

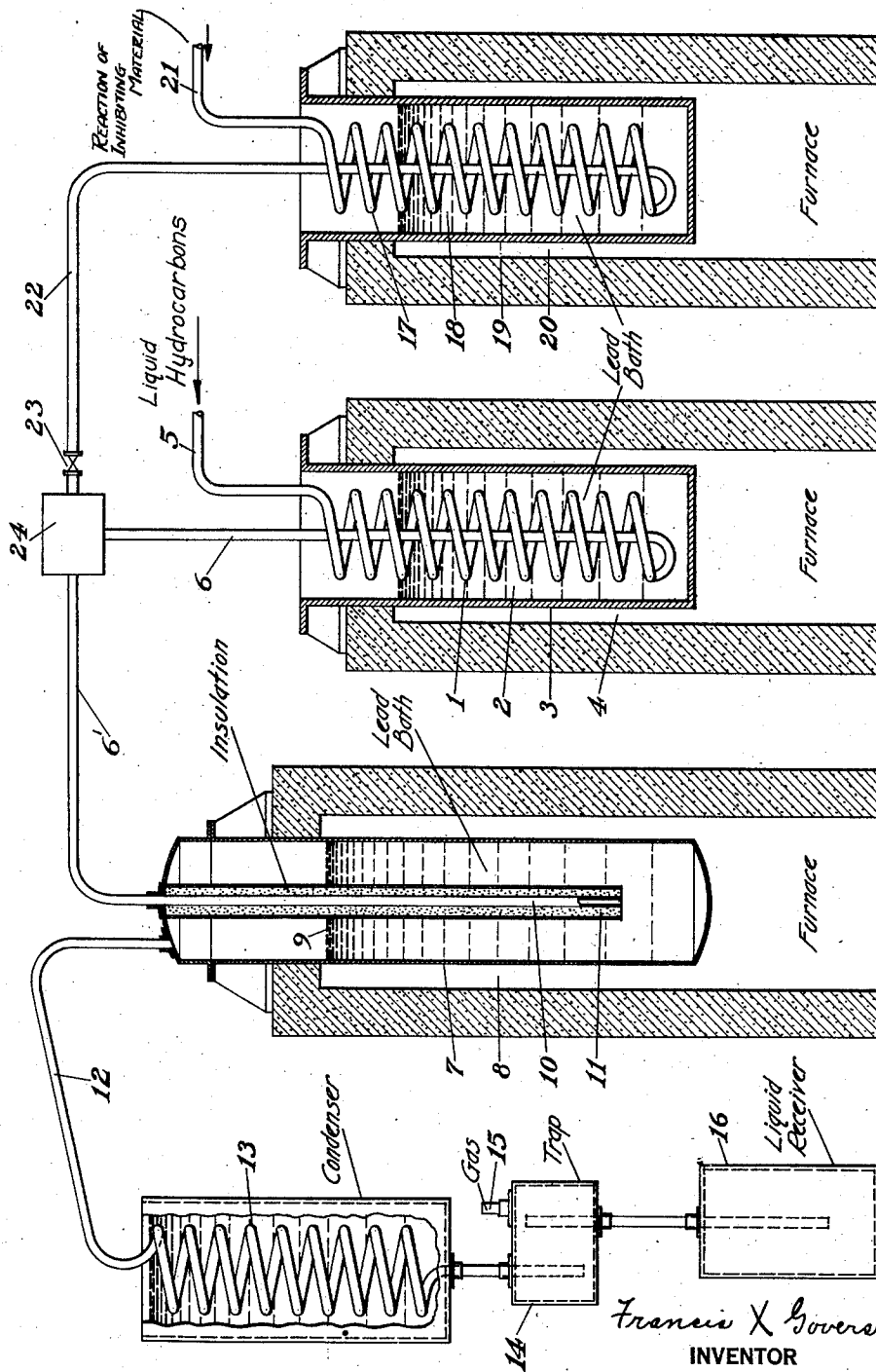
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PYROLYSIS OF HYDROCARBONS

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PYROLYSIS OF HYDROCARBONS

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6 Claims. (Cl. 196—70)

This invention relates to the pyrolysis of hydrocarbons under controlled conditions.

The invention broadly contemplates an improved process for the pyrolysis of hydrocarbons, particularly such as petroleum hydrocarbons, wherein the hydrocarbons are subjected to pyrolytic treatment under controlled conditions, such as that of time and temperature of treatment, for the maximum production of desired products. The invention also contemplates treating the hydrocarbons under such controlled conditions in the presence of catalytic agents, if desired, with material adapted to influence the nature and extent of the reaction, as may be desired, in order to produce products of desired characteristics.

In the pyrolysis of all petroleum hydrocarbons whether the products of such pyrolysis are to be used for motor fuels or, with chemical or other treatment, for products other than motor fuels, it is most essential that the pyrolysis or break down and recombining of the petroleum hydrocarbons takes place in such a manner as to be easily controllable and in such manner that the greatest amount of desired products or products of desired characteristics may be obtained. Various suggestions have been made in regard to preserving the equilibrium of various constituents in order to produce the greatest amount of desired products. Suggestions have been made for the addition of inert substances to slow down undesirable reactions, or active substances to accelerate desired reactions. But no suggestion hitherto made has called for the definite pyrolytic decomposition in steps, neither has any suggestion been made at any time for limiting the effect of reacting agencies and catalysts to a definite part and place in the process.

In many desired reactions time and temperature are interchangeable, that is, long exposures to relatively low temperatures give approximately the same effect as a short exposure to relatively high temperatures. In all the methods heretofore proposed there has been an inter-stage, so as to speak, which is not controllable by the operator, that is, a period of time between the mere heating up of the material under treatment and the point at which the desired reaction occurs. Frequently during this intermediate period of time, either due to structural features of the apparatus employed or to the method of heating and temperature and pressures applied, undesired intermediate reactions occur which influence to a marked extent the final desired end reactions. Thus comparative long time factor low temperature treatment gives as unsatisfactory results as short time high tem-

perature treatment, this being particularly the case where direct heat is used and spotty or local overheating occurs. Quite a portion of the heat is used up in heat of vaporization and many compounds due to their complex nature under rapid heating tend to break down in the period of vaporization, particularly where the compounds are of high boiling point and are poor conductors of heat.

I have discovered that by a method of controlled heat in a two-phase system, the first phase embracing heating the material under controlled temperature conditions, advantageously by means of indirectly applied heat, such heating being carried only to the point where no substantial pyrolysis of the compounds under treatment occurs, and a second phase whereby the heat is applied by means of direct contact with a molten mass maintained at a temperature high enough to cause immediate disassociation and reassociation that entirely different products are obtained than by the ordinary methods of heating.

By means of my invention I am able to subject the oil or hydrocarbon fractions to what may be referred to as "flash cracking". That is, the oil is brought up to a decomposing temperature and advantageously in a vaporous state, under conditions such that substantially no cracking occurs or, if desired, only a very small amount occurs, but without giving rise to any undesired effects, following which it is immediately discharged in the midst of the molten contact mass wherein the vapors bubble through the hot mass with a minimum time of contact therewith, and during which time of contact substantially all of the cracking or at least the major portion thereof is brought about with the shortest possible time of exposure to high temperature conditions.

I have discovered that by the use of inert gases undesired side reactions can be prevented. I have also discovered that by the use of hydrogen, polymerization can be prevented to a great extent without affecting the products as in hydrogenation under high pressures. Furthermore, by suspending solid catalysts in the molten mass reactions can be retarded or accelerated as desired. As an illustration, in the manufacture of motor fuels from gas oil or the equivalent thereof, I have discovered by this method it is possible to produce a motor fuel having not only marked characteristics in its anti-knock properties but in addition thereto having the properties of producing more power for a given cubic displacement of piston with less fuel consumption for H. P. developed than with the ordinary

type of fuel. I have also discovered that by the pyrolysis of wax distillate fractions containing appreciable percentages of wax it is possible to break down these waxes to desired products that permit of their utilization in the production of lubricating oils having characteristics differing from the ordinary lubricating oils of commerce.

I have found that the dehydrogenation and condensation of hydrocarbon compounds can be effected under controlled two-phase conditions more easily than in any method before practiced.

On the drawing the single figure is a diagrammatic showing of the principal parts of the hydrocarbon treating apparatus. For the purpose of illustration, the size and materials of an apparatus which has been operated successfully will be described, but it is to be understood that the invention is not limited to these details since the size and shape and materials of the apparatus may be altered without departing from the principles of my invention.

In practice, the coils 1 and 17 are made of seamless steel tubing, which are 750 feet long and .840 inches external diameter and .539 inches internal diameter, submerged in baths 2 and 18 of molten lead supported in vessels 3 and 19 within the furnace chambers 4 and 20. The coil 1 is supplied with liquid hydrocarbons by means of a pressure pump, which is not shown, through the inlet pipe 5 and the resulting heated vapors pass from coil 1 by way of pipe 6 to the decomposer which comprises the closed chamber 7 supported in furnace chamber 8 containing a bath 9 of molten lead or other molten material such as cryolite, et cetera, into which the pipe 10, which communicates with pipe 6', and is jacketed with heat insulating material, extends. The chamber 7 communicates through pipe 12 with condenser 13 which in turn communicates with trap 14 having a gas or vapor outlet 15 and a liquid receiver 16.

The coil 17 is supplied through pipe 21 by means of a pressure pump or pressure turbo fan with gases or liquid reacting inhibiting or inert material as desired, and the heated vapors or liquid pass from coil 17 by way of pipe 22 provided with stop valve 23 to the mixing chamber 24, in which mixing chamber it is mixed with heated vapors from coil 6 and thence is conveyed by means of pipe 6' to the decomposer before described.

As an example, in carrying out the process in the apparatus just described a fraction of mineral oil having an initial boiling point of 360° F., final boiling point of 550° F. and a mean boiling point of 450° F. is delivered to the coil 1 at the rate of about 3 gallons per minute. The bath 2 is maintained at about 400° C. (752° F.) and petroleum fraction vaporized in the coil 1 passes through pipe 6 into the mixer 24 where it is mixed with a stream of hydrogen supplied through pipe 21 by means of a turbo fan, not shown, the bath 18 is maintained at a temperature of about 600° C. (1112° F.) and the hydrogen is supplied at approximately the rate of 20 cu. ft. per minute. The mixed stream of vaporized hydrocarbons and heated hydrogen passes through pipe 6' and 10 into the bottom of lead bath 9 which is maintained at about 700° C. (1292° F.). The outlet pipe 10 advantageously is about 8 feet below the surface of bath 9 and the surface area of the bath may be about 5 sq. ft. In passing through the bath 9, the hydrocarbons are heated to approximately the temperature of

the bath and decompose and recombine without polymerization, the highly unsaturated molecules tending to combine with the hydrogen. The highly heated vapors pass through pipe 12 to condenser and cooler 13 and the condensed and cooled liquid and cooled gas go to the gas trap 14 where the gas is separated from the liquid, the liquid going to the liquid receiver 16 and gas being conducted away through pipe 15.

In the example the conversion of the above treated oil results in approximately 40% of hydrocarbons boiling below 190° C. (374° F.) and of such a nature that the low boiling hydrocarbons have a high octane number and result in the production of more power with a given piston displacement and with less fuel consumption than does ordinary fuel. In addition thereto due to the prevention of polymerization the higher boiling point hydrocarbons are in a condition to be retreated, the resulting retreatment giving about the same results in percentages as the original treatment. Thus the process not only gives a superior fuel but in addition thereto results in greater economy due to the greater total percentage conversion.

As another example, a fraction of mineral oil wax distillate having an initial boiling point of 500° F., final boiling point of 600° F. under 4 m. m. absolute pressure, and a pour test of 85 is delivered to the coil 1 at a rate of about 2 gallons per minute. The bath 2 is maintained at about 350° C. (662° F.) and the petroleum fraction heated in the coil 1 passes through pipe 6 into mixer 24 where it is mixed with a stream of methane supplied through pipe 21 by means of a turbo fan, not shown, and bath 18 being maintained at a temperature of 600° C. (1112° F.) and methane being supplied at approximately the rate of 30 cu. ft. per minute. The mixed stream of heated hydrocarbons and methane passes through pipe 6' into the bottom of lead bath 9 which is maintained at from about 600° to 725° C. (1112° to 1337° F.). The outlet pipe 10 advantageously is about 10 feet below the surface of bath 9 and the surface area of the bath may be about 5 square feet. In passing through the bath 9 the hydrocarbons are heated to approximately the temperature of the bath and wax and other paraffinic hydrocarbons are decomposed and recombined without substantial polymerization. The highly heated vapors pass through pipe 12 to condenser and cooler 13 and the condensed and cooled liquid and cooled gas go to the gas trap 14 where the gas is separated from the liquid, the liquid going to the liquid receiver 16 and gas being conducted away through pipe 15. The conversion of the wax into a series of hydrocarbons containing less hydrogen than the paraffin hydrocarbons is practically complete and the resulting heat treated material has a pour test below -0° F. with an initial boiling point of 350° F. and a final boiling point of 650° F. under 4 m. m. absolute pressure. The decomposed and reconstructed hydrocarbons being of a nature readily affected by aluminum chloride or other catalysts tending to promote polymerization and condensation.

While the examples given show the use of hydrogen or methane, it is found that the results can be altered to a marked extent by the addition of other reacting gases such as a mixture of CO₂, nitrogen, et cetera. The method of my invention is particularly well adapted to carrying out the pyrolysis of natural gas and gasoline hydrocarbons to form aromatic hydrocarbons.

As an additional example, a mixture consisting

primarily of hydrocarbons of a greater molecular weight than methane and ethane and lower than pentane are delivered to the coil 1 at the rate of 3 gallons per minute. The bath 2 is maintained at 600° C. (1112° F.) and the vaporized hydrocarbons pass through pipe 6 into mixer 24 where they are mixed with carbon monoxide and nitrogen in the proportion of 20 parts of carbon monoxide to 80 parts nitrogen. The bath 18 is maintained at a temperature of 700° C. (1292° F.). The mixed hydrocarbons and gases pass from the mixer through pipe 6' to the decomposing bath, comprising molten cryolite, which is maintained at from 600° to 1000° C. (1112° to 1832° F.) where the hydrocarbons are decomposed and highly unsaturated compounds formed unite and form additional substitution products giving alcohols, ketones and aldehydes. These go to the condenser and cooled, and the liquid hydrocarbons are separated and fractionally distilled and the gas separated and kept for further treatment.

The apparatus may be made of suitable material, the container for baths 2 and 18 may be of hammer welded steel, and the container for the bath 9 may advantageously be made of "Fahrite" or some other heat and hot metal resisting material. The molten bath may be of lead, cryolite or other suitable material and depending on the materials used in the molten bath catalysts such as flake nickel, flake iron, etc., may be suspended in the molten mass. In place of heating the decomposing bath by means of the furnace shown, the molten material may be heated in a furnace apart from the decomposing bath and circulated to and from the decomposing bath.

While not shown in the drawing, the apparatus may include suitable fractionating means with which to subject the vapors issuing from the decomposer or reaction vessel to fractionation to produce different fractions as may be desired.

Furthermore, while the treatment of hydrocarbons derived from petroleum sources has been described in the examples, the invention is not limited to the treatment of such hydrocarbons but may equally well embrace the pyrolytic treatment of hydrocarbons derived from other sources.

Obviously many modifications and variations of the invention, as hereinbefore set forth, may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

I claim:

1. A method of cracking mineral oil to produce a relatively high yield of hydrocarbons of motor fuel boiling range without subjecting said hydrocarbons to substantial secondary cracking which comprises preheating the oil to a temperature of around 750° F. at which cracking would occur if maintained at that temperature for a sufficient period of time for the cracking reaction to proceed, removing the oil from the preheating zone before substantial cracking occurs, thereupon momentarily exposing the thus heated oil to direct contact with molten material maintained at a temperature in excess of about 1000° F. whereby conversion of the oil to the desired extent is effected substantially instantly, immediately removing the converted oil from further contact with the molten material, and cooling it to avoid undesired secondary cracking reactions.

2. A method of cracking mineral oil to produce a relatively high yield of hydrocarbons of motor fuel boiling range without subjecting said hydrocarbons to substantial secondary cracking which

comprises preheating the oil to a temperature at which cracking would occur if maintained at that temperature for a sufficient period of time for the cracking reaction to proceed, removing the oil from the preheating zone before substantial cracking occurs, thereupon momentarily exposing the thus heated oil to direct contact with molten material maintained at a temperature of from around 1000° to about 1800° F., whereby conversion of the oil to the desired extent is effected substantially instantly, immediately removing the converted oil from further contact with the molten material, and cooling it to avoid undesired secondary cracking reactions.

3. A method of cracking mineral oil to produce a relatively high yield of hydrocarbons of motor fuel boiling range without subjecting said hydrocarbons to substantial secondary cracking which comprises preheating the oil to a temperature at which it is substantially completely vaporized and at which cracking would occur if maintained at that temperature for a sufficient period of time for the cracking reaction to proceed, removing the oil from the preheating zone before substantial cracking occurs, thereupon momentarily exposing the thus heated oil to direct contact with molten material at a temperature of about 300°-600° F. above the preheating temperature of the oil whereby conversion of the oil to the desired extent is effected substantially instantly, immediately removing the converted oil from further contact with the molten material, and cooling it to avoid undesired secondary cracking reactions.

4. A method of cracking mineral oil to produce a relatively high yield of hydrocarbons of motor fuel boiling range without subjecting said hydrocarbons to substantial secondary cracking which comprises rapidly preheating the oil to a temperature of around 750° F. at which the oil is substantially completely vaporized and at which cracking would occur if maintained at that temperature for a sufficient period of time to permit the cracking reaction to proceed, removing the oil from the preheating zone before substantial cracking occurs, intimately mixing it with a substantial proportion of gaseous material of the character of carbon dioxide, nitrogen, hydrogen, methane and mixtures thereof, which has been preheated to a temperature substantially above the decomposition temperature of the oil, passing the mixture through and in direct contact with a mass of molten material maintained at a temperature in excess of about 1000° F. in such proportion of vapor to molten material that the oil is only momentarily exposed to said high temperatures whereby conversion of the oil to the desired extent is effected substantially instantly, immediately removing the converted oil from further contact with the molten material, and cooling it to avoid undesired secondary cracking reactions.

5. A method of cracking mineral oil to produce a relatively high yield of hydrocarbons of motor fuel boiling range without subjecting said hydrocarbons to substantial secondary cracking which comprises rapidly preheating the oil to a temperature of around 750° F. at which the oil is substantially completely vaporized and at which cracking would occur if maintained at that temperature for a sufficient period of time to permit the cracking reaction to proceed, removing the oil from the preheating zone before substantial cracking occurs, intimately mixing it with a substantial proportion of hydrogen previously heated to around 1000° F., passing the mixture through and in direct contact with a mass of

molten material maintained at a temperature in excess of about 1000° F. in such proportion of vapor to molten material that the oil is only momentarily exposed to said high temperatures whereby conversion of the oil to the desired extent is effected substantially instantly, immediately removing the converted oil from further contact with the molten material, and cooling it to avoid undesired secondary cracking reactions.

6. The process of subjecting natural gas and gasoline hydrocarbons to instantaneous pyrolysis by direct exposure to a mass of molten material comprising conducting a stream consisting mainly of natural gas and low-boiling gasoline hydrocarbons through a heating zone maintained at around 1000° F. wherein it is heated by indirect means to a temperature at which cracking would occur if maintained at that temperature for a sufficient period of time to permit the cracking reaction to proceed, removing the thus heated hydrocarbons before substantial cracking occurs, intimately mixing them with a substantial proportion of a gas consisting of a mixture of carbon dioxide and nitrogen which has been preheated to a temperature of around 1000° F. or higher, immediately thereafter and before substantial cracking occurs, passing the mixture into the midst of a body of molten material maintained at a temperature of from 1000° F. to around 1800° F. in such proportion of combined hydrocarbon vapor and gas to molten material that the hydrocarbons are only momentarily exposed to said high temperatures whereby conversion of the oil to the desired extent is effected substantially instantly, immediately removing the converted oil from further contact with the molten material, and cooling it to avoid undesired secondary cracking reactions.

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