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APPARATUS FOR PYROLYZING HYDROCARBONS

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Fig. 1

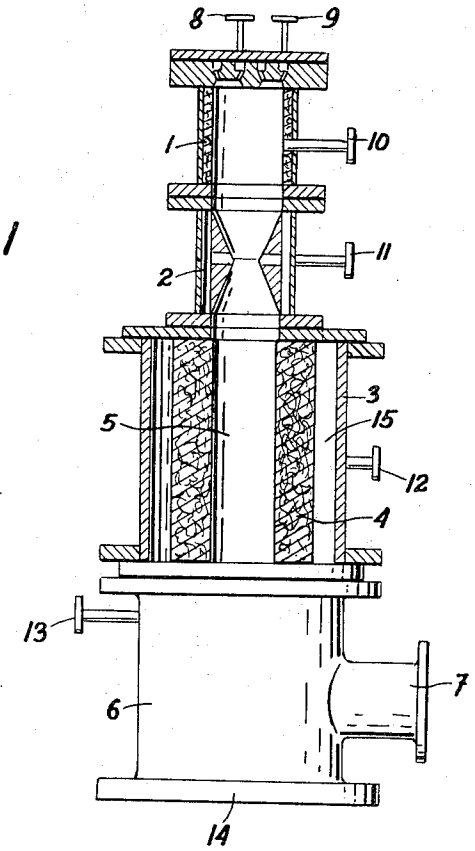
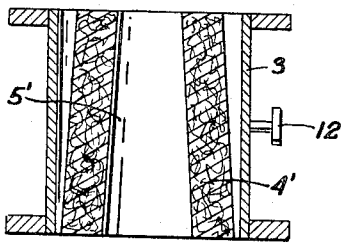


Fig. 2



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APPARATUS FOR PYROLYZING HYDROCARBONS

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Int. Cl. C10g 9/36

U.S. Cl. 23—277 4 Claims

ABSTRACT OF THE DISCLOSURE

A hydrocarbon raw material is pyrolyzed to lower unsaturated aliphatic hydrocarbons by mixing the raw material with hot combustion gases at a rate sufficient to heat the mixture above the pyrolyzing temperature. The endothermic reaction is performed in a porous tube while oxygen is being forced into the tube through the wall to supply the thermal energy consumed and to maintain the pyrolysis temperature by oxidation of a portion of the pyrolysis product, particularly hydrogen. The reaction mixture is then quickly cooled.

This application is a continuation-in-part of our copending application Ser. No. 674,570, filed on Oct. 11, 1967, now abandoned.

This invention relates to the pyrolysis of hydrocarbons to unsaturated aliphatic hydrocarbons having fewer carbon atoms, and particularly to a pyrolyzing method and to apparatus for performing the method.

It is known to mix a hydrocarbon raw material with gaseous combustion products in order quickly to raise the raw material to a temperature at which pyrolitic decomposition takes place. The ensuing reaction is endothermic so that the temperature of the raw material quickly reaches a maximum during mixing with the combustion gases, but then drops. Yet, it is known that the most desirable pyrolysis products are obtained by maintaining the temperature or by even gradually increasing the temperature during pyrolysis. The afore-described known process cannot achieve optimum results and the formation of carbonaceous solids in substantial amounts cannot be avoided.

It is also known to raise the temperature of the raw material while the same passes through a tube having a porous wall. Either a hot combustion gas or oxygen is forced into the tube under pressure. If oxygen is so admixed to the hydrocarbon, combustion of the latter provides the heat for reaching pyrolysis temperature and the formation of carbonaceous deposits on the reaction vessel is prevented. If hot combustion gas or oxygen is supplied through the permeable walls of a conduit holding the flowing raw material, the latter can be heated only relatively slowly. It dwells for relatively long periods in zones where the temperature is sufficiently below the proper pyrolysis temperature to favor the formation of undesirable by-products. Moreover, it has not been practical to build such permeable, tubular conduits of a size useful in industrial production. A sizable portion of the space in the reaction chamber actually serves as a preheating chamber. If hot combustion gases are forced into the chamber through the wall, the thermal losses significantly affect the cost of operation.

Attempts at overcoming the difficulties outlined above have been hampered by the high cost of materials capable of withstanding the temperatures necessary for pyrolysis and the even higher cost of shaping such materials.

A primary object of the invention is the provision of a continuous pyrolysis method for a hydrocarbon raw material in which the temperature can be controlled at will along the stream of reactants, more particularly, the raw material is heated almost instantaneously to the pyrolysis temperature, and the thermal energy consumed by the endothermic reaction is replenished as needed to provide constant or even rising temperature through the reaction zone. Another object is the provision of reliable and practical apparatus for performing the method.

In the method of the invention, a stream of fuel is burned with an oxygen-bearing gas to produce a stream of hot combustion gas. The latter is mixed with a stream of the hydrocarbon raw material to be pyrolyzed at a rate sufficient to raise the temperature of the mixture so produced to the pyrolysis temperature of the raw material. The mixture is then passed through a conduit having a porous wall while at pyrolysis temperature, whereby a major portion of the raw material is thermally decomposed in the conduit. An additional amount of oxygen bearing gas is introduced inward of the conduit through the porous wall at a rate sufficient to supply the thermal energy consumed by the endothermic pyrolysis reaction, whereby the temperature is at least substantially maintained, but may be increased by oxidation of a portion of the reaction products. The remainder of the products is then withdrawn from the conduit.

The apparatus employed includes the burner required for burning the fuel, a reaction chamber having a wall of permeable material, and a source of hydrocarbon raw material. A mixing device is interposed between the burner and the reaction chamber and is connected to the raw material source for receiving the combustion gas and the raw material, mixing the same, and discharging the mixture so produced into the reaction chamber. A pressure chamber is in contact with a face of the aforementioned wall outside the reaction chamber and means are provided for feeding an oxygen bearing gas to the pressure chamber. The reaction chamber has an outlet for discharge of a reaction mixture formed therein, and a cooling device is provided for cooling the discharged reaction mixture.

Further objects, additional features, and many of the attendant advantages of this invention will readily be appreciated as the same becomes better understood by the following detailed description of preferred embodiments when considered in connection with the appended drawing in which:

FIG. 1 shows a pyrolysis apparatus of the invention in side elevation, and partly in section; and

FIG. 2 shows a modified element for use in the apparatus of FIG. 1.

Referring initially to FIG. 1, there is seen a sectional tower whose topmost element is a combustion chamber **1** flanged to a Venturi mixer **2**. The latter is mounted atop an upright tubular vessel **3** whose cavity is divided by a coaxial, cylindrical wall **4** of porous material into a central reaction chamber **5** and an annular pressure chamber **15**. The bottom section of the tower which supports the vessel **3**, the mixer **2**, and the combustion chamber **1**, is a cooling chamber **6** having a wide outlet **7** in its curved vertical wall. The chamber **1**, **5**, and **6** and the diverging-converging passage of the mixer **2** jointly form a straight vertical conduit.

The otherwise closed top wall of the combustion chamber **1** is separately supplied with fuel and oxygen through supply lines **8**, **9**, and the length of the flame and the temperature of the combustion gas can be controlled in a known manner by a steam inlet **10** on the lower portion of the combustion chamber near the mixer **2**.

A fluid hydrocarbon raw material is admitted to the throat or mixing chamber of the Venturi mixer **2** by a pipe **11**. A flanged nipple **12** on the vessel **3** admits oxygen under pressure to the chamber **15**. A pipe **13** communicating with the cooling chamber **6** near the top of the latter permits a cooling fluid to be introduced into the chamber **6** above the outlet **7**. The bottom flange **14** of the chamber **6** may be apertured in a conventional manner, not shown, to permit discharge of pyrolysis products not passing through the outlet **7** and of an excess of liquid cooling fluid if employed.

It will be understood that the apparatus is further equipped with control valves in the several supply lines for proper adjustment of process variables, and with indicating or recording instruments for measuring flow rates of materials entering the illustrated apparatus and for indicating temperatures wherever of interest.

The combustion chamber **1**, the mixer **2** and the cooling chamber **6** are lined with refractory material in a conventional manner. The wall **4** is made of sintered spherical particles of phosphor bronze having a nominal composition of 92% copper and 8% tin, and a solidus temperature of 880° C. Other materials which have been used successfully include a similar bronze wall prepared by sintering short length of wire, walls of sintered nickel and stainless steel, and sintered ceramic materials such as alumina, zirconia, mullite, or cermets consisting mainly of alumina or chromium oxide and Cr, Mo, Co, W as the metallic constituent. It is preferred to prepare the porous wall **4** by sintering, but other methods of construction may be resorted to.

Hydrogen or a gas rich in hydrogen content is the preferred fuel which is admitted to the combustion chamber **1** through the supply line **8**. It is burned with a stoichiometrically equivalent amount of oxygen discharged from the line **9**. The gaseous residue recovered from the work-up of the pyrolysis products is usually a suitable fuel and may be recycled to the combustion chamber **1**. Any gas containing elementary oxygen may be employed for combustion if commercially pure oxygen is not available or if the resulting dilution of the product is acceptable. Atmospheric air or air enriched with oxygen may thus be employed.

The temperature of the combustion gas can reach as much as 3000° C. and may be adjusted by introducing steam through the inlet **10**.

The hot gas is mixed in the throat of the Venturi mixer **2** with the hydrocarbon raw material that is to be pyrolyzed and which is initially in the liquid state. The temperature of the hydrocarbons is raised almost instantaneously to the desired pyrolysis temperature by suitable control of the feed rates. Typically, the reaction temperature is 750° C. for the preparation of propylene and ethylene as the predominant pyrolysis products, and somewhat higher if it is desired to prepare mainly ethylene and acetylene, the necessary conditions of pyrolysis being well known among those skilled in the art and not different in the method of this invention from the usual operating conditions.

The period during which the raw material is heated through the temperature range below the pyrolysis temperature is extremely short, and the percentage of undesired products known to be generated at the lower temperatures by polymerization, dehydrogenation, or cracking is minimal. It is further reduced if the temperature in the reaction chamber **5** is controlled to rise in the direction of fluid flow.

Thermal energy is supplied to the stream of material in the chamber **5** by partial combustion of the pyrolysis products with secondary oxygen supplied through the porous wall **4** from the pressure chamber **15**. Hydrogen, methane, and carbon monoxide in the mixture are preferentially oxidized to maintain the initial pyrolysis temperature, or to raise the temperature of the gaseous stream for further pyrolysis of compounds of relatively low molecular weight formed in the initial stage of pyrolysis.

The oxygen or oxygen bearing gas employed in the secondary combustion enters the pressure chamber **15** through inlet **12** at relatively low temperature, and thus protects the wall **4** against the high temperatures prevailing elsewhere in the reaction chamber **5**. The flow of gas through the pores of the wall **4** is rapid enough to prevent the deposition of carbon on the inner wall surface which would impede further entry of secondary oxygen.

The reaction mixture is quickly cooled in the chamber **6**, typically to about 500° C., by a fluid coolant introduced through the pipe **13**. Any suitable and available process fluid may be employed as coolant, and it may be liquid or gaseous. Water in the liquid form or as steam may be employed, but liquid or gaseous hydrocarbons have also been employed. An excess of liquid coolant, if any, is withdrawn through the bottom flange **14** whereas the gaseous pyrolysis products together with combustion products and volatile coolant are withdrawn from the illustrated apparatus through the outlet **7** for recovery of thermal energy and fractionation in a conventional manner.

The temperature in the several axial zones of the reaction chamber **5** may be controlled more precisely by axially dividing the pressure chamber **15** and by individually controlling the admission of oxygen to the compartments so formed. FIG. 2 illustrates a different method of controlling the temperature distribution in a combustion chamber **5'** radially bounded by a porous wall **4'** which flares conically in a direction from the Venturi mixer **2** toward the cooling chamber **6**. The mixer and cooling chamber are not shown in FIG. 2, and it will be understood that the apparatus of FIG. 2 is identical with that illustrated in FIG. 1 as far as not specifically shown in the drawing.

Because of the conical shape of the wall **4'**, its permeability to oxygen entering from the pressure chamber **15** through an axial unit length of the wall increases in a direction away from the combustion chamber **1**. Conversely, the ultimate flow rate of the pyrolysis mixture in the chamber **5'** is lower than in the cylindrical chamber **5** if the initial flow rate was the same. It is therefore easier to maintain an increasing temperature in the flowing pyrolysis mixture in the chamber **5'** than in the chamber **5**.

Obviously, the shape of the reaction chamber in the pyrolysis chamber of the invention may be modified otherwise to adapt it to specific processing conditions. It has been found, however, that one of the advantages of the apparatus illustrated is its great versatility, and its ability to operate successfully over the entire range of conditions normally required for pyrolysis of hydrocarbon raw materials to compounds having shorter carbon chains, more specifically lower alkenes and lower alkynes.

The following examples are further illustrative of the method of invention as performed in apparatus of the type illustrated:

EXAMPLE 1

A laboratory reactor of the type shown in FIG. 1 was used for pyrolysis of a gasoline fraction boiling between 80° and 180° C. The porous wall **4** of the reactor had an internal diameter of 40 mm., and other dimensions of the combustion chamber **1**, the Venturi mixer **2**, and the vessel **3** may be read from the drawing which is substantially to scale with respect to elements **1, 2, 3, 4.**

The gasoline entered the mixer **2** through the pipe **11** at a rate of 5 kg. per hour and a temperature of 500° C. For each kilogram of raw hydrocarbon stock, the combustion chamber was supplied with 0.415 cubic meter of a fuel gas consisting of 42% hydrogen, 38% carbon monoxide, and 20% methane, and having a net heating value of 4.792 cal. per $m.^3$. It will be understood that all percentage values are by volume unless stated otherwise, and that absolute values of gas volume relate to measurements reduced to standard conditions of temperature and pressure.

Oxygen was supplied to the combustion chamber **1** at a rate of 0.440 m.^{3} and to the pressure chamber **15** at a rate of 0.140 m.^{3} per kg. of hydrocarbon stock. The dwell time of the reaction mixture in the tube **4** was 0.01 to 0.001 second, and the temperature in the tube had an average value of approximately 1,000 to 1,100° C., and increased by about 200° C. in the direction of gas flow. The pressure in the tube **4** was approximately 7 p.s.i.g., and the pressure differential across the wall **4** was approximately 20 mm. Hg.

The effluent gas contained, on a dry basis, 20.7% ethylene, 3.9% acetylene, 4.5% propylene, and 28.9% hydrogen, the remainder being carbon monoxide, carbon dioxide, methane, and smaller amounts of ethane, propane and butane. The material recovered by condensation per kilogram of raw gasoline feed consisted of 0.418 kg. ethylene, 0.074 acetylene, and 0.139 propylene.

EXAMPLE 2

The reactor of Example 1 was supplied with the same gasoline fraction at a rate of 5 kg. per hour. The combustion chamber was supplied, per kilogram of hydrocarbon stock, with 0.480 m.^{3} fuel gas and 0.510 m.^{3} oxygen while 0.162 m.^{3} oxygen were fed to the pressure chamber **15**.

The temperature in the tube **4** varied from 1,500° C. near the Venturi mixer **2** to 1,700° C. near the cooling chamber **6**. The dwell time in the pyrolysis zone was approximately 0.001 to 0.0001 second and the pressure about 7 p.s.i.g. The pressure differential across the porous wall was 25 mg. Hg.

For each kilogram of gaseoline fed to the reactor, 0.24 kg. ethylene and 0.23 kg. acetylene were recovered, the remainder of the reaction products consisting essentially, in the order of decreasing quantities, of hydrogen, carbon monoxide, carbon dioxide, methane, ethane, propane, and butane.

The effect of higher operating temperature on the average chain length of the pyrolysis product is evident. Other variations in the operating conditions of the reactor may obviously be resorted to, and their results are predictable.

We claim:

1. A pyrolysis apparatus comprising, in combination:

(a) sources for the supply of a portion of the total amount of oxygen bearing gas to be used and of fuel;

(b) combustion means for burning said fuel to a combustion gas;

(c) a reaction chamber having a wall of permeable material;

(d) a source of hydrocarbon raw material;

(e) mixing means interposed between said combustion means and said reaction chamber for receiving said combustion gas and said raw material, for mixing the received combustion gas with said raw material, and for discharging the mixture so produced into said reaction chamber;

(f) a pressure chamber in contact with a face of said wall outside said reaction chamber;

(g) means for feeding the remaining portion of oxygen bearing gas to said pressure chamber, said reaction chamber having an outlet for discharge of a reaction mixture formed therein; and

(h) cooling means for cooling the discharged reaction mixture.

2. In the apparatus according to claim **1**, said wall of permeable material forming said reaction chamber, extending longitudinally, and being cylindrically shaped, a vessel constituting said pressure chamber, said vessel surrounding, and being coextensive and cocentric with, said reaction chamber.

3. An apparatus as set forth in claim **1**, wherein said combustion means, said mixing means, and said reaction chamber constitute respective portions of a continuous conduit, said conduit flaring in cross section in said combustion chamber in a direction away from said mixing means.

4. An apparatus as set forth in claim **3**, wherein said wall of said combustion chamber is frustoconical.

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