

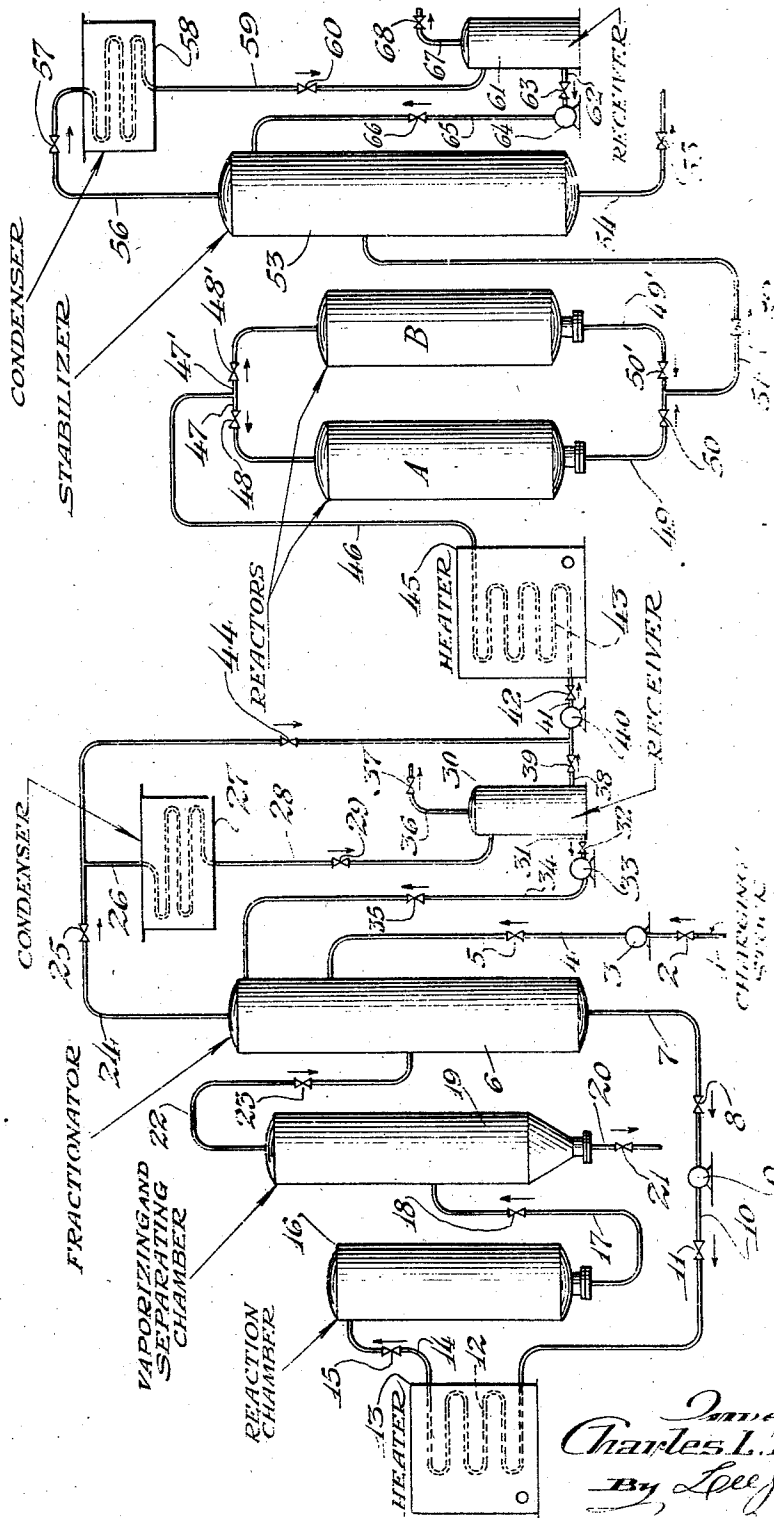
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PRODUCTION OF MOTOR FUEL

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PRODUCTION OF MOTOR FUEL

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6 Claims. (Cl. 196—52)

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This is a continuation in part of my co-pending application Serial No. 380,963, filed February 28, 1941.

The present invention relates to a process for converting high boiling hydrocarbons into high antiknock gasoline by a combination of pyrolytic and catalytic steps which are so integrated as to produce the desired result.

The charging stock for the process may comprise any petroleum fraction boiling above the range of gasoline such as a gas oil, a topped crude, or a reduced crude. I have found by extensive experimentation the combination of process conditions which will produce the optimum results desired in my process. My process employs a combination of thermal and catalytic reactions so as to accomplish the desired result with a minimum of carbon deposition and catalyst regeneration costs.

In one specific embodiment, my invention comprises a process for the production of a high octane motor fuel by subjecting a hydrocarbon oil boiling above the range of gasoline to thermal cracking at a temperature within the approximate limits of 900 to 1050° F. while at a pressure within the approximate limits of 15 to 150 pounds per square inch when said temperature is below 975° F. and at a pressure within the approximate limits of 15 to about 250 pounds per square inch when the temperature is above 975° F., fractionating the products from said thermal cracking step, separating the gasoline from the higher boiling products and subjecting said gasoline to the action of an olefin isomerizing catalyst at a temperature within the approximate limits of 800 to 1100° F. while at a pressure within the approximate limits of substantially atmospheric to about 100 pounds per square inch and for a time of contact such that cracking does not cause more than 5 percent liquid volume loss in said isomerizing step and separating from the products of said olefin isomerizing step the gasoline fraction as a product of the process.

The accompanying drawing diagrammatically illustrates one arrangement of apparatus for accomplishing the process of my invention.

Referring now to the drawing, charging stock for the process which may comprise a gas oil, topped crude, reduced crude, or the like, is supplied to the system through line 1, controlled by valve 2, from which it is supplied to pump 3 which discharges through line 4, pump 5, to fractionating column 6. Fractionating column 6 fractionates the products of the thermal cracking step in commingled state with the aforesaid charging

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stock. This column separates gasoline and gaseous products from the higher boiling hydrocarbons, the latter being removed from the column by way of line 7, controlled by valve 8. After passing through valve 8, this fraction is supplied to pump 9 which discharges through line 10, controlled by valve 11. After passing through valve 11, the oil is supplied to heating coil 12 which is so disposed as to receive heat from furnace 13.

The oil is heated in coil 12 to a temperature which may vary from about 900° F. to about 1050° F. using a pressure at the exit of the coil of about 15 to 150 pounds per square inch gage when the temperature is not higher than about 975° F. When temperatures above 975° F. are used such as, for example, 1000 or 1020° F., the pressure may be allowed to exceed 150 pounds per square inch gage, 200 pounds per square inch gage being a very satisfactory exit pressure in that temperature range. When cracking such stocks as topped crudes, I preferably employ a temperature of about 940° F. at the exit of the heating coil while utilizing a pressure within the range of 15 to 100 pounds per square inch gage. When the charging stock is a gas oil, I may employ a somewhat higher temperature, such as, for example, 950 to about 1000° F. With such a stock very satisfactory results may be obtained operating at a temperature of 980° F. at the exit of the heating coil while utilizing pressures below 100 pounds per square inch but which are preferably at least mildly superatmospheric. In the case of some charging stocks which are particularly high in constituents boiling within the kerosene range, I may operate with cracking above 1000° F. for example, 1020 to 1035° F. and in such cases, the pressure may be equal to 200 or 225 or even as much as 250 pounds per square inch gage. When processing fractions consisting largely of constituents within the kerosene boiling range, a temperature as high as 1050° F. may be used.

The extent of cracking per pass, in a coil is an important feature in my process. In general, the soaking time is so adjusted for each stock such that about 5 to 8 or 10 per cent of the oil is cracked in the coil for each passage therethrough.

Referring again to the drawing, the cracked products leaving the heating coil 12 by way of line 14 and after passing through valve 15, are supplied to insulated reaction chamber 16 wherein further cracking is allowed to take place. I find that a very satisfactory operation may be obtained when the extent of cracking in the reaction chamber is about equal to that in the heating

coil. The reaction chamber may be entirely omitted with all the thermal cracking taking place in the coil in which case I prefer no more than about 15 to 20 per cent cracking in each pass through said coil.

The products leave reaction chamber 16 by way of line 17 and after passing through valve 18 enter vaporizing and separating chamber 19. The pressure in flash chamber 19 may, if desired, be lower than in reaction chamber 16, it being quite commonly reduced to a value mildly superatmospheric but sufficient to permit the subsequent separation steps. The separation process taking place in flash chamber 19 is promoted by quenching the reactants by means well known but not indicated in the drawing. A side cut removed from fractionator 6 may be used for this purpose, a portion of the quenching medium being introduced in line 17 that is the transfer line to the flash chamber, while another portion may be introduced in the top of flash chamber in the form of a spray. The liquid separated from the reaction products is removed from flash chamber 19 by way of line 20, controlled by valve 21. This residue constitutes a product of the process. The vapors separated from flash chamber 19 are removed as overhead by way of line 22 and after passing through valve 23, are supplied to fractionating column 6 wherein they are fractionated in commingled state with the charging stock as hereinbefore indicated.

The overhead, from fractionating column 6, consisting of gasoline and normally gaseous products, is removed by way of line 24 and after passing through valve 25, is supplied to line 26 from which it enters cooler and condenser 27. The mixture of liquid together with the undissolved and uncondensed gases leave cooler and condenser 27 by way of line 28 and after passing through valve 29, enters receiver and separator 30. A portion of the liquid collected in receiver 30 is returned to fractionating column 6 for cooling and refluxing. This portion of the liquid enters line 31 and after passing through valve 32, enters pump 33 which discharges through line 34, valve 35 to the top of fractionating column 6. The gases collected in receiver 30 are removed by way of line 36, valve 37 and constitute a product of the process. The olefinic constituents present in said gases may be polymerized to form a motor fuel or, if desired, these olefins may be alkylated with isoparaffins also, to form an aviation fuel. The portion of the liquid not returned to the column for refluxing, is removed from receiver 30 by way of line 38 and after passing through valve 39, is supplied to pump 40 which discharges through line 41, valve 42, into heating coil 43. In some cases, it may be desired to omit the separation of the gasoline from the normally gaseous products before directing the former to the subsequent reforming step. In this method of operation, the overhead product from fractionating column 6 is directed through valve 44 into line 38, from which it is supplied to pump 40 and is charged through line 41, valve 42 into heating coil 43.

The gasoline with or without the normally gaseous products is heated in coil 43 by furnace 45 with a temperature within the approximate limits of 800-1100° F. and at a pressure which may vary from mildly superatmospheric to about 100 pounds per square inch at the exit of said heating coil. The heated vapors are discharged from coil 43 into line 46 from which they are directed to either of reactors A or B. The cat-

alyst used in the reforming of the olefinic gasoline is preferably one which comprises the oxides of silicon and aluminum such as some of the natural occurring montmorillonite clays after acid purification but more preferably the synthetically prepared composites of silica and alumina. Catalysts consisting of alumina alone may be used although blends of silica and alumina are to be preferred. More complex composites such as those of silica, alumina, and zirconia may also be used as is the case in the example subsequently cited.

The catalyst used in the reforming step becomes contaminated with carbonaceous material and must be regenerated at certain intervals which is accomplished by the oxidation of the deposits on the catalyst. This oxygen may be supplied in the form of air or air diluted with products of combustion in order to dilute the oxygen and to more accurately control the reactivation temperature. In order to insure continuity of operation two or more reactors are used so that when one is being used in processing hydrocarbons the catalyst in the other may be regenerated. The heated charge in line 46 is then directed into line 47 and after passing through valve 48 is supplied to reactor A wherein the conversion takes place. After the catalyst in reactor A becomes contaminated the charge is then directed into line 47', controlled by valve 48', and supplied to reactor B. Reactors A and B are preferably of the adiabatic type on account of the simplicity of the construction of such reactors. The time of contact depends on the temperature and space velocities of the order of 5 to 50 volumes of liquid charging stock per hour per unit volume of catalyst when the temperature is 950° F., will give satisfactory results. Lower temperatures, of course, require greater contact time while temperatures above 950° F. permit correspondingly higher space velocities.

The principal reactions taking place in the catalytic reforming process of my invention appear to be the isomerization of the olefinic hydrocarbons. Other reactions undoubtedly take place to a certain extent, the amount of cracking being such that the liquid volume loss usually equals two or three percent, the time of contact being so adjusted that the liquid recoveries of 95 percent and greater are obtained. While the reactions taking place in the reforming step are not thoroughly understood, it appears that the double bonds formed in the thermal cracking step are not in the position of the most stable equilibrium and the function of the catalyst at least in part, is to shift these double bonds with a consequent increase of the octane number of the olefinic gasoline. In addition to the shift in the position of the double bond a certain increase in the branching of the olefinic hydrocarbons undoubtedly takes place. The pressures are so regulated that the amount of polymerization taking place is kept to a minimum. Owing to the difficulty of operating under sub-atmospheric pressures it is usually preferred to introduce the heated gasoline to the catalyst at pressures which are mildly superatmospheric. When operating at the higher reforming temperatures a pressure as much as 100 pounds per square inch may be used although at this upper limit the results are less satisfactory than when reforming at pressures of 5 to 10 pounds per square inch gage.

The reaction products, in case reactor A is being used in processing, enter line 49, controlled by valve 50, from which they are supplied to line

51. In case reactor B is being used in processing, the reactants enter line 49', controlled by valve 50', and are then directed to line 51. The process of regenerating a catalyst contaminated with carbonaceous deposits is well known in the art at the present time and for the sake of simplicity, the regeneration circuit has been omitted from the drawing. The reaction products in line 51 pass through valve 52 from which they are supplied to stabilizer 53. The stabilized gasoline leaves column 53 by way of line 54, controlled by valve 55 and constitutes a product of the process. The normally gaseous products separated from stabilizer 53, enter line 56 and after passing through valve 57, are supplied to cooler and condenser 58. The liquid together with the undissolved and uncondensed gases leaves condenser 58 by way of line 59 and after passing through valve 60 are directed to receiver and separator 61. The liquid collected in receiver 61 is returned to the stabilizer column for cooling and refluxing. This liquid enters line 62 and after passing through valve 63 is directed to pump 64 which discharges through line 65, valve 66, to the top of the stabilizing column. The gases collected in receiver 61 are removed from the system by way of line 67, valve 68.

The following example shows the results obtainable by the process of my invention. A 25.6 A. P. I. Mid-Continent topped crude was processed in an apparatus corresponding in its essential features to that described in the drawing. The pressure at the exit of the heating coils are varied from 100 to 300 pounds per square inch gage while maintaining transfer temperatures at the inlet of the reaction chambers of 920, 940, and 960° F. A recycle operation was employed in these cases with the residue production amounting to around 35 volume per cent of the topped crude. The gasoline produced in the process was subjected to contact with a catalyst comprising a composite of chemically precipitated and purified silica, alumina and zirconia, the temperatures in the reforming step corresponding to 950° F. while utilizing a space velocity of 15 volumes of liquid per hour per unit volume of catalyst. The resulting gasolines all stabilizing to a 10 pound R. V. P. were as follows:

Table I

Temperature, ° F. entrance to reaction chamber	Pressure, pounds per square inch gage	Octane No. of reformed gasoline, 1939 research method
920	100	82.8
920	200	80.3
920	300	80.1
940	100	84.0
940	200	81.6
940	300	80.0
960	100	81.3
960	200	80.4
960	300	80.1

In another series of runs a 37.6 A. P. I. Pennsylvania gas oil was processed in the same apparatus as hereinbefore referred to. Recycle conditions were again employed and the process operated so as to produce on the order of 10 to 13 volume per cent of residue. The gasoline obtained was subjected to contact with the same silica, alumina and zirconia deposit used in the preceding set of runs while again employing a catalyst temperature of 950° F. and a 15 liquid hourly

space velocity. Table II indicates the results obtained in this set of runs.

Table II

Temperature, ° F. entrance to reaction chamber	Pressure, pounds per square inch gage	Octane No. of reformed gasoline, 1939 research method
940	100	85.5
940	200	84.5
940	369	80.7
980	25	88.4
980	34	88.1
980	100	87.8
980	200	85.7
980	276	82.7

I claim as my invention:

1. A process for the production of a high octane motor fuel which comprises subjecting a hydrocarbon oil boiling above the range of gasoline to thermal cracking at a temperature within the approximate limits of 900 to 975° F. and a pressure within the approximate limits of 15 to 150 pounds per square inch gage, fractionating the products to separate a gasoline and intermediate conversion products and subjecting said gasoline to the action of an olefin isomerizing catalyst at an isomerizing temperature within the approximate limits of 800 to 1100° F. and a pressure of from substantially atmospheric to mildly superatmospheric and for a time of contact such that cracking liquid volume loss is maintained below 5% and olefin isomerization is the principal reaction, and separating from the products of said olefin isomerizing step the reformed gasoline as a product of the process.

2. A process for the production of a high octane motor fuel which comprises subjecting a hydrocarbon oil boiling above the range of gasoline to thermal cracking at a temperature within the approximate limits of 975 to 1050° F. and at a pressure within the approximate limits of 15 to 250 pounds per square inch gage, fractionating the products to separate a gasoline fraction and subjecting said gasoline fraction to the action of an olefin isomerizing catalyst at an isomerizing temperature within the approximate limits of 800 to 1100° F. and a pressure of from substantially atmospheric to mildly superatmospheric and for a time of contact such that cracking liquid volume loss is maintained below 5% and olefin isomerization is the principal reaction, and separating from the products of said olefin isomerizing step a gasoline fraction as a product of the process.

3. A process for the production of a high octane motor fuel by a combination of thermal cracking and catalytic reforming which comprises subjecting a hydrocarbon oil boiling above the range of gasoline to thermal cracking under such conditions of temperature and pressure that the cracking takes place at a temperature within the approximate limits of 900 to 1050° F. and at a pressure within the approximate limits of 15 to 150 pounds per square inch gage when said temperature is below 975° F. and at a pressure within the approximate limits of 15 to about 250 pounds per square inch gage when the temperature is above 975° F. and for such a period of time that not more than 20 weight percent of the oil is cracked per pass, fractionating from the products of said thermal cracking step a gasoline fraction and subjecting said gasoline fraction to the action of an olefin isomerizing catalyst at a temperature

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within the approximate limits of 800 to 1100° F. and at a mildly superatmospheric pressure and for a time of contact equivalent to an hourly liquid space velocity of about 5 to 50 volumes of gasoline per hour per volume of catalyst when the reacting temperature is 950° F. so as to cause less than 5 percent liquid volume loss in said isomerizing step and separating from the products of said olefin isomerizing step the gasoline fraction as the product of the process.

4. A method of producing high octane number motor fuel which comprises subjecting a hydrocarbon oil boiling above the range of gasoline to thermal and non-catalytic cracking at a temperature of about 925° F. and a pressure within the approximate limits of 50 to 250 pounds per square inch, fractionating the products to separate a gasoline therefrom, subjecting said gasoline to contact with an olefin isomerizing catalyst at a temperature within the approximate limits of 850 to 1100° F. and a pressure from about atmospheric to about 100 pounds per square inch and at a space velocity within the approximate range of 5 to 40 volumes of gasoline (liquid basis) per

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volume of catalyst space per hour such that a volume per cent liquid yield of motor fuel of about 95 and greater is obtained.

5. A process for increasing the octane number of a thermally and non-catalytically cracked gasoline which comprises subjecting said gasoline to contact with an olefin isomerizing catalyst at a temperature within the approximate limits of 800° to 1100° F. and at a space velocity within the approximate range of 5 to 50 volumes of gasoline (liquid basis) per volume of catalyst space per hour such that a volume per cent liquid yield of motor fuel of about 95 and greater is obtained.

6. A process for increasing the octane number of a thermally and non-catalytically cracked gasoline which comprises subjecting said gasoline to contact with an olefin isomerizing catalyst at a temperature within the approximate limits of 850° to 1100° F. and at a space velocity within the approximate range of 5 to 40 volumes of gasoline (liquid basis) per volume of catalyst space per hour such that a volume per cent liquid yield of motor fuel of about 95 and greater is obtained.

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