

June 18, 1963

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3,094,479

CONVERSION PROCESS AND APPARATUS

Filed Feb. 7, 1958

2 Sheets-Sheet 1

FIG. 1

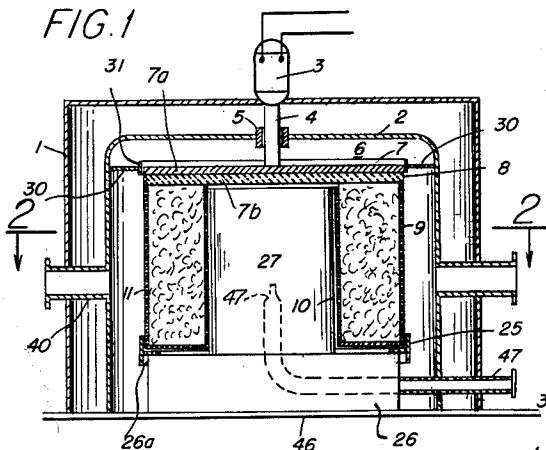


FIG. 2

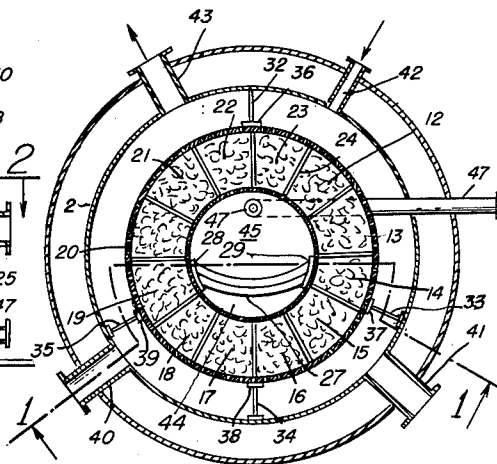


FIG. 3

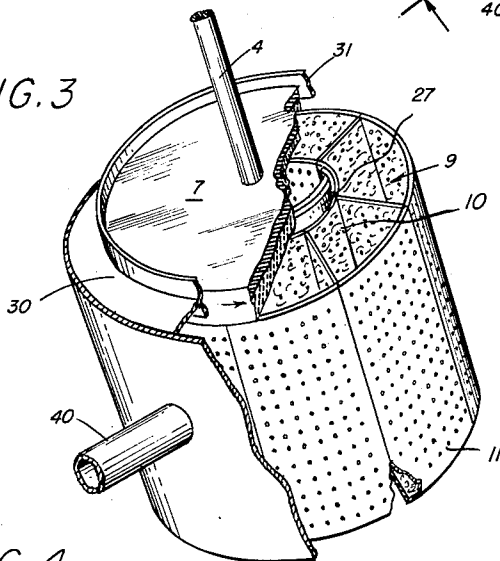


FIG. 4

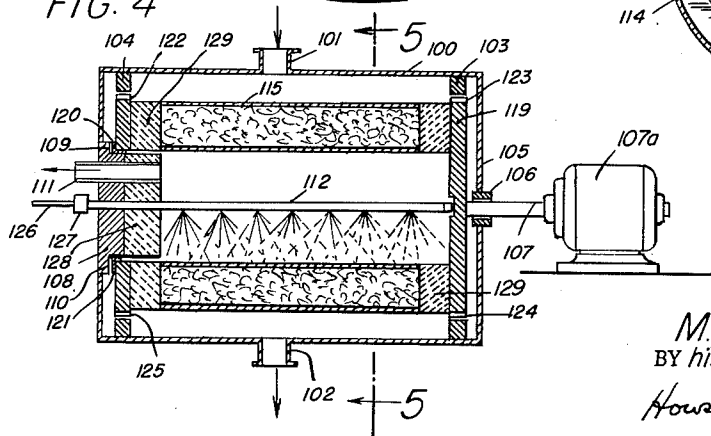
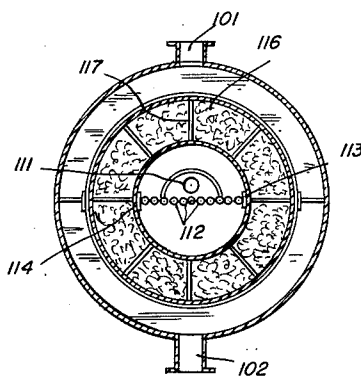


FIG. 5



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2 Sheets-Sheet 2

FIG. 6

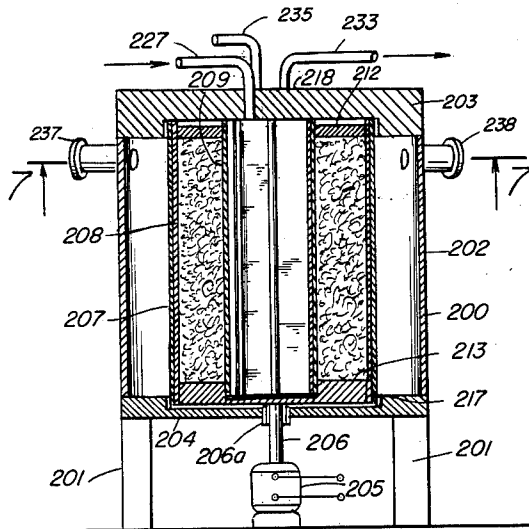
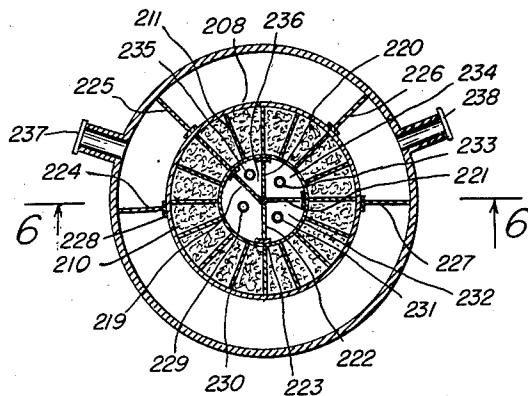


FIG. 7

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3,094,479

CONVERSION PROCESS AND APPARATUS

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Filed Feb. 7, 1958, Ser. No. 713,863

4 Claims. (Cl. 208—176)

This invention pertains to a process and apparatus for the pyrolytic conversion of hydrocarbonaceous materials.

In many chemical processes, it is desirable to carry out the pyrolysis of hydrocarbonaceous materials. For example, acetylene and ethylene, which are used in constantly increasing quantities for a variety of different synthetic resins are often made by thermally cracking or converting lower value hydrocarbons such as methane, ethane, propane, butane or petroleum oils. These same raw materials can also be used to make Fischer-Tropsch synthesis gas ($\text{CO} + \text{H}_2$), and ammonia synthesis gas ($\text{H}_2 + \text{N}_2$) in processes which involve a pyrolysis step. Waste materials, such for example as sulphite base waste liquor from pulp mills, are also treated by methods employing pyrolysis.

A great variety of different techniques have been suggested for carrying out these pyrolysis processes. In recent years, for example, much attention has been given to the fluidized bed technique, in which the hydrocarbon to be converted is sprayed into a mass of hot fluidized solids, and thereby pyrolyzed. This technique is satisfactory for certain applications, but involves large plants which are expensive to build and operate. Moreover, there is a minimum contact time in such beds which cannot be lessened and when products such as acetylene are desired, this time is too long, because the acetylene will polymerize or decompose before it can be taken from the bed.

To achieve a shorter contact time it has been proposed to inject the hydrocarbonaceous material to be pyrolysed into a flame, followed by sudden quenching with water. Maintaining a flame in a reducing atmosphere converts the carbon burned mainly to CO instead of CO_2 , thus giving less than one third as much heat, fails to burn much of the hydrogen, burns some of the desired product, and completely wastes the large amount of sensible heat in the product gases; thus, this is an expensive technique using large quantities of fuel and the gaseous products are always greatly contaminated with carbon oxides, and with nitrogen if air is used as the oxidizing medium.

It is an object of the present invention to provide a process for the conversion of low value hydrocarbonaceous material which is more economical to operate than existing systems.

It is another object of the invention to provide an apparatus of the class described which is smaller and less expensive to build and operate than existing systems.

It is another object of the invention to provide a method and apparatus for the pyrolysis of hydrocarbonaceous materials which can be used to provide valuable unsaturated compounds in which contamination by nitrogen or oxides of carbon is minimized.

It is another object of the invention to provide a method and apparatus for the pyrolysis of hydrocarbonaceous materials in which the reaction time can be varied from extended to very brief periods.

It is a further object of the invention to provide a method for removing, and thus preventing excessive build up of solid deposits formed during a pyrolysis process at or near the pyrolysis zone.

It is a further object of the invention to provide an economical method for rapidly quenching products of high temperature pyrolysis.

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In accordance with a principal aspect of the invention, these and other objects are attained by passing the hydrocarbonaceous material to be pyrolysed through a mass of fibrous heat exchange or heat storage material, at least a portion of said heat exchange material being at a temperature sufficient to cause pyrolysis of the hydrocarbonaceous material. Preferably, the mass of heat exchange material is passed in a circuitous path which includes a pyrolysis zone and a reheating zone. Hydrocarbonaceous feed is passed through the heat storage material in the pyrolysis zone and is heated and thereby pyrolysed to give vaporous products, which are at least partially cooled by the heat storage material, and a non-vaporous residue which remains on the heat storage material. The heat storage material is then removed from the pyrolysis zone to the reheating zone where it is brought into contact with oxygen. By this means the residue is burned off and the heat exchange material is at least partially reheated.

In a preferred arrangement the fibrous heat storage material is arranged in an annular mass and rotated about an axis. Hydrocarbonaceous feed is continuously passed through one section of the mass and pyrolysed and air, or other oxygen containing gas, is continuously passed through another section to burn off pyrolysis residue thereby partially reheating the heat storage material. Additional fuel may also be added to the air to furnish the remainder of the heat required.

If desired, the vaporous products of pyrolysis removed from the pyrolysis section may be passed through a quenching section where further pyrolytic decomposition is arrested.

The composition of the fibrous heat exchange or heat storage material used will depend on the particular reaction being conducted. For low temperature pyrolysis, i.e. below about 1200° F. materials such as glass wool, asbestos, or metallic wires may be used. Preferably, however, and particularly where the temperatures involved are above about 1200° F., aluminum silicate fibers, such as those manufactured by the Carborundum Company and sold under the trade name "Fiberfrax" are employed. Recently graphitic fibers have been developed and these may also be used in certain embodiments, or if they are properly treated to become non-oxidizable.

The physical form of the apparatus employed may vary from one application to another. Basically the preferred apparatus consists of an annular container having perforated walls and divided into sections by radial partitions. The sections are filled with heat exchange material. Means are provided for introducing feed into and removing product from one set of sections, for passing oxygen or an oxygen containing gas through another set of sections and for rotating the annular container about its axis.

The hydrocarbonaceous feed employed in the present invention may be drawn from a wide variety of materials including gases such as methane, ethane, propane and butane and liquids such as recycle gas oil, bunker C fuel oil, coke oven tar, low temperature coal carbonization tar, and waste sulphite liquor. Solids such as coal, lignite or peat may also be used; however, here serious practical difficulties are encountered and the advantages of the invention are less attractive. As used the feed must be fluidized. If it is a liquid it is preferably either vaporized before being brought into contact with the fibrous material, evenly sprayed on the fibrous material, or is dispersed in some innocuous carrying gas such as steam or nitrogen. Solids must be gasiform, e.g. finely divided and entrained in a carrying gas, in a disperse phase before introduction or dissolved in a recycle oil or the like.

As noted, the process can be applied to a number of

different pyrolysis reactions. Some of the most important are:

- (1) Conversion of methane to acetylene;
- (2) Conversion of butane and propane to acetylene, ethylene, butylene and butadiene;
- (3) Conversion of methane to Fischer-Tropsch synthesis gas;
- (4) Conversion of methane to ammonia synthesis gas;
- (5) Conversion of methane, ethane, propane, or butane to aromatics;
- (6) Conversion of heavy oils (e.g. bunker C fuel oil) to various products including acetylene, butadiene, and aromatics;
- (7) Recovery of SO_2 and NH_3 from ammonia base waste sulphite liquor.

The conversion of various hydrocarbons to acetylene is of particular interest because the use of the novel technique permits extremely short reaction times at high temperatures, i.e. as low as about 0.001 second, to be obtained, thus preventing destruction of the acetylene as it is produced.

The invention will be further described with reference to the accompanying drawing in which:

FIG. 1 is a view, partly in elevation and partly in vertical section (along the line 1—1 of FIG. 2) of a pyrolysis unit for use with the present invention.

FIG. 2 is a view in horizontal section of the unit of FIG. 1, taken along the line 2—2 of FIG. 1.

FIG. 3 is a perspective view showing the construction of the rotor of FIGS. 1 and 2.

FIG. 4 is a view in vertical section of a modified form of a pyrolysis unit according to the invention, especially adapted for processing liquid feeds.

FIG. 5 is a view in vertical section taken along the line 5—5 of FIG. 4.

FIG. 6 is a view in vertical section of still another form of the invention, suitable for use in processes where there is a liquid feed or in processes where a somewhat larger contact time is desired.

FIG. 7 is a view in horizontal section along the line 7—7 of FIG. 6.

Referring first to FIG. 1, a pyrolysis unit according to the invention comprises a shell 1, enclosing a casing 2. The shell 1, which may be of sheet steel or other structural material, supports a motor 3 having a shaft 4 which extends downwardly through the casing 2. A stuffing box 5 is provided on top of the casing 2 to furnish a gas-tight seal and journal for the shaft 4. Suspended from the bottom of shaft 4 is a rotor indicated generally as 6. The rotor 6 comprises an upper plate 7 which is formed of a sheet of structural material such as steel 7a and a lower sheet 7b of insulating material such for example as magnesite. Its outer edge 8 is provided with a sealing surface such for example as graphite for reasons which will become apparent. Attached to the lower surface of the plate 7 is an annular chamber indicated generally as 9. This chamber 9 is formed by two perforated walls 10 and 11. These walls may be formed of perforated silicon carbide plates or heat resistant metal screening; for example, screening made of a high temperature alloy such as one composed of 94% nickel, 3% manganese, 2% aluminum, and 1% silicon. The chamber is divided into a number of sections 12—23 by radial walls 24. Each section is filled with a fibrous heat exchange or heat storage material such, for example, as "Fiberfrax." The walls 24 may be made from Carborundum or from a heat resistant alloy and the fibrous material may simply be placed at random in the spaces between the walls. Alternatively, and this is preferred where a substantial pressure different exists from one section to another, the fibrous material is used in the form of a web or blanket which is wrapped around the inner wall 10. The walls 24 are built up during the wrapping of the fibrous material by spraying the material with a

temperature-resistant adhesive at each point where it is desired to form the walls 24.

In some instances, where the fibrous material has substantial structural strength the inner wall 10 of the annular chamber 9 may be eliminated.

At the bottom of the chamber 9 a sealing ring 25 is secured. This provides a sealing surface for the lower section of the rotor. Beneath the rotor is a base block 26 formed of some refractory material such as fire brick or magnesite. A stationary sealing ring 26a is provided on the upper corner of the block 26 for cooperation with the sealing ring 25 of the rotor 9. The base block 26 has extending upwardly from it a sealing divider 27. The divider 27 is again made of a refractory material such as silicon carbide and has at its extremities sealing shoes 28 and 29. It divides the inside space into two zones 44 and 45. The casing 2 is further provided with an upper sealing ring 30 having a circular shoe 31 which extends around the rotor and cooperates with the surface 8 on the upper plate of the rotor. Vertical sealing legs 32—35 are provided on the casing 2. These legs are also provided with sealing shoes 36—39 which are in close cooperation with the outer wall 11 of the rotor. They divide the annular space between the inner casing 2 and the rotor into 4 compartments as will be noted from FIG. 2. A duct 40 is provided emptying into the annular space bounded by the casing 2, the outer wall 11 of the rotor, the vertical sealing legs 34 and 35, base 46, and the upper sealing ring 30. Another duct 41 is provided connecting into the space defined by the casing 2, the outer wall 11 of the rotor, the vertical sealing legs 33 and 34, base 46, and the upper sealing ring 30. A third duct 42 is provided connecting with the space defined by the casing 2, the outer wall 11 of the rotor, the vertical sealing legs 33 and 32, base 46, and the upper sealing ring 30. A fourth duct 43 is provided connecting with the space defined by the casing 2, the outer wall 11 of the rotor, the vertical sealing legs 32 and 35, base 46, and the upper sealing ring 30.

In operation, the motor 3 is energized and causes the rotor 9 to rotate on its axis. Hydrocarbonaceous material to be pyrolysed is introduced through the duct 40. It flows into the casing 2 and then through the holes in the outer wall 11 of the rotor. The fibrous material in the sections 17—18, as will later appear, is hot from previous treatments and at least at the inner surface is at a temperature sufficient to cause pyrolysis of the hydrocarbon. The hydrocarbon flows through the fibrous material and is pyrolysed to form vaporous products and a residue which may consist of carbon, tars, and other heavy material. The vaporous product flows into the central chamber 44 while the residue remains on the fibrous material. Pyrolysis continues in chamber 44. From the chamber 44 the vaporous product flows radially outwardly through the sections 15—16 where it is rapidly cooled to a temperature below that at which it would be further decomposed and normally to a temperature somewhat above the inlet temperature in duct 40. The cooled product flows into the space between the rotor and the casing and is thence removed from the unit through duct 41.

At the same time that hydrocarbonaceous feed is introduced through duct 40, an oxygen-containing gas such as air is introduced through the duct 42. It flows through the space between the rotor and the casing 2 and thence through the sections 23, 12, 13, and 14. Here it burns the pyrolysis residue from the fibrous heat exchange material, heating up the material. The hot products of combustion still containing excess air flow into the central chamber 45, wherein auxiliary fuel is introduced through nozzle 47, which burns with at least a portion of the excess air. The products of combustion then flow radially outwardly through the sections 21, 22, 20 and 19, where additional combustion occurs with concomitant heating. The products of combustion flow through the

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space between the rotor and the inner chamber and are removed through duct 43. Considering the same operation from the standpoint of the matrix of fibrous heat exchange material it will leave the reheating zone which point, assuming that the rotor is moved counter-clockwise (see FIG. 2), is indicated by the vertical sealing leg 35, at an inner temperature which is dependent upon the amount of combustion that has been carried out but which will normally be on the order of 1600° F. to 3000° F., and an outer temperature normally on the order of 150° F. to 500° F. A radial temperature gradient between these end temperatures will exist within the intermediate zones of the matrix. As it moves away from the sealing leg 34 it is met with fresh hydrocarbonaceous feed at a temperature of say 50° F. to 700° F. This will cause cooling of the fiber matrix and heating of the hydrocarbonaceous feed so that by the time the matrix has reached the vertical sealing leg 35 its peripheral portion will approach closely the temperature of the fresh feed. The inner portion on the other hand will be at the temperature required to pyrolyse the feed. As the matrix passes beyond the vertical sealing leg 34 it receives hot products of pyrolysis from the central chamber 44. These products flow through the matrix and upon emerging from the peripheral portion of the matrix are somewhat above the temperature of the feed introduced through duct 40. As the fiber moves toward the vertical sealing leg 33 the temperature of its peripheral portion increases. This increase, however, is not sufficient to cause decomposition or recombination of the products of pyrolysis. As it moves past the vertical sealing leg 33 the fiber is met by air which may be preheated in an external apparatus (not shown), if desired, say to 600° F. In any case, the pyrolysis residue is burned off. The temperature of the inner fibers increases to say 1500° F. to 2500° F. by the time the matrix reaches the vertical sealing leg 32. In between sealing legs 32 and 35 the inner fibers increase in temperature still further, normally to about 1600° F. to 3000° F., and the outer fibers will also increase in temperature, usually to about 150° F. to 600° F.

The embodiment of FIGS. 1-3 is preferred for situations where the hydrocarbonaceous feed is gaseous. A somewhat different embodiment is preferred for a liquid feed, and a system which is particularly valuable in the pyrolysis of waste sulphite liquor is shown in FIGS. 4 and 5. In the embodiment of FIGS. 4 and 5 the rotor is moved about a horizontal rather than a vertical axis and the feed is introduced through a series of pipes in the center of the rotor. Referring specifically to FIGS. 4 and 5, the pyrolysis unit shown there comprises a casing 100 having an inlet duct 101 in its top and an outlet duct 102 at the bottom. Inside and disposed about the periphery of the casing 100, at one end thereof is a sealing ring 103. A similar ring 104 is located at the opposite end. An end wall 105 of the casing is provided with a stuffing box 106 adapted to receive a shaft such as 107 driven by a motor 107a. At the opposite end of the casing there is provided a bearing block 108 having shoulders 109 and 110 and insulation 128. A duct 111 with internal insulation (not shown), is provided in the block and the block is also provided with an aperture to receive a row of spray pipes 112. These spray pipes are welded together to provide a gas impermeable surface and are fitted with sealing shoes 113 and 114 (FIG. 5). Inside the casing there is mounted a rotor 115. This rotor is of the general type described above in connection with FIGS. 1-3 and comprises a series of sections 116 defined by radial partitions 117 and filled with fibrous heat storage material. As in the embodiment of FIGS. 1-3 the walls of the rotor may be made of perforated silicon carbide plates or some alloyed metal. The partitions 117 may be made of a similar material or may be built up by a temperature resistant adhesive being applied to succeeding courses of fibrous material along axial lines, thereby forming radial partitions. The rotor 115 has end walls 118 and 119 which are separated from the

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high temperature zone by insulation 129. The inner corners of these walls, as indicated at 120 and 121, and their outer edges 122-125 are provided with bearing surfaces for providing a moving contact with the bearing rings 103 and 104 and the bearing surfaces of the block 108. In operation, a liquid hydrocarbonaceous feed, such as waste sulphite liquor is introduced through pipe 126 and manifold 127 and flows through the spray pipes 112. It is sprayed into the interior of the rotor 115 and comes against the lower interior surface of the rotor. This surface is extremely hot, having previously been contacted with hot products of combustion. The liquor is therefore vaporized to give steam, sulphur gases, ammonia and oily products which are removed through the duct 102. As the rotor is revolved by the shaft 117 and comes into the upper half of the pyrolysis unit, air, a mixture of air and fuel, or a mixture of air (or oxygen), and hot products of combustion formed in an external burner (not shown), is introduced through duct 101 and moves downwardly through the mass of fibrous material. The oxygen in these gases burns off the pyrolysis residue formed in the lower portion of the unit. It heats the fibrous material to say 1200° F. to 2500° F., at its hottest zone. The resulting products of combustion are removed through duct 111.

FIGS. 6 and 7 show a further modification of the invention which is also suitable for use with liquid feeds as well as with processes where a somewhat longer contact time is desirable.

The embodiment of FIGS. 6 and 7 comprises a casing 200 supported by legs 201. The casing has a cylindrical side wall 202, a cover 203 and a floor 204. A motor 205 is located beneath the floor 204 and has a shaft 206 extending up through the floor. A stuffing box 206a provides a gas-tight seal for the shaft 206. Supported within the casing 200 on the shaft 206 is a rotor 207. The rotor is provided with a perforated cylindrical outer wall 208 and a perforated cylindrical inner wall 209. The space between the walls 208 and 209 is divided into sections 210 by partitions 211. The sections are filled as in the embodiment of FIGS. 1-5 by fibrous heat exchange material such as "Fiberfrax." A cover plate 212 and a floor plate 213 are provided for the rotor. The edges of the floor and cover plates 212 and 213 are finished with sealing surfaces 214 and 215 which cooperate closely with similar surfaces 216 and 217 on the cover 203 and floor 204 of the casing 200. Extending downwardly from the cover 203 of the casing 200 is a sealing member 218. This sealing member has four vanes 219, 220, 221, and 222, each of which is provided with a sealing shoe 223. The sealing shoes 223 are each at least as wide as the narrow end of sections 210. The casing 200 is further provided with vertical sealing legs 224, 225, 226, and 227. These legs extend inwardly from the casing and each is terminated with a sealing shoe 228 which cooperates closely with the outer wall 208 of the rotor 207 to minimize leakage across the face of the sealing shoes.

A duct 229 is provided in cover 203 for supplying fluid to the compartment 230 between vanes 219 and 222. A duct 231 is provided in cover 203 for removing fluid from compartment 232 between vanes 222 and 221. A duct 233 is provided through cover 203 for supplying fluid to compartment 234 between vanes 220 and 221. A duct 235 is provided through cover 203 for supplying fluid to compartment 236 between vanes 219 and 220. Ducts 237 and 238 are provided through the casing 200 for furnishing an innocuous sealing fluid to the spaces between legs 224 and 225; and 226 and 227, respectively.

In operation, a fluid to be pyrolysed is introduced through duct 229 and passes into the space between vanes 219 and 222. It flows radially outwardly through the sections of the rotor which are available to it. The fibrous material within these rotor sections is, at least in part, at a temperature sufficient to cause pyrolysis of the hydrocarbonaceous material. As it emerges from the rotor the partially pyrolysed material moves into the space between

the rotor and the casing 200. It then flows circumferentially through this space around the rotor and is drawn inwardly through the adjacent rotor sections into the central chamber 232 extending between partitions 222 and 221. From here it flows out through duct 231. In its inward passage through the rotor the hydrocarbonaceous material is first further pyrolysed and is then cooled or quenched as it leaves the rotor. The rotor is, of course, constantly turning during the above described sequence and the sections of the rotor upon which pyrolysis residue has been deposited are brought into a position between the vertical sealing legs 226 and 227.

Steam or like innocuous gas is charged through duct 238 and enters the space between rotors 226 and 227. It then flows inwardly through the rotor section opposite this space, purging the fibrous material of residual gases and carrying them into the compartment 234.

Air or other oxygen containing gas is introduced into space 234 through duct 233. The oxygen containing gas then passes radially outwardly through the rotor into the space between sealing legs 226 and 225. As the oxygen containing gas passes through the rotor, pyrolysis residue is burned from the fibrous material in the rotor, heating the material. The products of combustion flow circumferentially through the space between legs 225 and 226 and then radially inwardly through the rotor to compartment 236, whence they are exhausted through duct 235.

Depending on the reaction being conducted it may be desirable to introduce fuel, e.g. methane, into duct 233 along with the air or other oxygen containing gas. The fuel is burned in the compartment 234, or in the fibrous material and furnishes whatever heat may be necessary beyond that derived from burning the products of pyrolysis, to raise the fibrous material to the required temperature.

In place of burning a fuel in the rotor, it is obvious a fuel may be burned in an external heater (not shown) and the resulting hot gases charged to duct 233.

The steam introduced through duct 238 not only purges residual gases from the fibrous material through which it flows, but forms a seal, preventing oxygen containing gas and products of combustion from contaminating the pyrolysis products in compartment 227.

Another stream of steam is introduced through duct 237 whence it flows into the space between legs 224 and 225, thence through the rotor into compartment 230, sealing compartment 230 from compartment 236.

The invention will be further described by the following specific examples which are given for purposes of illustration only and are not intended in any way to restrict the invention beyond the scope of the appended claims.

Example I

An apparatus is constructed according to FIGS. 1-3, the volume of chamber 44 being such that the residence time at conversion temperature is about 0.005 second. The rotor has an inner diameter of 10 inches, an outer diameter of 20 in., and a height of 11 inches. Into the annular space provided by this rotor are packed 150 lbs. of "Fiberfrax" yarn in the form of a porous cloth. The apparatus is rotated at about 40 r.p.m. To start the operation a mixture of air and fuel gas is introduced through duct 42, and additional fuel gas through nozzles 47. When the average temperature of the inner zone of the "Fiberfrax" reaches about 2300° F., 300 lbs./hour of natural gas at about 1 atmosphere are introduced through duct 40. The products of pyrolysis removed through duct 41 comprise (mol percent):

Acetylene	12.5
Hydrogen	72.5
Methane	12
Other	3
	100

Example II

The conditions of Example I are repeated except that natural gas is fed at the rate of 750 lbs./hour, the average temperature of the matrix is about 2000° F. and the residence time is about 0.05 second. Of the natural gas connected, the gasiform products are distributed as follows (wt. percent):

Light oils	39
Heavy oils	28
Hydrogen	19
Other	14
	100

Example III

An apparatus is constructed according to FIGS. 4 and 5 of the drawing. The rotor has an inside diameter of 20 inches, an outside diameter of 40 inches and a length of 12. It is rotated at a speed of 100 r.p.m. To start the unit in operation the rotor is rotated and a mixture of air and fuel gas is introduced through the duct 101 and ignited in the upper central chamber. When the temperature of the "Fiberfrax" reaches about 1500° F., 5000 lbs./hour of ammonia base waste sulphite liquor having a solids content of about 25% is introduced through the pipes 112. Fluid product is removed through duct 102. On a dry basis, this product analyzes as follows (mol percent):

SO ₂	35
NH ₃	32
Combustibles	13
Other	20
	100

Example IV

The apparatus of FIGS. 6 and 7 is constructed using a rotor having an interior diameter of 20 inches, an exterior diameter of 40 inches, and a height of 12 inches. In starting up, the rotor is turned at a speed of 100 r.p.m. Flue gas at a temperature of 1600° F. is introduced through the duct 233. When the "Fiberfrax" packing has reached a temperature of about 1500° F. air at 500° F. is substituted for the flue gas and when the inner temperature of the matrix has decreased to about 600° F., fuel gas is added to the air in an amount sufficient to maintain the temperature within the matrix at about 1500° F., and 5000 lbs./hour of a fuel oil, dispersed in 10,000 lbs. steam are introduced through duct 229. The products of pyrolysis removed through line 231 comprise (wt. percent of feed)

Ethylene	16
Butadiene	5
Other gases	15
Light oils	8
Tar oils and pitch	48

From a consideration of the foregoing description, it will be evident that the invention provides a simple and convenient method for converting low value hydrocarbonaceous materials into products having greater value. Many variations in the process and apparatus described will be obvious to those skilled in the art. For example, although in the apparatus specifically described, fluid flow through the fibrous material is radial, it can obviously be axial if desired. Moreover, although only one inlet for feed is shown in each apparatus, evidently a plurality of feed inlets may be employed. Again, air or other oxygen containing gas may be introduced at a variety of different points to aid in combustion of pyrolysis residue and auxiliary fuel.

What I claim is:

1. A method for pyrolytic conversion which comprises passing fluid-form hydrocarbonaceous material to be converted radially through a first section of a rotating an-

nular fibrous mass, said first section of said mass having a temperature which increases in the direction of flow of said hydrocarbonaceous material from a degree not substantially below that at which said hydrocarbonaceous material is introduced to a point at least equal to that at which said hydrocarbonaceous material is pyrolysed and thereby effecting pyrolysis of said material to give a vaporous product and a non-vaporous residue and cooling of said mass, removing said vaporous product from said first section, passing vaporous pyrolysis product through a second section of said annular mass, at least a portion of said second section having a temperature substantially below that at which said vaporous product becomes unstable, to quench said product, removing the quenched product from said second section, passing an oxygen-containing gas in contact with a third section of said mass to burn off pyrolysis residue previously deposited thereon and to preheat said third section for subsequent contact with fresh material.

2. A method for pyrolytically converting fluid-form hydrocarbonaceous material which comprises passing said material through a mass of fibrous heat exchange material, said mass having a temperature which increases in the direction of flow of said hydrocarbonaceous material from a degree not substantially below that at which said hydrocarbonaceous material is introduced, to a point at least equal to that at which said hydrocarbonaceous material is pyrolysed, thereby pyrolysing said hydrocarbonaceous material to give a vaporous product and a non-vaporous residue and cooling said mass, and passing the vaporous product through said cooled mass of fibrous heat exchange material to cool it.

3. The method claimed in claim 2 wherein the last named mass of heat exchange material has a temperature which decreases in the direction of flow of said vaporous product from a degree not substantially below the

pyrolysis temperature of the hydrocarbonaceous material, to a degree not higher than that at which the vaporous products of pyrolysis will remain substantially stable during passage therethrough.

4. Pyrolysis apparatus comprising a casing having a wall, a rotor in said casing positioned to rotate about its axis, said rotor comprising an annular mass of fibrous heat storage material, said rotor defining an annular space between itself and said casing and a central cylindrical space, first sealing means dividing said outer annular space into a first portion and a second portion, second sealing means dividing said central cylindrical space into a first portion and a second portion, inlet means in said wall for introducing a fluid into the first portion of said outer space, duct means for withdrawing fluid from the first portion of said central space, spray means for introducing liquid into the second portion of said central space, outlet means for withdrawing fluid from the second portion of said outer space, and means for rotating said rotor.

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