containing valve 65, recovered as a product of the process or subjected to any desired further treatment.

Light reflux condensate separated in fractionator 53 is directed through line 66 containing valve 67 to pump 68 which discharges through line 69 containing valve 70 into line 27 and the light reflux condensate subjected to treatment in the manner previously described. Heavy reflux condensate separated in fractionator 63 is directed through line 71 containing valve 72 to pump 73. Pump 73 discharges through line 74 containing valve 75 into heating coil 76 which receives heat from furnace 77. The heavy reflux condensate in passing through coil 76 is heated to a thermal cracking temperature which may range, for example, from 850 to 975° F., or thereabouts. Reaction products leaving coil 76 at a superatmospheric pressure of the order of 100 to 500 pounds per square inch are directed through line 78 containing valve 79 into line 3 and these reaction products subjected to treatment in reaction chamber 5 in the manner previously described.

An example of one specific operation of the process as it may be accomplished in an apparatus such as illustrated and above described is approximately as follows:

A 24° A. P. I. gravity topped crude oil is subjected to thermal cracking in a conventional coil and chamber type cracking system at a cracking temperature of 920° F. and at a pressure of 250 pounds per square inch. Instead of returning all of the insufficiently converted hydrocarbons to the cracking system, a light oil fraction is separated which is commingled with the cracked residue and this mixture is non-destructively hydrogenated in the presence of a nickel catalyst at a temperature of 800° F. and under a superatmospheric pressure of 750 pounds per square inch. The products from the non-destructive hydrogenation are fractionated to separate gasoline produced in the treatment from the higher boiling hydrocarbons and the latter condensed in a fractionator as light and heavy reflux condensate. The light reflux condensate is supplied to the original cracking step while the heavy reflux condensate is subjected to thermal cracking in a separate heating coil at a temperature of 900° F. and at a superatmospheric pressure of 250 pounds per square inch. The conversion products from the latter heating step are commingled with the products from the original heating step and the mixture subjected to treatment in the conventional type treatment.

In an operation employing conditions as above described one may obtain approximately 62% of 72 octane rating gasoline whereas a conventional type process will produce approximately only 50% of gasoline of a relatively low octane rating, the balance of the reaction products being principally liquid residue, gas, and loss.

I claim as my invention:

1. A hydrocarbon oil conversion process which comprises cracking a hydrocarbon oil to form vaporous and liquid conversion products, separating resulting cracked vapors from non-vaporous liquid residue, fractionating said cracked vapors to condense and separate selected relatively low and relatively high boiling reflux condensates, recovering the fractionated vapors, combining said relatively low boiling condensate with said liquid residue, subjecting the mixture to non-destructive hydrogenation, fractionating the resulting vaporous products of hydrogenation to form reflux condensate and to separate fractionated vapors, and supplying at least a portion of said reflux condensate to the cracking step.

2. The process of claim 1 further characterized in that the cracked vapors are fractionated in the presence of charging oil and high boiling reflux condensate thus formed is supplied to the cracking step.

3. A hydrocarbon oil conversion process which comprises cracking a hydrocarbon oil to form vaporous and liquid conversion products, separating resulting cracked vapors from non-vaporous liquid residue, fractionating said cracked vapors to condense and separate selected relatively low and relatively high boiling reflux condensates, recovering the fractionated vapors combining said relatively low boiling condensate with said liquid residue, subjecting the mixture to non-destructive hydrogenation, fractionating the resulting vaporous products of hydrogenation to condense and form a light reflux condensate and a heavier reflux condensate, and supplying said light reflux condensate to the cracking step.

4. The process of claim 3 further characterized in that said heavier reflux condensate is subjected to independently controlled cracking conditions, and the resulting vaporous and liquid conversion products combined with the first mentioned vaporous and liquid conversion products.

5. The process of claim 1 further characterized in that the non-destructive hydrogenation treatment is accomplished in the presence of added hydrogen and a finely divided hydrogenation catalyst suspended in the mixture to be hydrogenated.

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