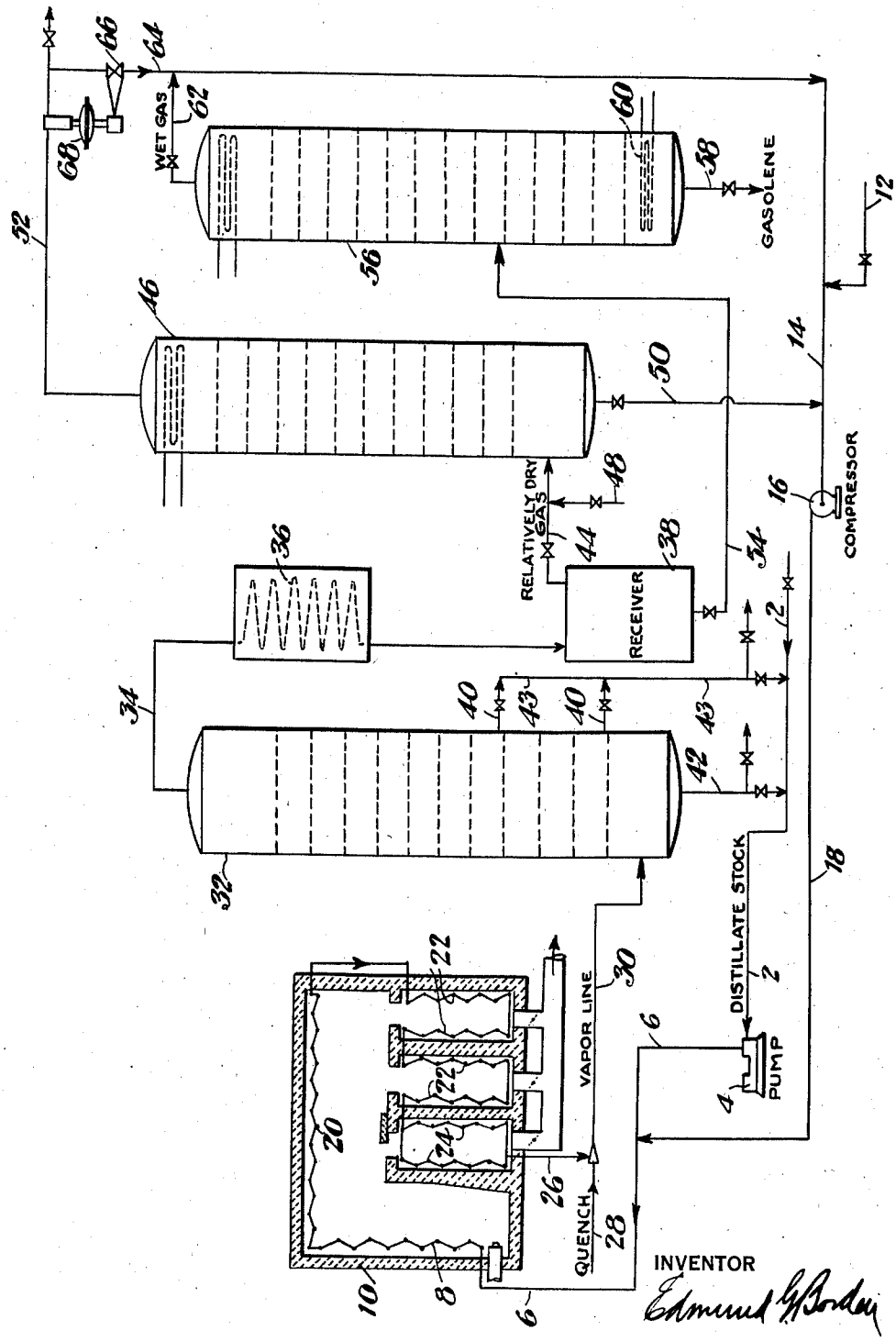
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CONVERSION OF HYDROCARBONS

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CONVERSION OF HYDROCARBONS

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This invention relates to a process for converting hydrocarbons into products suitable for motor fuels, and more particularly to a process which includes the conversion of specific types of gaseous hydrocarbons into liquid hydrocarbons of high anti-knock value boiling within the gasoline range of boiling points.

The production of cracked gasolines for use as motor fuels involves the simultaneous production of considerable amounts of unsaturated hydrocarbon gases or constituents having boiling points below that suitable for any appreciable proportion of the gasoline. Various proposals have been made for the polymerization of such hydrocarbons to produce liquid constituents, but such proposals have not taken into account the fact that cracked gases produced in cracking operations contain suitable proportions of relatively inert gases which cannot be polymerized under reasonable operating conditions.

The primary object therefore of the present invention is the provision of a cracking process for converting distillate oil stocks into high anti-knock gasoline and at the same time carry out a conversion of particular types or fractions of normally gaseous hydrocarbons.

A further object of the invention is the provision of a conversion process in which a selected olefinic hydrocarbon or fraction is converted into normally liquid constituents having high anti-knock properties without subjecting the olefin hydrocarbon to excessive temperature conditions.

Accordingly, the improved process of the present invention comprises an operation in which a distillate charging stock such as gas oil, kerosene or naphtha type paraffin distillates are subjected to a relatively long time conversion reaction at a moderate temperature of approximately 1020° to 1050° F. in admixture with an unsaturated hydrocarbon gaseous fraction such as propylene, the mixture being subjected to a relatively long time heating while flowing in a stream of restricted cross section through a reaction zone upon which a relatively high pressure is imposed, discharging the highly heated converted products from the reaction zone, suddenly chilling them to a temperature below that of further decomposition or reaction and fractionating the resulting products to recover the desired gasoline material.

Other features, objects and advantages of the present invention will be apparent to those skilled in the art from the following more detailed description thereof taken in connection with the accompanying drawing in which:

The single figure is a diagrammatic flow sheet showing a series of apparatus elements particularly adapted for carrying out the improved process.

Referring to the drawing, the distillate stock to be cracked and converted to gasoline is introduced into the apparatus through a supply line 2 and forced by means of a pump 4 at a pressure of from 400 to 800 lbs. per square inch through a line 6 into radiant heating tubes 8 mounted in furnace 10. Propylene or a selected narrow gaseous fraction containing substantial proportions of olefin hydrocarbons is introduced into the system through a line 12 and conducted through a line 14, a compressor 16 and introduced into the line 6 through a connecting line 18. The fraction may be comprised of olefine hydrocarbons containing not more than four carbon atoms to the molecule. In the line 6 the olefin fraction or propylene is intimately mixed with the distillate which is preferably preheated to a temperature of approximately 550° F. The proportion of propylene or other olefin fraction mixed with the charging stock in the line 6 is preferably controlled in accordance with the degree of conversion obtained in the process, but usually comprises from 10% to 20% by weight of the mixture.

The mixture of oil charging stock and olefin fraction is conducted through the side radiant tubes 8 and then through a roof radiant bank of tubes 20 in which the mixture is heated while flowing rapidly through the tubes to a temperature of approximately 950° F. At this temperature the oil constituents are cracked at a moderately rapid rate into lower boiling products but considerable time and somewhat higher temperatures are necessary for completing the desired conversion reactions. The mixture therefore is conducted from the roof tubes 20 through a series of tube banks 22 and parallel banks 24. The temperature of the oil mixture is preferably raised to a point of about 1020° to 1060° F. by the time it is discharged from the banks 24, and it will then contain very considerable proportions of aromatic hydrocarbons formed by the interconversion of the olefin gases and the relatively high boiling cracking stock.

In ordinary practice, the tube banks 8 and 20 may comprise about 2000 feet of 4" tubing, while the total length involved in the banks 22 and 24 preferably comprises about 3500–6000 feet of 4" tubing. The furnace 10 also preferably includes the separately controlled heating chambers containing the respective groups of tube banks 22 and 24 as shown. The amount of combustion

gases sent to these heating chambers may be regulated either by suitable furnace blocks at the inlet of the chambers or by suitable valves in the flue gas outlets.

It has been found that the soaking or conversion reaction of the mixture of gas and vapor to promote the cracking and polymerization reactions can be more effectively controlled by maintaining the mixture in a stream of comparatively small cross section and under a controlled uni-flow velocity.

The heating and conversion of the oil and gaseous constituents in the tube banks **22** and **24** is preferably carried out in such a manner that the mixture is raised to a temperature of approximately 1020° to 1040° F. by the time it leaves the second of the tube banks **22**, so that the remaining tube banks **22** and the banks **24** will be available for effecting the desired time reaction which appears to have a marked influence on the character of the product obtained.

The highly heated conversion products formed in the tube banks **22** and **24** are conducted from the latter through a transfer line **26** and suddenly chilled to a temperature below that of further reaction by intimate contact with a cooling fluid such as water or an oil distillate injected into the transfer line through a quench line **28**. The resulting cooled mixture preferably at a temperature below 700° F. is conducted through a vapor line **30** into the lower portion of a fractionating tower **32**. The vapor products are fractionated in the tower **32** under conditions such that the normally gaseous hydrocarbons as well as the gasoline constituents are taken overhead through a vapor line **34**, condensed in a condenser **36**, and the gasoline or pressure distillate collected in a receiver **38** which serves as a gas separator. A relatively high superatmospheric pressure is preferably maintained throughout the vapor line **30**, tower **32**, condenser **36** and receiver **38**. A pressure of from 200 to 600 lbs. per square inch may be used to advantage under certain variations of the process but for the major operations, a pressure of approximately 250 lbs. has been found suitable in the receiver **38**. The fractionation carried out in tower **32** produces some higher boiling fractions, the lighter fractions of which may be withdrawn from one of the bubble trays in the tower by means of valved lines **40**, while the higher boiling product may be withdrawn through a valved line **42**.

If the original charging stock introduced through the line **2** is a heavy gas oil or topped crude material then the product removed from the dephlegmator **32** will be a residual oil suitable for fuel oil, or it may be flash evaporated to recover a recycle gas oil. Such recycle gas oil may be introduced through the line **2** to augment the charging stock. The reflux condensate recovered in the lower part of the dephlegmator **32** is adapted for recycle cracking and this product which is shown as taken off of the lower trays of the dephlegmator tower through lines **40** would be returned hot by a line **43** to the pump **4** to help make up the charging stock. If a product such as naphtha or gasoline is being reformed in the cracking coils then all of the product which is recovered through the outlets **40** and **42** may be returned to the hot oil pump for recycling through the coil.

Because of the temperature and pressure maintained in receiver **38**, the gases separated from the pressure distillate will comprise a relatively low proportion of constituents containing more than three carbon atoms to the molecule. This gas which is relatively "dry", and which contains substantial proportions of propylene as well as a small amount of butylenes, hydrogen, methane, ethane and ethylene, is withdrawn through a valved line **44** and conducted into the lower part of a rectifying tower **46**. The gases introduced into the tower **46** through the line **44**, or any other outside gases of similar character introduced through a valved line **48** are subjected to rectification in the tower for the purpose of condensing and fractionating out the propylene and other constituents boiling at approximately the same temperature or higher. The condensed and rectified fraction is withdrawn from the tower **46** through a valved line **50** and is either mixed with the distillate stock in the line **2**, or with the gaseous materials in the line **14**, and sent to the conversion coils mounted in the furnace **10**. This fraction is particularly adapted for conversion into higher boiling products along with the gas oil, kerosene or naphtha distillate introduced through the line **2**. The fraction is substantially free of rather large proportions of hydrogen and methane which are separated out in the fractionating tower **46**. This separated hydrogen and other relatively light constituents are discharged from the tower **46** through a gas line **52**.

The pressure distillate separated out in the high pressure receiver **38** is conducted through a valve controlled line **54** into the mid-portion of a stabilizing tower **56** in which the pressure distillate is subjected to rectification conditions under substantially reduced pressure. The pressure in the tower **56** may be 50 lbs. per square inch or lower and the rectification is carried out under conditions such that a stabilized gasoline having the desired vapor pressure is withdrawn through a valved line **58** and sent to storage.

The tower **56** as well as the tower **46** may be provided with a cooling coil for the purpose of giving the desired amount of refluxing, and the tower **56** is preferably provided with a steam heating coil **60** for maintaining the proper bottom temperature on the tower.

The light constituents removed from the pressure distillate in the stabilizer **56** usually comprises such dissolved constituents as propylene, propane, butane and some butylenes. These hydrocarbons are removed as gases or vapors from the top of the stabilizer through a valved line **62** and are discharged into a line **64** which connects line **52** with supply line **14**. The gas or vapor fraction removed through the line **62** is particularly adapted for augmenting the fraction removed from tower **46** through the line **50**.

In some cases it is particularly desirable to return some of the hydrogen and constituents such as methane to the conversion coils in order to suppress the formation of such materials during the conversion reaction. Accordingly the line **64** is connected to line **52**, and suitable arrangements made for removing a regulated proportion of the gases discharged through the line **52**. This arrangement comprises an automatically controlled valve **66** which is operatively connected to a control mechanism **68**, in such a way as to permit a definite proportion of the gas passing through the line **52** to be conducted through the line **64** and thence through lines **14**, **18** and **6** to the conversion coils. The regulator **68** is preferably adjusted so that approximately 10% to 20% of the gases in the line **52** are allowed to pass through the line **64**. The remain-

ing gases are discharged from the system through the valved line 52. Instead of returning gas from the line 52 the desired proportion of hydrogen and methane or similar constituents may be introduced into the system through the line 12 and sent to the conversion coils along with the relatively greater proportion of unsaturated olefinic gases.

In order to suppress the formation of hydrogen by influencing the mass reaction carried on in the cracking coil, it is desirable to return not more than 25% of the dry gas removed from the gasoline. Although this amount of gas constitutes only 25% of the weight of the gas produced, however, 25% of the gas produced in some cases may amount to as much as three to seven times by volume of the amount of liquid oil products introduced into the system as charging stock. It has been found that by circulating a large amount of gas, the formation of free hydrogen and methane may be substantially suppressed and at the same time the cracking and polymerizing operation may be very accurately controlled. Furthermore, the circulation of the large amount of gas permits feed rates through the coils of such a volume of liquid materials introduced into the coils, that a very long time reaction may be obtained while holding the products at a comparatively high temperature. If an attempt is made to circulate only liquid products through the coils there is a very great tendency for the coils to carbonize when using the high temperatures which are desirable for the simultaneous cracking and polymerization reaction to be carried out. The presence of a large amount of gas however shields and controls the cracking and polymerization reaction so that desirable cracking and polymerization may be carried on at comparatively high temperatures without coke formation.

While it is understood that the fractions separated and withdrawn through lines 50 and 62 will usually contain at least a small proportion of saturated hydrocarbons, a relatively narrow fraction of unsaturated olefinic hydrocarbons may be introduced into the system through the line 12 and sent to the conversion coils. It is furthermore to be understood that the gases fractionated in the tower 46 may comprise coke oven gases and other commercial gases containing substantial proportions of unsaturated olefin constituents. These gases are introduced through the valved line 48.

The reactions taking place in the tube banks 22 and 24 appear to involve not only the breaking up of the higher boiling oil constituents, with formation of aromatic hydrocarbons, but also the polymerization of gaseous constituents either with themselves or with aromatic hydrocarbons for the formation of branched chain benzenes and other derivatives. The gasoline withdrawn from the line 58 under normal operating conditions comprises a yield of from 32% to 45% of the charging stock mixture sent to the conversion coils, and this gasoline contains from 55% to 80% of aromatic hydrocarbons, the majority of which are side chain benzene derivatives. The aromatic character of the gasoline can be built up to 92% of the product if a sufficiently long time reaction is provided. The production of the high aromatic product is accompanied by a high production of gas.

The distillate products withdrawn through the lines 40 and 42 also include very substantial proportions of aromatic hydrocarbons, particularly derivatives of the type of naphthalene, anthracene and their side chain derivatives. These products are particularly adapted for the manufacture of individual compounds or fractions which may be recovered by suitable processes of fractionation and extraction.

The gases formed in the cracking reaction may be polymerized by heat or pressure alone or may be polymerized by heat or pressure in conjunction with a catalyst which materially affects the polymerization action and allows the polymerization to be carried on at materially lower pressures and temperatures. In the present invention it has been found desirable to carry on polymerization and cracking of the gaseous products formed in the cracking reaction as well as gaseous products introduced into the system in the presence of higher boiling point hydrocarbons wherein a very desirable result may be obtained. When a liquid hydrocarbon is subjected to cracking and long time soaking or conversion in a coil, it has been found that if sufficient time is provided at comparatively high temperatures (1000° to 1050°) that, irrespective of the source of the hydrocarbon raw material, and although it may be a paraffine hydrocarbon, the final product recovered is of an aromatic nature, that is, it contains benzene, benzene derivatives or alkylated benzene derivatives.

The conversion may be carried to such a point that the product will be substantially all aromatic compounds, that is, up to 95% by volume. When such a reaction is carried on much of the gas formed in the cracking reaction is polymerized in the soaking or conversion reaction so that this product is available as a gasoline along with the cracked product. By polymerizing the gas formed in the process as well as gas formed externally from the process in conjunction with the hydrocarbons having higher boiling points than gasoline, it has been found that the polymerization of the gaseous products produces similar aromatic compounds to those produced from the higher boiling hydrocarbons. This reaction, therefore, results in an aromatization of all of the hydrocarbon products. It has been found furthermore that the resulting product is a different type of aromatic product than that produced when gas alone is polymerized, and this resulting product has a higher blending value and gives a higher octane rating to the gasoline with which it is blended, than a gasoline made from the polymerization of gas alone.

An example of the operation of the process of the present invention includes the use of a paraffin base gas oil charging stock of about 38° Bé gravity which is supplied to the pipe still furnace under a pressure of 575 lbs. per square inch. With this oil charging stock was supplied approximately 12% by weight of a cracking still gas fraction having approximately the boiling point range of propylene. The mixture was heated in the tube banks 8 and 20 to a temperature of about 935° F. and the first tube banks 22 to a temperature of about 1025° F. The heating in the second tube banks 22 and banks 24 was continued and the products discharged through the transfer line 26 at a temperature of 1035° F. The pressure in the transfer line 26 was 255 pounds per square inch and this pressure was substantially maintained up to and in the receiver 38 except for the pressure drop through the tower 32 and other intervening elements of the apparatus. The heating time of the materials in the pipe still furnace was approximately seventeen minutes.

Various modifications may be made in the process of the present invention without departing from the spirit and scope of the invention as described, and it is understood that the invention is not to be limited except as so limited by the accompanying claims.

Having thus described the invention in its preferred form, what is claimed as new is:

1. The process of converting hydrocarbons which are unsuitable for use as motor fuel into a high anti-knock motor fuel product, which comprises passing a distillate oil at a pressure of from 400 to 800 pounds per square inch through a long heating coil in the initial portion of which the oil is raised to a temperature of approximately 950° F., thereafter continuing the heating of the oil in the latter portion of the coil to a temperature of approximately 1020° to 1050° F. and maintaining the oil therein for a sufficient length of time to convert a substantial proportion of it into constituents boiling within the gasoline range of boiling points, discharging the resulting converted products into a fractionating zone and separating the fraction containing the gasoline constituents and gases from the higher boiling constituents, condensing the gasoline under high pressure and separating the uncondensible gases from the resulting gasoline condensate while maintained under said high pressure, fractionating the resulting gases in a rectifying zone to recover a relatively narrow fraction containing such constituents as propylene and other hydrocarbons of similar boiling point, fractionating the separated gasoline at a lower pressure to remove dissolved hydrocarbon constituents of relatively low boiling point which are not desired in the gasoline, and passing the separated fraction of said gases free of lower molecular weight gases together with the dissolved hydrocarbon constituents removed from the gasoline into the long heating coil to be converted into constituents boiling within the gasoline range along with the oil charging stock being converted in said coil.

2. The process of converting hydrocarbons which are not suitable for use as motor fuel into a high anti-knock motor fuel, which comprises passing a mixture of an oil distillate such as gas oil, kerosene or naphtha together with a relatively narrow range gaseous fraction containing substantial proportions of unsaturated hydrocarbons through an elongated coil reaction zone in which the mixture is raised to a cracking temperature and then heated while flowing through a substantial proportion of said coil after it reaches a comparatively rapid cracking temperature, maintaining an outlet temperature of approximately 1050° F. and an outlet pressure of approximately 250 lbs. per square inch on the constituents leaving said coil, suddenly chilling the highly heated constituents leaving the coil by intimately contacting them with a relatively cool fluid, thereafter fractionating the resulting mixture to separate the gasoline and gaseous constituents from the higher boiling materials contained in the mixture, condensing the gasoline vapors and separating the normally gaseous constituents therefrom, and recovering a relatively narrow boiling fraction of the normally gaseous constituents which is substantially free of inert products such as hydrogen and methane by rectifying the normally gaseous constituents separated from the gasoline, and introducing said fraction into the oil charging stock being delivered to the conversion coil.

3. The process of converting hydrocarbons which are unsuited for use as motor fuel into a motor fuel product having high anti-knock properties, which comprises passing a mixture of a hydrocarbon distillate such as gas oil and a relatively narrow gas fraction containing substantial proportions of unsaturated olefin constituents through a long heating zone in the initial portion of which the mixture is raised to a temperature of approximately 950° F. and thereafter heated for a substantial period of time and raised in temperature to approximately 1040° F. for the conversion, condensation and polymerization of light and heavy hydrocarbons, removing the converted products from said zone and condensing all of the more readily condensible constituents including the gasoline hydrocarbons while maintaining a relatively high pressure thereon, separating out the uncondensable gases and passing the uncondensed gases thus separated into a fractionating zone in which the higher members of the gas mixture are condensed under rectifying conditions and separated from the lower molecular weight members such as methane and hydrogen, and introducing the resulting condensate produced from the said gases substantially free of said lower molecular weight members into said heating zone to be converted into constituents boiling within the gasoline range.

4. The process of converting hydrocarbons which are not suitable for motor fuel into a high anti-knock motor fuel which comprises, mixing a high boiling hydrocarbon oil with a substantial proportion of a hydrocarbon gas containing hydrogen, rapidly bringing the gas-oil mixture to a vapor and to a cracking temperature, circulating the gas-vapor mixture in a confined stream of comparatively narrow cross sectional area under controlled heating conditions to promote the cracking and polymerization of the hydrocarbons in the mixture to aromatise the hydrocarbon mixture, and quenching the mixture at the completion of the conversion operation to immediately and suddenly reduce the temperature of the products below that at which further reaction either polymerization or cracking occurs, the gas of said mixture constituting less than 25% of the dry gas formed in the cracking and polymerization reaction and containing hydrocarbons having C_2 to C_4 carbon atoms in the molecule.

5. In the process of converting hydrocarbons boiling below the gasoline range into a motor fuel product having high anti-knock characteristics and boiling within the gasoline range in which a normally gaseous hydrocarbon fraction is subjected to thermal conversion conditions at relatively high pressure in a conversion zone and in which the resulting gasoline product is separated from the normally uncondensable constituents at high pressure, the improvement which comprises passing the separated normally uncondensable constituents into a rectifying tower and therein rectifying and fractionating the constituents to produce a narrow fractional condensate containing such constituents as propylene and other hydrocarbons of similar boiling point and passing said condensate fraction from said rectifying tower into said conversion zone to be converted into products boiling within the gasoline range.

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