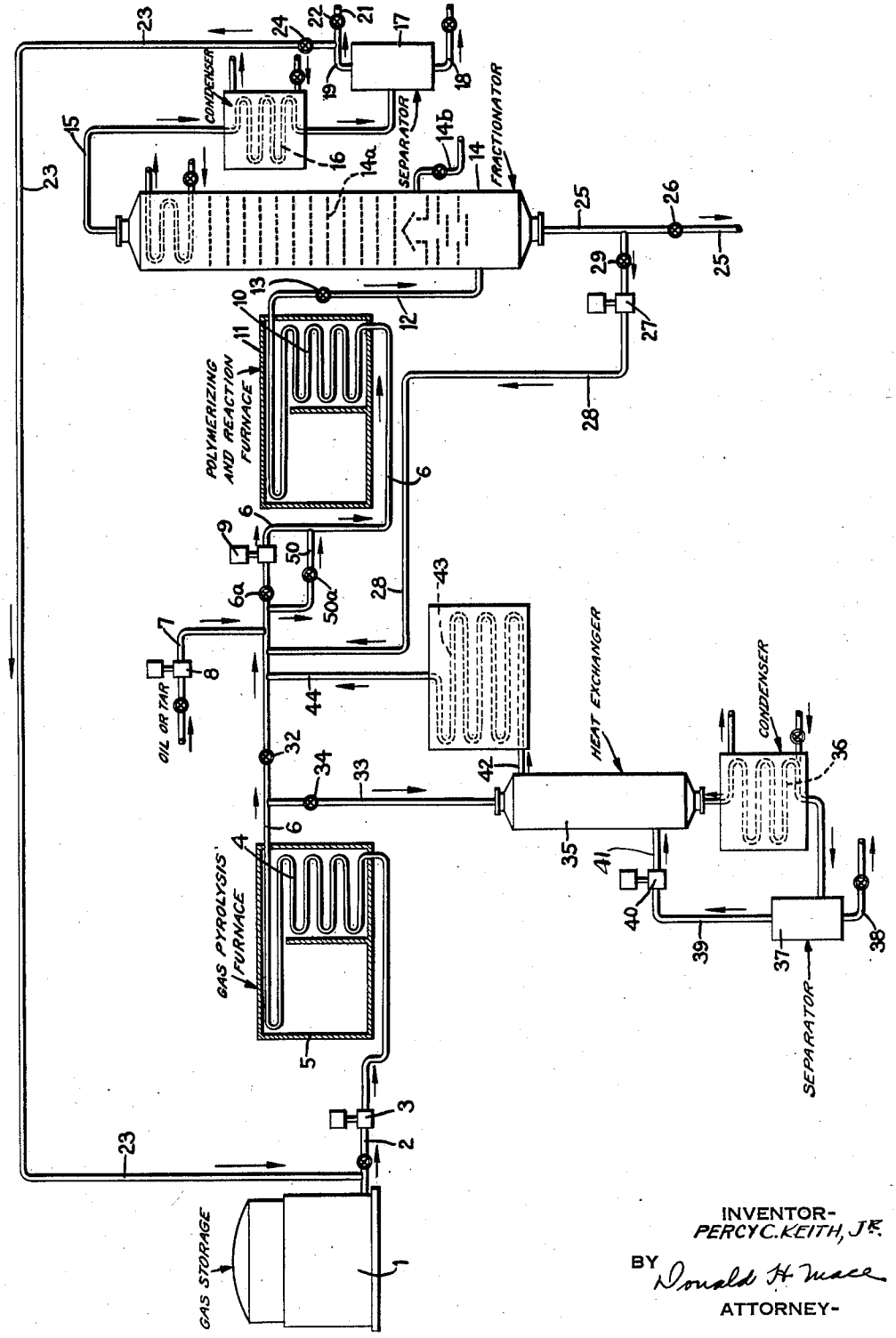
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PYROLYTIC TREATMENT OF HYDROCARBONS

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PYROLYTIC TREATMENT OF HYDROCARBONS

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My invention relates to the pyrolytic treatment or conversion of hydrocarbons and the recovery of valuable products therefrom.

In the pyrolytic decomposition or cracking of hydrocarbons, and more particularly petroleum oils, the primary products are lower boiling liquids such as gasoline or other normally liquid materials of relatively high volatility, normally gaseous hydrocarbons including fixed gases, and relatively high boiling hydrocarbons varying from gas oil to heavy tars approaching coke in character. The value of these gases and liquids is relatively low as compared with motor fuels such as gasoline and the intermediate products, but these materials represent potential sources of valuable materials such as normally liquid hydrocarbons either aromatic in character or resembling aromatics in having desirable anti-knock properties when used as motor fuel.

My invention therefore has for objects the production of hydrocarbon liquids from normally gaseous hydrocarbons and from relatively high boiling hydrocarbon materials and, in one aspect at least, reduction of the amounts of gases and tarry material produced in plants for cracking petroleum oils.

My invention has for further objects such additional specific operating advantages and results as may hereinafter be found to obtain.

My invention contemplates the contacting of low-boiling or normally gaseous hydrocarbons with relatively high-boiling hydrocarbons, such as heavy, substantially non-volatilizable or tarry material derived from pyrolytic decomposition of hydrocarbon materials such as petroleum oils and coal, under such conditions that unsaturated hydrocarbon constituents, such for example as olefins, are polymerized or otherwise converted to heavier or lighter products by inter-reaction between the low-boiling or gaseous hydrocarbons and the tarry material.

This inter-reaction is carried out under such conditions that it results in the formation of valuable products of normally liquid character, more or less intermediate between the gaseous material and the heavier material and capable of separation in a form suitable for use as motor fuel or for admixture with motor fuel or capable of conversion by pyrolytic decomposition, that is to say, either by cracking or straight distillation, to produce motor fuel or material advantageously employed for admixture with gasoline or other motor fuel to increase the anti-knock character of the latter.

In general, the normally gaseous hydrocarbon materials which I prefer to employ are those containing substantial proportions of unsaturates, that is to say, not less than 10%, and preferably 25% or more, of unsaturates such as olefins.

I may, however, employ, as a source of such gases, gases containing hydrocarbons of the paraffin series, preferably ethane, propane and butane. Methane, being more stable, is less desirable, although it may be employed under suitable conditions and is, as a matter of fact, present in many gases which it may be desirable to employ in my process.

Thus I may initially employ natural gas, especially that which contains substantial amounts of ethane, prop ne and butane, or gaseous products resulting from the decomposition of hydrocarbon materials such as hydrocarbon oil and coal More specifically, I may employ substantially "dry" gases resulting from the more or less drastic cracking of petroleum oil, or mixtures of liquefiable materials, such for example as "stabilizer reflux" containing considerable amounts of butane and pentane.

Such gaseous hydrocarbons are preferably first subjected to pyrolytic conversion or cracking to promote the formation of unsaturates such as olefins, capable of polymerization or conversion to hydrocarbons of a normally liquid character. However, such conversion or cracking may be dispensed with when gases containing substantial proportions of olefins and other unsaturates are employed, for example, those gases produced in relatively high temperature oil-cracking operations such as vapor phase operations conducted at temperatures of the order of 1000° F. or higher.

The relatively high-boiling hydrocarbons which I employ in my process are preferably those which contain substantial amounts of unsaturated hydrocarbon constituents. Thus, I may employ certain cycle stocks or gas oils rich in unsaturates. I prefer, however, to employ so-called "pressure tars" produced in the pyrolytic decomposition of petroleum oil, for example, a final tar from the flash tower of a cracking plant, which tar has been separated from relatively light constitutents, or a lighter tar or residuum from the high-pressure distillation zone or evaporator of a cracking plant, which tar contains considerable amounts of relatively light constituents. While I prefer to employ oils produced in the destructive decomposition of petroleum oils, I may use oils or tars derived from other sources, for example, coal tar and water-gas tar.

While I prefer to subject the normally gaseous

or very low boiling hydrocarbons initially to pyrolytic conversion or cracking for the purpose of producing or increasing the proportion of polymerizable unsaturated hydrocarbons and then to lead the products, preferably after removal of any normally liquid constituents therefrom, into a separate polymerization and reaction stage, the initial pyrolytic conversion and the polymerization or reaction in the presence of the heavier material may take place together or may to some extent overlap.

Where, however, the initial pyrolytic conversion stage is performed separately from the subsequent polymerization and reaction stage, I prefer to so limit the time element in the pyrolysis stage as to make it possible to carry out in the reaction stage, in contact with the heavier material, as much as possible of the polymerization of the unstable materials resulting from the initial pyrolytic conversion.

The polymerization of the unstable or unsaturated products resulting from the initial pyrolytic conversion of the normally gaseous or low boiling hydrocarbons or present as such in the gaseous material and the reaction between the polymerized or unpolymerized products and the heavier material or constituents thereof, is carried out under such elevated pressure and temperature as to promote polymerization of unsaturates such as olefins. The products of reaction from the polymerization and reaction stage are removed and fractionated to effect the separation therefrom of normally liquid products and normally gaseous products.

All or a portion of the lighter liquid products from the polymerization and reaction stage may then, if unsuitable for use directly as motor fuel or for direct addition to motor fuel, such as gasoline, be subjected to distillation or cracking to further refine the same, and to produce motor fuel or material adapted to be combined with motor fuel and having the property of increasing the anti-knock character of or otherwise improving said motor fuel.

Such tar as is separated may either be removed from the system or recycled through the polymerizing and reaction stage, while any gas oil may be subjected to further cracking.

It will readily be understood that the temperatures and pressures employed and the proportions of materials caused to react with each other may vary considerably with the nature of the materials themselves and the results desired. Ordinarily, however, I employ in the polymerization and reaction stage temperatures of from 600° to 1250° F., preferably temperatures below those at which active coke formation takes place, for example, temperatures of from 700° to 900° F., and pressures of from 750 to 3000 pounds per square inch and preferably from 1000 to 2000 pounds per square inch. In the initial gas pyrolysis stage, the pressures employed are preferably much lower, but may be similar to those employed in the subsequent polymerization and reaction stage, while higher temperatures are preferred, for example, temperatures of from 1100° to 1750° F. The temperatures maintained in the gas pyrolysis stage may, however, be reduced by the employment of suitable catalysts.

The pressures employed in the two stages may be made equal or substantially equal to avoid the difficulty of increasing the pressure upon the highly heated materials between the two stages, but it is possible according to my invention to employ lower pressures in the pyrolytic conversion stage than are employed in the subsequent polymerization and reaction stage without mechanical difficulty. For example, the pressure maintained in the pyrolytic conversion stage may be from substantially atmospheric to about 150 pounds per square inch, whereas the pressure maintained in the polymerization and reaction stage may be from 1000 pounds to 3000 pounds per square inch, it being understood that the polymerization and reaction are favored by high pressures which may not be necessary in the preliminary conversion stage.

Where desired, catalysts may be employed in either or both of the aforesaid stages. Such catalysts may comprise those ordinarily used in the pyrolysis of hydrocarbons, as, for example, metallic halides such as aluminum chloride and zinc chloride, and in the polymerization and reaction stage may alternatively comprise such known catalysts as are commonly employed in hydrogenation processes, for example, activated carbon, fuller's earth, oxides of chromium, nickel and cobalt, and oxides and salts of vanadium and molybdenum, and copper.

In the drawing accompanying and forming a part of this specification, the single figure is intended to represent more or less diagrammatically a preferred form and manner in which my invention may be embodied and practiced.

Referring to this drawing, a hydrocarbon gas, such for example as "dry" gas obtained in the pyrolysis of petroleum oil, is drawn from a source 1 and is delivered through a conduit 2 at high pressure by means of a pump 3 to a heating coil 4 situated in a furnace 5 of suitable character. The hydrocarbons passing through the coil 4 are preferably subjected to a temperature of from 1500° to 1600° F. and a limited pressure of for example up to 200 pounds per square inch, and preferably the time of travel of the hydrocarbons through the coil 4 is limited to a few seconds or even a fraction of a second.

During their passage through the coil 4, the normally gaseous or low-boiling hydrocarbons such as ethane, propane and butane contained in the gas supplied from the source 1 are subjected to pyrolysis, with the result that relatively unstable unsaturated hydrocarbons such as olefins are produced.

In the preferred instance, the resultant highly heated products of conversion then pass through a conduit 6 to be commingled with cool heavy or tarry hydrocarbon material introduced from a suitable source (not shown) through a conduit 7 by means of a pump 8.

By thus "quenching" the products of conversion from the coil 4, the extent of pyrolytic conversion initiated in the coil 4 may be controlled, and compression of the commingled materials is facilitated. In this instance, the relatively cool commingled gases and tar are delivered by means of a pump 9 to a polymerizing or reaction coil 10 located in a suitable furnace structure 11, where they are brought to the reaction temperature of from 600° to 1250° F., under a pressure of from 750 to 3000 pounds per square inch.

During the passage of the commingled hydrocarbon materials through the reaction coil 10, the unstable unsaturated products resulting from the pyrolytic conversion of the normally gaseous or low-boiling hydrocarbons are polymerized or otherwise converted to materials of higher boiling points, whereas by reaction of these materials with constituents of the tarry hydrocarbon material the latter are converted into materials of dif-

ferent character from the original constituents of the tar. The ultimate result of this polymerization and inter-reaction is the formation of increased quantities of normally liquid hydrocarbons having boiling points intermediate between those of the principal constituents of the original gaseous or low-boiling hydrocarbons and the tarry hydrocarbons, and a consequent reduction in the amounts of normally gaseous hydrocarbons and heavy or tarry hydrocarbons ultimately yielded.

The products of reaction pass from the reaction coil 10 through a conduit 12 having a reducing valve 13 to a low-pressure flash tower or fractionating tower 14, where they are separated into vapors and liquids under the reduced pressure and temperature at which the flash tower is maintained. The flash tower 14 may be provided with an upper fractionating section 14a where, by suitably cooling or refluxing the vapors, an intermediate fraction may be recovered, this fraction being withdrawn through a conduit 14b.

The uncondensed vapors pass off from the fractionator 14a through a vapor conduit 15 to a suitable condenser 16 and separator 17. The normally liquid light hydrocarbon products condensed in the separator 17 are withdrawn through an outlet 18 while the uncondensed gases pass off through a conduit 19 either to be used as fuel or to be recirculated through the pyrolytic conversion stage as desired. In the former instance these gases may be withdrawn through an outlet 21 having a valve 22, whereas in the latter instance they may be delivered by means of a conduit 23 having a valve 24 to the conduit 2 at a point ahead of the pump 3.

The tar or other liquid fraction separated in the flash tower 14 is withdrawn through a conduit 25 having a valve 26 or all or any portion of it may be returned to the reaction coil 10 by means of a pump 27 through a conduit 28 having a valve 29.

When the conditions of pressure and temperature to which the hydrocarbons are subjected in the coil 4 are such that normally liquid materials are present in substantial amount in the gases leaving the coil 4, I may remove these liquid materials prior to commingling the products from the coil 4 with tarry material. For this purpose I provide a valve 32 located in the conduit 6 and a branch conduit 33 having a valve 34.

With the valve 32 closed and the valve 34 open, the products coming from the coil 4 pass through a heat exchanger 35, where they are partially cooled, and into a cooler 36, where normally liquid constituents are condensed. The condensate collects in a separator 37, from which it is withdrawn through a conduit 38, while the uncondensed gases pass through a conduit 39 to a pump 40, where they are raised to a pressure at least equal to that obtaining in the reaction coil 10. The compressed gases then pass through a conduit 41, the heat exchanger 35, a conduit 42, a heating coil 43, and conduits 44 and 6 to the coil 10. In this instance the pump 9 may be bypassed through a line 50 provided for that purpose, by closing a valve 6a in the conduit 6 and opening a valve 50a in the conduit 50. When this is done, the tarry material may also be preheated prior to commingling it with the products of conversion from the coil 4.

The coil 43 is, when used at all, ordinarily employed simply as a preheater, although, if desired, the temperature at this point may be made high enough to effect some cracking or conversion of the gases.

The distillate withdrawn at 18, and also that withdrawn at 38, will ordinarily comprise desirable light hydrocarbon oil having a boiling point range which will permit the use of this distillate as a motor fuel or for blending with other motor fuel to increase the anti-knock value of the latter, although it may be subjected to further treatment if desired.

The fraction recovered at 14b will ordinarily comprise heavier hydrocarbon oil, and may be subjected to distillation or pyrolytic decomposition to recover therefrom a motor fuel or an oil suitable for blending with motor fuel, while the still heavier residual oil or tar removed at 25 may be withdrawn from the system or recycled as set forth hereinabove.

If the gaseous materials employed in the operation already contain the necessary or desired unsaturates, such as olefins, the coil 4 may be employed mainly in the capacity of a preheater for raising the gases to the desired temperature prior to their introduction into the reaction coil 10. Such gaseous materials may, of course, include those gases produced during relatively high temperature oil cracking or naphtha reforming operations, or gases derived from the cracking or conversion of any hydrocarbon materials including natural gas, refinery gas, casinghead gas, and the like.

Moreover, the conversion of saturated hydrocarbons to unsaturated hydrocarbons may be caused to take place more or less simultaneously with the polymerization and inter-reaction, that is to say, in the presence of the tarry material, especially where the temperatures maintained in the coil 10 are relatively high. In this instance, the temperature maintained in the coil 10 may be as high as from 1500° to about 1750° F.

While in the specific instance illustrated in the drawing, the polymerizing and reaction stage is shown as taking place in a pipe coil; such a coil may be followed or replaced by an enlarged chamber or vessel, which may be insulated where so desired. The choice of apparatus at this point will of course depend upon the temperatures to be maintained and the temperatures of the products about to be treated, as well as the time factor. Since the polymerization reaction is exothermic in character, in instances where the polymerization reaction takes place vigorously, the coil 10 may be provided with means for removing excess heat developed in the reaction. Thus I may supply the coil 10 externally with a cooling fluid, as for example by spraying water over the coils 10 or by immersing the coil 10 in a bath of water, oil or other cooling fluid, or by passing cool gas around the coil 10.

It will be obvious to those skilled in the art that my invention is susceptible of considerable modification in detail, and is therefore not limited to the specific example or examples set forth and described hereinabove by way of illustrative example, but may variously be embodied within the scope of the claims hereinafter made.

I claim:

1. The process which comprises subjecting normally gaseous hydrocarbons of the paraffin series substantially free from normally liquid hydrocarbon oil to a temperature of from 1,100° to 1,750° F. to effect a pyrolytic conversion of such hydrocarbons to olefinic hydrocarbons and liquid products, cooling the gaseous products to remove therefrom liquid products formed during said pyrolytic conversion, intimately contacting gaseous products resulting from said conversion

after separation of said liquid products with normally liquid oil, reacting the commingled gaseous products and normally liquid oil prior to the separation of any heavy oil therefrom and in the absence of added catalyst at an elevated temperature while being maintained under superatmospheric pressure for a sufficient period of time to effect the formation of normally liquid low boiling hydrocarbon oil and fractionating the resultant products to recover said low boiling hydrocarbon oil in liquid form.

2. The process which comprises subjecting normally gaseous hydrocarbons of the paraffin series substantially free from normally liquid hydrocarbon oil to a temperature of from 1,100° to 1,750° F. to effect a pyrolytic conversion of such hydrocarbons to olefinic hydrocarbons and liquid products, cooling the gaseous products to remove therefrom liquid products formed during said pyrolytic conversion, compressing the remaining gaseous products to a pressure of at least 750 pounds per square inch, intimately contacting the gaseous products with normally liquid residual oil obtained in the pyrolytic decomposition of hydrocarbons, reacting the gaseous products while under pressure and at a temperature of from 600° to 1,250° F. with said residual oil obtained in the pyrolytic decomposition of hydrocarbons prior to the separation of any heavy oil therefrom and in the absence of added catalyst for a sufficient period of time to effect the formation of normally liquid low-boiling hydrocarbon oil, and fractionating the resultant products to recover said low-boiling hydrocarbon oil in liquid form.

3. The process which comprises subjecting normally gaseous hydrocarbons of the paraffin series substantially free from normally liquid hydrocarbon oil to a temperature of from 1,100° to 1,750° F. under a pressure of not more than about 150 pounds per square inch to effect a pyrolytic conversion of such hydrocarbons to olefinic hydrocarbons and liquid products, cooling the gaseous products to a low temperature by passing them through a heat exchange zone, further cooling the gases to effect a condensation and separation of liquid products formed during said pyrolytic conversion, compressing the gases to a high superatmospheric pressure in excess of that obtaining in the pyrolytic conversion zone, passing the compressed gases through said heat exchange zone to heat the same, intimately contacting the gaseous products with normally liquid residual oil obtained in the pyrolytic decomposition of hydrocarbons, further heating the compressed gases and said oil to a temperature of from 600° to 1,250° F. prior to the separation of any heavy oil therefrom and in the absence of added catalyst, maintaining them at this temperature and under such pressure in the presence of said residual oil obtained in the pyrolytic decomposition of hydrocarbons for a sufficient period of time to effect the formation of normally liquid low-boiling hydrocarbon oil, and fractionating the resultant products to recover said low-boiling hydrocarbon oil in liquid form.

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