

April 9, 1940.

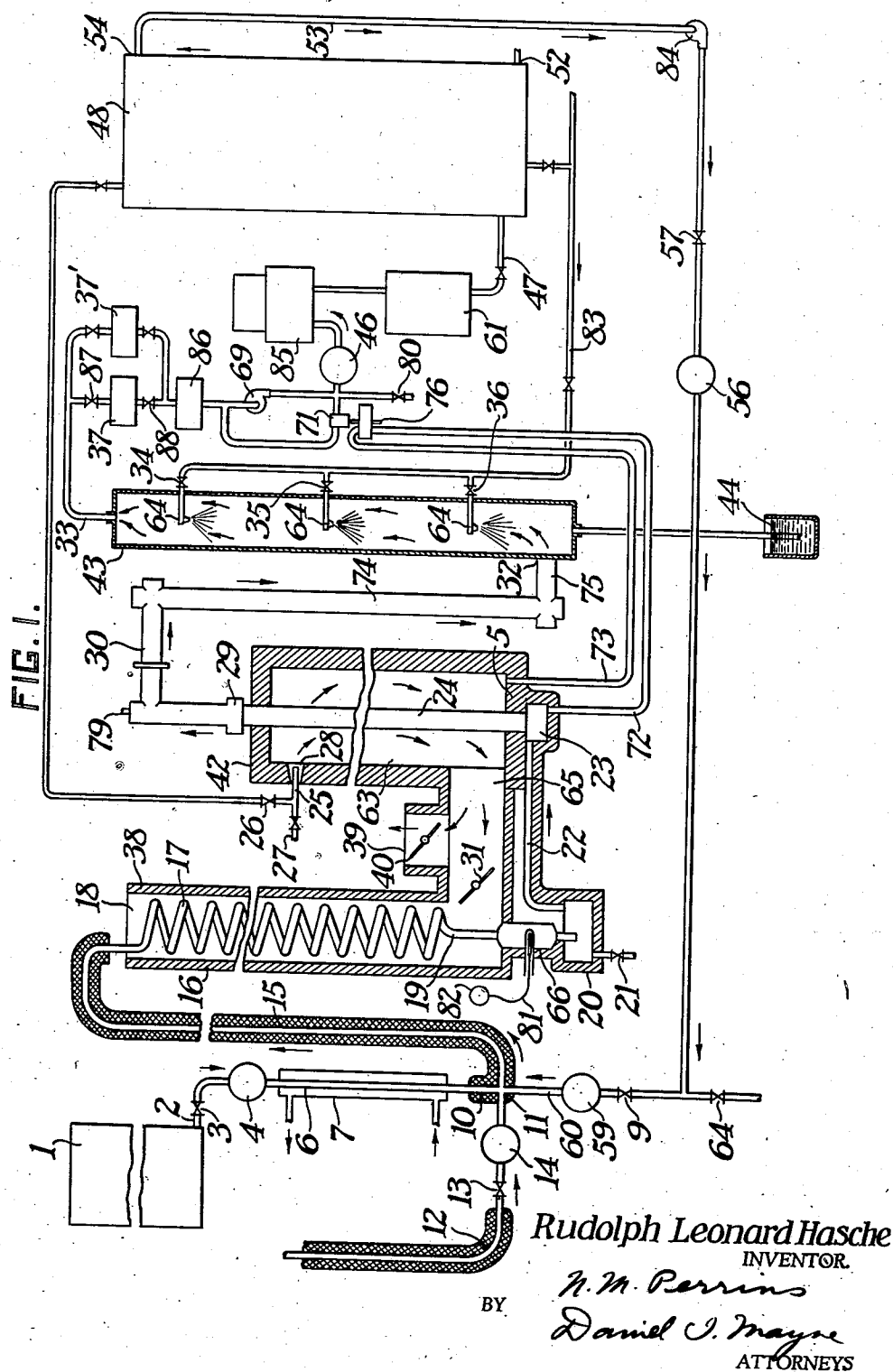
R. L. HASCHE

2,196,767

PYROLYSIS APPARATUS

Filed July 10, 1937

3 Sheets-Sheet 1

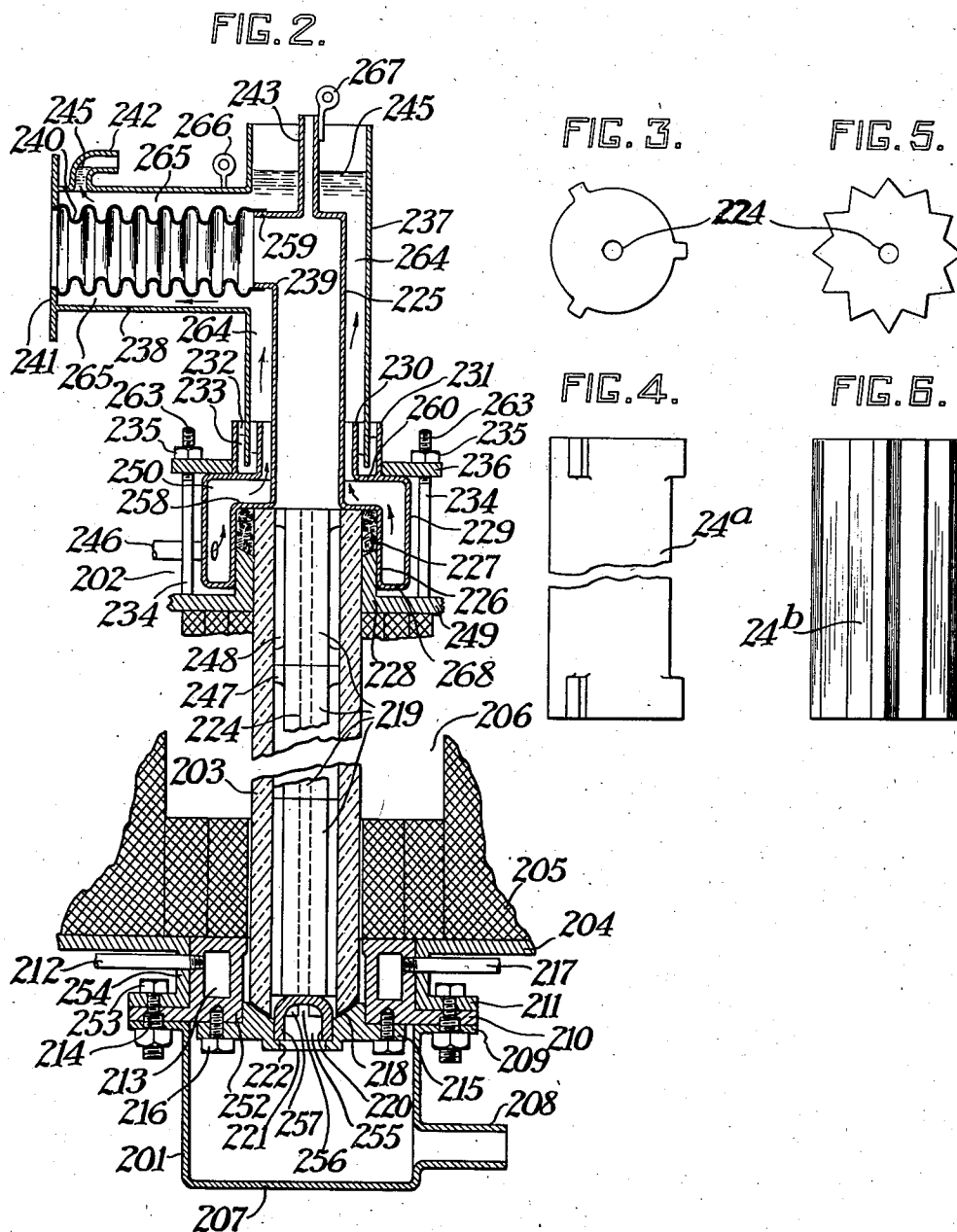


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3 Sheets-Sheet 2



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PYROLYSIS APPARATUS

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11 Claims. (Cl. 23—277)

This invention relates to apparatus for carrying out high temperature treatments and more particularly to pyrolysis apparatus for the high temperature conversion of saturated hydrocarbons to unsaturated hydrocarbons.

While considerable apparatus has been constructed and designed in the prior art for reactions to be carried out at increased temperatures, such apparatus was not designed or constructed for use at temperatures as high as those contemplated herein. That is, for example, in the oil cracking industry various apparatus has been constructed for pyrolysis of oils to various other materials. However, it will be noted that such equipment in most instances is constructed entirely of metal thereby evidencing that the temperature of operation is low when compared with the temperatures with which my novel apparatus is adapted to withstand. In such prior art processes the temperatures have in many instances not exceeded 700° C., whereas my novel apparatus is suitable for operation at temperatures above twice this magnitude.

While some prior art apparatus has been constructed of refractory materials to withstand high temperatures, such apparatus has in many instances only been constructed on a small scale more or less suitable for laboratory uses. In other instances where refractory construction has been employed, since construction was not gas-tight, it would be unsuitable for the hydrocarbon materials because of various hazards, as well as the possibility of losses and contaminations due to leakages.

I have found that an apparatus may be constructed in accordance with the several novel features set forth herein which apparatus is capable of satisfactorily withstanding excessively high temperatures. My apparatus produces particularly satisfactory heating and conversion of the materials treated therein.

This invention has for one object to provide apparatus capable of use at high temperatures. Still another object is to provide pyrolysis apparatus satisfactory for the high temperature conversion of saturated hydrocarbons to unsaturated hydrocarbons. A still further object is to provide apparatus, for use at high temperatures, which is substantially leak-proof with respect to the components to be treated therein. A still further object is to provide apparatus for use at high temperature operations wherein the pressures therein may be varied or controlled. Still another object is to provide high temperature apparatus including means for separating and re-

covering products produced therein. A still further object is to provide pyrolysis apparatus having in combination therein means for cooling, recycling or otherwise treating products or by-products produced therein. A still further object is to provide apparatus for use in high temperature pyrolysis processes, that is particularly adapted to continuous operation. Other objects will appear hereinafter.

For a more complete understanding of my invention, reference is made to the accompanying drawings.

Fig. 1 is a diagrammatic side elevation view showing one form of general arrangement of high temperature apparatus in accordance with my invention.

Fig. 2 is a semi-diagrammatic side elevation view on a larger scale, with certain parts broken away and in section for clarity, showing in more detail one of the high temperature units of my apparatus.

Figs. 4 and 6 are additional views of a type similar to Fig. 2, showing in further detail certain parts which may be employed in the construction of my apparatus.

Figs. 3 and 5 are end views of the parts shown in Figs. 4 and 6.

Fig. 7 is a semi-diagrammatic side elevation view of a type similar to Fig. 2 showing an enlarged furnace unit which might be employed in my apparatus.

Fig. 8 is a semi-diagrammatic side elevation view of the type shown in Fig. 1 of a modified horizontal apparatus arrangement in accordance with my invention.

Fig. 9 is a detailed view showing manner of fastening tubes.

In high temperature apparatus the parts which are subjected to high temperatures for heating may be comprised of various refractories and ceramic materials such as silicon carbide, aluminum silicate, zirconium silicate, fire clay, alumina and various fused compositions. Such materials are more or less inflexible and if rigidly joined to metal or cemented into other refractories, subsequent heating and the distortion produced thereby, produce the breaking of joints, the forming of cracks or other openings in various parts of the apparatus. In my apparatus I have found a construction whereby such defects may be avoided and at the same time refractory materials employed in the construction of my apparatus which will resist high heating.

For a more complete understanding of my invention and general functioning of my invention

in apparatus set-up, reference is made to Fig. 1.

In Fig. 1, the stock to be pyrolyzed may be supplied from the container 1. Any force required for putting it in flow may be available from the natural pressure of stock in the container 1, or from superposed gaseous pressure above the liquid therein, or by any other suitable means (not shown), such as by introducing a pump into the line 2. In the line 2 may be a valve 3 for regulating the rate of flow. Following valve 3 may be a flow meter 4, followed in turn by a heater 7. The said heater is preferably put in use if the stock tends to condense, solidify or otherwise exert resistance to flow. The heater 7 may operate in the conventional manner by admitting a heating medium around the tube 6. At the pipe juncture 11 the stock may join with another material such as diluent furnished under pressure through the pipe 12 if it is desired to add such material. Valve 13 serves for adjusting the rate of flow of this other material, and 14 is a flow meter in the line. A pipe 60 may also make communication with the point of juncture 11 for admitting further material in a manner to be described hereinafter.

The various materials to be pyrolyzed thereby become intimately mixed in the pipe 15 which may carry the feed to a preheater 16. This preheater comprises a housing 38 and a heating coil 17 that receives the feed from pipe 15. The heating medium for the feed in coil 17 may be flue gas in countercurrent, coming from the furnace 42 operating in conjunction. Flue gases forming in the combustion chamber 63 of the said furnace, pass into a duct 65, and may be divided into two streams by manipulation of the two dampers 31 and 40, which construction therefore serves as means for controlling the degree of preheat for the feed in coil 17. From the coil 17 the feed passes into the pipe 19, in which there may be a chamber as at 66. If a chamber is not desired, the pipe 19 may lead directly to the trap 20. The purpose of this trap is to catch residues such as oils, resins, tars and the like that may form from the feed at times due to the action of the preheater 16. Any accumulation in trap 20 may be drained at will through valve 21.

Material that is not removed in the trap 20, continues through pipe 22, and enters the main pyrolysis tube 24 through a fitting 23. The tube 24 is heated by one or more burners as at 25, supplied with fuel and air, respectively, through valves 26 and 27 for regulating the degree of temperature in the said pyrolysis tube. Preferably there are at least two such burners, disposed to give a more or less uniform heating of the said tube. Pyrolyzed mixture leaves the tube 24, passes through a fitting 29, and enters pipes 30, 74, and 75 which may convey it to a cooler, quencher or other device 43, which it enters at a point 32. The said pipes 30, 74, and 75 are preferably water-jacketed or otherwise cooled, and preferably both fittings 23 and 29 are of artificially-cooled design, as will be brought out in full later.

Thermocouples or other devices 79 and 81 may be inserted in my apparatus at suitable places. It is also apparent that flow meters and other such instruments may be employed in my apparatus at other points than those shown. The indication of such instruments in Fig. 1 has merely been for the purposes of illustration and is not to be construed as limiting my invention.

The means 43 is according to the embodiment

shown, preferably a tower fitted with water connections such as 34, 35, and 36, each of these having a valve as indicated for adjustment, and a spray device 64 within the tower in operating relation to the said water connection and valve. The pyrolyzed materials cooled by the pipe 30, on entering tower 43, at 32, may be suddenly chilled by the water sprays within. At the same time any diluent, if of boiling point substantially higher than that of the final gas temperature in the tower, will for the most part be condensed. Together with such diluent, will be removed from the cracked mixture, the greater part of any high boiling materials such as oil, asphalt or tar vapors, particles of solid organic matter, and particles of carbon that the said products may contain as a result of the pyrolysis operation in tube 24. Such material removed by the liquid spray will generally be in a fluid condition, making possible its removal from the tower at will, as through the liquid seal 44.

Cooled pyrolyzed materials make exit from tower 43 at a point 33, containing perhaps residues also of liquid and solid by-products. Pyrolyzed gas will be so termed herein till reaching the point 47 of the unit 48, regardless of intermediate changes in its character. Filters 37' and 37, are provided where there are removed particles of oil and asphalt fog, and particles of solid organic matter and carbon. Deposit in the filters may be removed by steaming, hence filtration is carried out in one filter while steaming the other. Steam connections are not shown, nor will alternate operation of the filters be detailed. An oil scrubber 86 may be provided which removes from the materials traces of the same kinds of deposits caught by the filters 37. The said scrubber is not detailed, but circulates an oil that makes intimate contact with the gas in a conventional manner and takes to itself further heavy impurities in the gas.

Beyond the oil scrubber 86 and connected therewith is the suction end of the pump 69, whose full function is to be explained later. 71 is a valve for by-passing part of the discharge of pump 69. The said valve 71 is operated by pressures in chambers 23 and 63 communicating through pipes 72 and 73, respectively. The purpose of this valve 71 is to maintain a desired ratio between the pressures in the chambers 23 and 63. From the exit end of the pump 69, the materials may be passed through a meter 46, a gas holder 85, and then preferably through a dryer 61 for removing traces of any liquids for the most part condensed in the quencher 43.

In combination with my apparatus may be one or more units 48, for treating the products produced in the pyrolysis apparatus. These units which may comprise scrubbing towers, absorbers and the like, may be connected with one another, and with the remainder of the system by conduits 47, 53 and 83. Conduits 83 and 53 may lead back to the pyrolysis apparatus as shown for recycling materials to the quencher 43 or other units. For example, the liquid used in treating the products produced might also be satisfactory as a cooling medium to supply to the quencher 43. By my apparatus arrangement such a liquid might be used in 48, conducted to 43 and further used. Such an arrangement assists in eliminating losses.

It should be repeated that Fig. 1 does not show each of the units of the process in its exact form, but diagrammatically. More particularly is this true of the unit 48, which is shown to indicate

points at which I would prefer to apply apparatus to accomplish separations, purification, or other treatment desired.

As indicated, I have provided apparatus to circulate some or all of products produced, allowing them to pass through valve 57 and the meter 56, so that they may enter pipe 60 which communicates with the point of juncture where is fed the original stock. In the case of such recirculation, then, necessarily the raw material to be pyrolyzed consists of mixed stock in the proportion as indicated on the meters 4, 56 and 59. It is clear that each of the said stocks at will may be analyzed so as to determine, in connection with the meter readings, the exact composition of the material resulting from them.

It will be plain that the passage of flue gas through the tunnel 65 at the rate desired, may be assured either through positive pressure from the burners as at 25, or through applying suction to the flue gases issuing from the preheater 16 and the by-pass 39. In the first case of course, the burners 25 should be in gas-tight relation to the furnace 42, while the said furnace in turn must be made to withstand the slight internal pressure needed to force the flue gases through the tunnel 65 as desired. In the second case the housing 38 of the preheater 16, and the stack (not shown) which receives flue gas from the by-pass 39, must be designed to deliver to a source of suction the gases passing through them. At the same time the furnace and connected chambers handling flue gas, must be sufficiently strong to withstand the suction applied, as is well known to those skilled in the art.

In the preceding paragraphs I have described in detail a complete assembly for my high temperature apparatus together with its associated parts such as feeding mechanism thereto, a preheater and means for controlling or otherwise treating the materials produced in the pyrolysis tube. As indicated above, one feature in the high temperature apparatus under description which requires particular consideration is my provision for assembling the heating conduit with other conduits, the furnace wall and associated parts in order to obtain a gas-tight relationship, yet provide a construction which under heating to extremely high temperatures does not break, crack or otherwise fail. For a more complete understanding of this feature of my invention, reference is made in particular to Fig. 2.

Fig. 2 shows in considerable detail a tube unit such as might be employed in Fig. 1, as at 23, 24, 29 and the manner in which these are assembled for accomplishing to best advantage the purposes of the said parts, separately and in conjunction. The said tube is shown connected to fittings bottom and top for receiving and delivering the material being processed. At 204 is shown the base-plate of the furnace, in which may be built a refractory housing as indicated at 205. The region 206 then forms the combustion space encircling the tube 203 and corresponds therefore with the space 63 of the furnace 42 of Fig. 1.

In Fig. 2 again, the tube 203 at its lower end is preferably spherically ground to fit a seat of spherical shape 218, and the said tube rests thereon in such a way that if it is tilted slightly from the vertical, there results but a slight sliding of two substantially concentric spherical areas that maintain snug contact, as is of course desirable. Preferably, there is placed between the said cooperating surfaces, a gasket such as of copper and asbestos, to improve gas-tight rela-

tionship as well as to facilitate the sliding of the surfaces. The said seat 218 is formed in a flanged fitting 215 which is made fast to a flanged hollow ring 252 by means of a plurality of cap-screws 216. The seat may be integral with the water-cooled casting, if desired. The annular chamber 213 carries water for water-cooling.

The said hollow ring 252 in turn has a flange 210 which is made fast to a flange 211 through the agency of a plurality of shouldered studs 214 co-operating with nut 253. Flange 211 becomes part of the furnace base-plate 204 by virtue of the collar 254 which is integral with both. The said collar 254 is of large enough diameter for the hollow ring 252 to slide within it, and dimensions of the two cooperating parts are such that when they are in operating relationship, the upper faces of the base-plate 204 and the hollow ring 252 substantially coincide. At the same time, water connection from the ring 252 to the outside is made through nipples 212 and 217 threaded into the said ring. The said nipples pass preferably through holes formed in the collar 254, to be threaded into the hollow ring 252 as shown, in water-tight relationship.

At 207 is a housing made fast to the studs 214 through the agency of nuts that draw up the flange 209 of the housing 207 against the flange 210 of the hollow ring 252, in gas-tight operating relationship, as preferably with a gasket between them. At 208 is a nipple integral with the housing 207 that connects with conduit 22 from the preheater 16 of Fig. 1.

Referring again to Fig. 2, the flanged fitting 215 that supports the tube 203 at the seat 218 may also support on an internal shoulder 222, the corebuster assembly within the tube 203. At 255 is a thimble with a cylindrical skirt 220 of diameter for fitting within the hole in the flanged fitting 215, and adapted to rest squarely on the shoulder 222 of the fitting. The thimble 255 at its upper end is approximately spherical, but contains perforations 257 for making communication from the housing 207 to the annular chamber 248 between the corebuster 219 and the tube 203. The said thimble with its perforations thus may form a sort of spider that can support at its top the weight of the corebuster, while at the same time giving passage to materials from the inside of housing 207 to the annular chamber 248.

The corebuster indicated at 219 can be of any of a number of different shapes, but is here shown cylindrical, and concentrically placed in the tube 203 by virtue of lugs 247 integral with each corebuster section. However, as will be pointed out hereinafter, there will be a definite area relationship in the unit. There may be a hole 224 in the corebuster axially concentric therewith, for the purpose of admitting a thermocouple or other devices therein.

In Fig. 2 again, the upper end of the tube 203 abuts a shoulder 258 integral with a tube-portion 225 of internal diameter approximately that of the inside of tube 203. At 239 the tube-portion 225 makes a turn from vertical to horizontal and continues for a short distance thus in the tube 259, making gas-tight connection with the corrugated flexible tube 240. The said flexible tube 240 in turn is made gas-tight at its far end, to the flange 241 which in turn serves for making connections to piping, as for instance the pipe 30 of Fig. 1. Thus as in Fig. 1 the materials may be carried from the pyrolysis tube 24 to the quencher 43 as described above.

Referring to Fig. 2 again, 243 is a nipple integral with the tube 259, and making communication to the inside of said tube. The said nipple 243 is also substantially concentric with the core-buster 219 within the tube 203, and thus serves for a means of introducing a thermocouple or other device within the corebuster as already referred to.

Gas-tight relationship between the cracking tube 203 and the tube-portion 225 is made through the gland 228 surrounding the said tube 203 and surrounded by a cylindrical wall 226 which is integral with the shoulder 258. Between the tube 203 and the wall 226 is a suitable packing 227, preferably of asbestos, which effects gas-tight cooperation between tube 203 and the tube-portion 225 by virtue of pressure exerted on said packing by the gland 226.

The wall 226 is integral with a flange 268 which in turn is integral with a cylindrical wall 229 of substantially larger diameter than that of the wall 226, and surrounding it so as to form an annular space 250. The said wall 229 also extends beyond the upper end of said wall 226, and is integral with an internal flange 260. The said flange 260 has a hole of diameter appreciably larger than the outside diameter of tube-portion 225, and concentric therewith, so that the said tube-portion may extend through the said flange without touching it, and in fact with the benefit of considerable clearance for reasons to be set out.

Coaxially integral with the internal flange 260 are two concentric tube-portions 230 and 231, the former having an internal diameter preferably that of the hole in the said flange 260, and the latter having an internal diameter approximately midway of those of the said tube-portion 230 and the cylindrical wall 229. Thus there is formed between the two tube-portions 230 and 231, an annular trough to serve as a seal in cooperation with a vertical tube 237 of diameter suitable for fitting loosely therein. The said tube 237 extends upwardly where a tube 238 of preferably the same diameter as tube 237, communicates therewith in a convention pipe-T relationship. The said tube 238 is further located at a point to be concentric with the flexible tube 240, and at its free end makes integral connection with the flange 241. With this spatial relationship, the vertical tube 237 extends well down into the trough 232, not so far as to touch the bottom of it, but in fact allowing considerable clearance, again for reasons to be made clear.

The flange 260, towards its outer edge, that is, beyond the tube-portion 231 offers a shoulder to receive a flange 236 loosely thereon. The said flange 236 has an external diameter considerably greater than that of the tube-wall 229, and approximately that of the flange 249 of the packing-gland 228. While the said gland flange 249 has a plurality of studs 234 integral therewith and extending upwardly and spaced approximately equally in a circle about the wall 229, the flange 236 has a circle of holes toward its outer edge consecutively coaxial with the said studs 234 so as to engage them. The upper threaded ends 263 of the said studs 234 pass through the said holes in the flange 236, so as to cooperate with nuts 235 that draw them upward. Thus is the gland 228 upwardly thrust against the packing 227 as desired.

The foregoing description of the fitting made fast to the upper end of tube 203, makes it clear that there is free communication between the

chambers 250, 264, and 265, which thus together form a jacket suitable for water-cooling the tube assembly that carries the hot pyrolyzed mixture from the upper end of the tube 203 to the flange 241. To make the said jacket function, nipple 246, is supplied for making communication with the chamber 250 for admitting water, while nipple 242, communicating with chamber 265, serves as an overflow for exit water, and mercury or other seal 233 in the trough 232, completes the requirements. Water entering through nipple 246 fills chambers 250, 264, and 265 in order, and rises in tube 237 to the level 245 maintained by the overflow nipple 242. Mercury in the trough 232 acts as a seal and prevents water from escaping at that point. In this manner it is obvious that all the piping handling pyrolyzed mixture delivered by the upper end of the tube 203 is effectively kept from burning, melting or otherwise depreciating. Particularly is this of advantage in the service of the corrugated tube 240, which necessarily is frail, but nevertheless important in assuring satisfactory service from the tube 203.

For it is to be expected that in the course of life of the tube 203, and particularly in beginning operations, there will be endwise expansion, and contraction, as well as bending and twisting according to the fortuitous demands of possible non-uniformity in the tube material, and irregularity in firing of the furnace. It is herein considered to be obvious from the description of the assembly as shown in Fig. 2, in view of the detail presented in the said figure, how the tube 203, while being held in perfectly suitable gas-tight relationship with its lower and upper cooperating fittings, is yet free to follow any thermal motions to which it may be subject. For with the spherical seat 216 it is clear that the upper end of the tube 203 without difficulty may remain substantially concentric with the tube 237 at some point between their opposed ends. Consequently, my apparatus is suitable for carrying out processes requiring temperatures substantially greater than 1000° C.

Thus though the tube 203 at its upper end may be tilted due to bending, ample clearance is provided between tubes 225 and 237 so as to obviate binding between them, while obviously the end of the flexible tube 240 affixed to the tube 259, follows the movements thereof. Twisting of tube 203 likewise is tolerated by the said flexible tube 240.

If desired, the assembly consisting of tubes 237 and 238, together with flange 241, may be counterweighted at a point indicated by the eye-bolt 266 integral with pipe 238. And if it is desired to relieve the weight resting on the tube 203 as described, this may be accomplished by counterweighting the assembly concerned at a point indicated by the eye 267 integral with the thermocouple nipple 243.

Thus, in short, the combination of parts shown in Fig. 2 and described, and cooperating as described, eliminate substantially all strain on the tube 203, with the one exception of compression at its upper end due to gland and packing. The value of this accomplishment will be clear when it is appreciated that heat resisting refractory ware such as may be used for tube 203, while in the service of being heated to 1000° C. or higher there is a severe temperature gradient not only through the wall of the tube, but also axially along the wall.

It may be pointed out also that at the bottom

of tube 203 cooling may be limited to what is necessary for keeping the gasket on the seat 218 in good condition. At the top of the tube, conversely, it may be desirable to perform as much cooling as possible, to assist in cooling and recovering the desirable products. Fig. 2 is developed in sufficient detail to make it obvious that the cooling functions are intended as described.

As indicated above, the tube 203 contains a filler, 24a or 24b such as shown in detail in Fig. 3-6. Such fillers possess a number of advantages in my apparatus, such as improving the heat transfer, and may be employed at other points such as in the preheater. Preferably, the size of this device is in accordance with the following wherein ratio of surface to volume will be expressed in square feet per cubic foot. For instance, in a preheater tube of 1.75 inches internal diameter, without corebuster, the said ratio might be

$$\frac{48}{1.75} = 27.4$$

If a corebuster is present, the sum of the internal areas exposed to the materials being pyrolyzed, is divided by the net volume bounded by said areas. If the corebuster is cylindrical, the volume is then annular. If the outer surface of the corebuster has a special shape, the area of that surface is measured or estimated for use as above.

Ratio of area to volume, hereinafter to be termed area ratio, in the preheater tube may range from as much as 250 to as little as 5. I have found that the range permissible here may be varied, since it may be compensated not only with temperature, but also with residence period. For the higher the area ratio, the more rapidly the gas will absorb heat, the less severe the temperature need be, or the less the period of heating. Wide fluctuation of area ratio brings wide fluctuation of residence period, but not such a great variation of temperature. Hence, the temperature range remains nevertheless rather well fixed.

While discussing the construction of my preheater, it is desired to point out that the preheater may be constructed of metal because it is not required to withstand such high temperatures as the pyrolysis tube. It is also apparent that the preheater is traversed by feed materials which are at a lower temperature than the products flowing in the pyrolysis tube, hence may be cooled somewhat by such feed. The preheater may be constructed of any of various metals of which may be mentioned chrome steels containing for example, between 15-40% chrome, chrome-aluminum steels containing from about 8-18% chromium, and a few per cent aluminum or various other steels such as chrome-molybdenum, chrome tungsten or the like. It is also possible to use chrome-nickel steels, and other heat-resisting alloys but the aforementioned types of materials are preferred.

Reference is now made to the interrelationships of variables in the apparatus shown in Fig. 2, for example.

Although any dense refractory of good heat conductivity and resistance to spalling may be used as wall material for the tubes 203, I prefer carborundum, zirconium silicate or the like. The corebuster within the tube can be made of either of these materials, or still others such as sillimanite since the corebuster is not usually subject to as high a temperature or such severe strains as the tube, and need not remain in such

superior mechanical condition. Whatever the material of the corebuster, it should not be such as not to slag down with the tube material.

I find that I can use tubes of any diameter, so long as I hold to a proper proportion of length to diameter, and to a reasonably light wall. The corebuster, if cylindrical, must be such as to maintain a reasonable range of clearance between corebuster and tube wall, regardless of tube diameter. If the corebuster is not cylindrical, as in Fig. 5, it should be such as to present a similar range of path section as the said cylindrical corebuster.

For example, a tube of 2-inch internal diameter may conveniently have a heated length of 36 inches, and a wall thickness of $\frac{1}{2}$ inch, while the corebuster may be of from 1.0 to 1.80 inches diameter. A tube of 4 inches internal diameter may have a length of 6 feet exposed to the combustion chamber, a wall thickness of $\frac{3}{8}$ inch, and a corebuster of from 2.0 to 3.70 inches. Again, a tube of 8-inch internal diameter may have an exposed length of 12 feet, a wall thickness of $1\frac{1}{2}$ inches, and a corebuster of from 4.0 to 7.60 inches.

The area ratios resulting from these assembly dimensions are, for the 2-inch tube, 48 to 240, for the 4-inch tube 24 to 160, and for the 8-inch tube 12 to 120. Fairly large values of ratios are preferred. With the large tubes, it is preferred to employ the cylindrical corebuster, one of increased contact area such as shown in Fig. 4. Particularly is this true in the hottest part of the tube.

Thus for illustration, in a 4-inch internal diameter tube of $\frac{3}{8}$ inch wall thickness, a very suitable diameter of cylindrical corebuster is $3\frac{1}{2}$ inches, giving an area ratio of 96. If instead of using the cylindrical corebuster, I adopt one such as in Fig. 6 giving the same net cross section of gas path, we may easily increase the area ratio to 200 and above. In general, then, I prefer to hold the area ratio above 100 in the largest tubes, of diameter greater than 8 inches.

In the preceding I have described apparatus comprising a single pyrolysis tube. In my apparatus a single pyrolysis tube functions satisfactorily and has considerable capacity. As pointed out, by my type of construction, it is possible to employ tubes of a considerably larger size than employed in the prior art. That is, certain prior constructions have employed tubes no larger than an inch in diameter.

However, my invention has wider application and may embrace constructions containing a plurality of tubes as will now be briefly described. Referring now to Fig. 7 which represents my pyrolysis apparatus on an enlarged scale, the unit 101 may be of a circular type containing a plurality of vertical ceramic tubes. These tubes may be the same construction as those described with respect to Fig. 2 and contain a corebuster. As already indicated, one of the important features for consideration is my novel arrangement for supporting the tubes so as to assure tightness yet freedom of movement to provide for expansion.

It will be noted that in this unit, tubes may be ground to fit a water-cooled metal seat at 103, as described under Fig. 2. The top is connected in a non-rigid manner as at 104.

After the tubes have been inserted through holes 106, the roof may be placed in position and connections made through the water-cooled packing gland 104 to which may be integrally connected water jacketed pipe 107 which extends

up to flange 108. This double walled cooled conduit is made flexible and free to move by the bellows construction 109. Cooling as shown serves several purposes. It makes possible a simple bellows construction for taking up movement of the tube. Also it provides a means for controlling the temperature of the products within the tube.

The several other features of my novel unit are clear from inspection of the drawings. A plurality of burners 111 of any construction suitable for the temperatures involved are distributed around the unit as shown. In the preferred arrangement indicated, a conduit 112 is provided for distributing combustion air and another conduit 113 is provided for distributing fuel.

The shape of the chamber surrounding the tubes has been arranged to produce rapid combustion and great heat liberation. The velocity of flow of the heating gases is increased and heating improved by means of the radiant reflectors 116 which forms the reflected annular passageway immediately below the combustion space. The slots 117 and passageway 118 are provided for conducting the combustion gases from the unit to the various preheating equipment already shown and described in Fig. 1.

The head construction of this unit may be composed of a number of suspended refractory parts designated 121. A removable section 122 may be provided for inspection of the inside of the unit and, also may be opened to prevent explosion.

The bottom of the unit is provided with the inlet conduits 123 which may be connected with conduit 22 of Fig. 1.

While in the preceding description vertical furnaces containing one or more pyrolysis tubes have been described, my invention has wider applications. The form of construction shown in Figs. 1-7 are preferred because it is possible to obtain better joint construction, weight distribution, freedom from sagging and other advantages. However, my invention may be carried out in a horizontal type of furnace in accordance with the following description with respect to Fig. 8.

In Fig. 8, 131 represents furnace construction within which may be positioned one or more pyrolysis tubes or units 132. These tubes are of the same construction as those designated 3, 24 and 102 in Figs. 1, 2 and 7. They are positioned within the furnace wall in a firm but non-rigid manner similar to that already described. That is, one end of the tube as at 133 may be more or less firmly fixed or seated in the furnace. The other end of the tube, as at 134 is attached in a firm but flexible manner which will permit the tube to move in all directions sufficient to take up movement, due to thermal distortion. Since this type of construction has already been described to some extent and will be further described with respect to Fig. 9, added description at this point appears unnecessary. A plurality of conduits 135 and 137 are provided for feeding materials to be pyrolyzed to the unit. In the instance of conduit 137, provision is made for preheating as at 138. In connection with this preheating device, it will be noted that heat from the burner 139 in the combustion chamber 141 escapes through a baffle construction 142. In this construction, it is possible to keep the preheating tubes out of radiative contact with the pyrolysis unit. Positioned above the preheating tubes may be still further units such as air heater 143, 181, 182, for air feed to the burners. Associated with

the other end of the pyrolysis unit as at 144 is a chamber from which the products produced in the apparatus may be withdrawn through a cooled conduit 146. The connection of this conduit with the apparatus may be rendered movable in a manner already described with respect to previous connections. This conduit is connected with a quencher or scrubber 147 of a construction similar to device 43 of Fig. 1. This quencher 147 may be connected through conduit 148 with one or more scrubbers or other devices 149 for further treating the materials produced. Conduit 151 is provided for conducting the materials away from the last of these units. As in Fig. 1, the heating chamber 141 is interconnected by means of the line 152 to a pressure balancing device 153 which in turn is interconnected with the pyrolysis chamber by means of line 154. A pressure-regulating device is interconnected by means of line 156 with a by-pass mechanism 157, 158.

The functioning of this by-passing arrangement is the same as the parts 60, 71, 76, 23, and 63 of Fig. 1, that is, as a further aid to providing apparatus in which the destruction thereof by high heating conditions is minimized. I have provided arrangement whereby the pressure inside of the pyrolysis unit may be equalized or maintained at some predetermined relationship with the pressure in the heating chamber. It is apparent that due to different temperature gradients there will also be different pressures developed within the apparatus at different points. Referring to Fig. 1, by my construction the pyrolyzed materials produced in the apparatus leaving the device 86 are picked up by pump 69 and may be ejected through the valve 80, which is open when starting the operation. The proper adjustment is then made on stud 76 of the by-pass valves 71 so as to hold the pressure within chamber 23 the same (or at any desired relationship) with respect to the combustion zone 63. Valve 71, of course, performs this function by relieving suction on the pump 69 through the by-passing line through which it operates. A similar function of the apparatus arrangement shown in Fig. 8 takes place.

Reference is now made to Fig. 9 wherein more detail is shown means for firmly yet non-rigidly connecting the pyrolysis unit into the furnace. 132 represents the tubes upon the end of which may be shrunk a steel sleeve 161. At either end of this steel sleeve flanges 163 and 164 may be welded or otherwise securely attached. To the end flanges a bellows construction 166 and 167 may be brazed or otherwise securely attached. These bellows are also fastened to a large central flange 168 which encircles the pyrolysis unit as do the bellows and other members. This flange may be bolted to a tube sheet 169 or other construction forming a part of the furnace wall. In this manner the tubes may be firmly attached to the furnace but at the same time be free to move sufficient for taking up expansion or other distortion due to extreme heating. Conduit means 171 and 172 are provided for circulating cooling fluid in the construction.

From a consideration of the various forms of my invention which have been shown, it will be observed that my novel apparatus possesses a number of advantages, a few of which are summarized below. In the constructions which I have shown, it will be observed that the pyrolysis chamber is firmly positioned in the heating or combustion chamber, yet by virtue of my novel non-rigid construction is free to move in sub-

stantially all planes. By this construction, extreme heating of the pyrolysis tube does not cause breakage thereof, pulling away from furnace walls, leakage and other defects encountered in prior art constructions. By my construction it is possible to employ pyrolysis tubes of several inches in diameter as contrasted to the use of very small sized equipment in prior art constructions. Although as indicated, a single large tube construction functions satisfactorily, my invention may be employed on a larger scale and a number of pyrolysis units positioned within the heating chamber.

As a further aid to the maintenance of conditions wherein gas leakage, strains and other destructive influences on the apparatus may be minimized, I have provided the aforementioned pressure-regulating mechanism between the pyrolysis tubes and heating chamber.

It is apparent, that in apparatus constructed for use at temperatures in excess of 800° C., the question of heat transfer and heating of the materials to be pyrolyzed is of considerable importance. As already pointed out, I have found certain important "area ratios" for obtaining maximum efficiency. In my furnace construction I have provided means for obtaining such area ratios as well as means whereby the area ratios may be changed or varied.

While the feature of preheating by means of flue gases is applied in a number of apparatuses, it will be noted that I have provided a construction wherein the preheater is out of radiative contact with the pyrolysis unit. I have found this to be a desirable feature in apparatus operating at extremely high temperatures; otherwise the preheater might tend to cool the pyrolysis unit.

The functioning of my apparatus is more or less apparent from the preceding description. However, brief reference is made to Fig. 1 for a consideration of the example which is set forth merely for the purposes of illustration and is not to be construed as a limitation of my invention.

Materials to be treated may be fed in through the several conduits shown, all joining at 11 and entering the preheater through conduit 13. Among the materials which may be treated are the various hydrocarbons such as methane, ethane, propane, butane, pentane, and the like. These materials may be mixed with steam, halogen or various other agents and may contain recycled materials supplied through 60. Materials fed in may include unsaturated compounds such as ethylene, propylene, and the like. The feed is preheated in the preheater and from the preheater pass through conduit 22 into the main pyrolysis chamber. It is, of course, apparent that a higher preheat, for example, in the neighborhood of 800-1000° C. alleviates to some extent the degree of heating necessary in the pyrolysis unit. Pyrolysis unit 24 may be heated by means of a burner 28 to a temperature in excess of 1000° C., say, for example, in the neighborhood of 1400° C. Such heating together with control of residence period in the pyrolysis unit will bring about various chemical changes depending upon the particular process being carried out and the exit products leaving the apparatus through conduit 14 may contain one or more of the materials, acetylene, benzene, naphthalene, olefines such as ethylene, propylene and the like. The material or various materials produced may be cooled, separated or otherwise processed in the various units 43 and 48. Certain of the residual

components may be recirculated as already indicated.

While my apparatus is particularly suitable for converting saturated hydrocarbons to unsaturated compounds, it is apparent from the preceding that my invention has a number of other uses, hence, I do not wish to be restricted, except insofar as may be necessitated by the prior art and the spirit of the appended claims.

What I claim is:

1. Apparatus for the continuous treatment of materials at temperatures in excess of 800° C., which comprises a furnace having a heating chamber with at least one exit passage therefrom, a preheater in an exit passage connected through a trap with at least one refractory pyrolysis tube of a diameter greater than one inch in the heating chamber, the preheater and pyrolysis unit being positioned out of substantial radiative contact with one another, means associated with the pyrolysis tube for fastening it to the furnace and to other elements in a gas-tight, non-rigid manner whereby temperatures in excess of 1100° C. may be applied thereto, said means including a double wall construction having a flexible bellows therein, thereby forming a chamber in which cooling fluid may be circulated, conduits leading to a plurality of units for treating the products produced in the apparatus, and return conduits leading to the apparatus from at least some of these treating units.

2. Apparatus for heating materials to high temperatures, which comprises a furnace having a heating chamber, a pyrolysis tube having a diameter greater than two inches, extending through the chamber and at least partially through the furnace walls, means associated with both the furnace and tube for holding the tube in a firm but non-rigid manner so that high heat may be applied to the tube without material dislodgment thereof from attachment to the walls, said means including a flexible double wall construction in which cooling water may be circulated, and a pressure regulating device connected with the apparatus for maintaining the pressure within the pyrolysis chamber at a predetermined relationship with the pressure exterior thereof.

3. Apparatus for the thermal treatment of materials to temperatures in excess of 800° C., which comprises a furnace having heating chamber with exit passages therefrom, a preheater having an area-ratio between 27-600, in an exit passage connected with at least one refractory pyrolysis unit having an area-ratio between 48-400, in the heating chamber, the preheater and pyrolysis unit being positioned out of substantially radiative contact with one another, means associated with the pyrolysis unit for fastening it to the furnace and to other conduits in a gas-tight, non-rigid manner whereby temperatures in excess of 800° C. may be applied thereto, said means comprising a double wall construction having a flexible bellows therein, in which cooling fluid may be circulated, a plurality of units for treating the products produced in the apparatus, and return conduits leading to the apparatus from at least some of these treating units.

4. Apparatus for the thermal treatment of gaseous hydrocarbon-containing materials to temperatures in excess of 800° C., which comprises a furnace having heating chamber with exit passages therefrom, a preheater having an area-ratio between 25-100, in an exit passage connected through a trap with at least one re-

fractory pyrolysis unit having an area-ratio between 100-400, in said heating chamber, means associated with the pyrolysis unit for fastening it to the furnace and to other conduits in a gas-tight, non-rigid manner whereby temperatures in excess of 800° C. may be applied thereto, said means comprising a double wall construction having a flexible bellows therein to form a chamber in which cooling fluid may be circulated.

5. Apparatus for carrying out a thermal treatment at temperatures in excess of 800° C., which comprises a furnace having a heating chamber with at least one exit passage therefrom, a preheater in an exit passage connected with at least one refractory pyrolysis unit in the heating chamber, means associated with the pyrolysis unit for fastening it to the furnace and to other conduits in a gas-tight, non-rigid manner whereby temperatures in excess of 800° C. may be applied thereto, said means comprising a spherical seat receiving one end of the pyrolysis unit, a hollow ring adapted for circulation of cooling fluid encircling the jointure, means on the hollow ring for the connection thereof with the seat, furnace and other parts, a metal conduit which terminates in a shoulder and flange, said shoulder and flange abutting and embracing the other end of the pyrolysis unit, a gland containing packing between the pyrolysis unit and flange, concentric collar means for exerting pressure on the packing and firmly connecting the unit with the furnace, a double wall construction having a flexible bellows therein, comprising at least a portion of the metal conduit to form a chamber in which cooling fluid may be circulated, and an outlet conduit leading from the apparatus.

6. Apparatus for heating materials to temperatures greater than 1000° C., which comprises a furnace having a heating chamber, a pyrolysis tube having a diameter greater than one inch and having an area-ratio between about 100-400, extending through the chamber and at least partially through the furnace walls, means associated with both the furnace and tube for holding the tube in a firm but non-rigid manner so that high heat may be applied to the tube without material dislodgment thereof from attachment to the walls, said means including a double wall construction having a bellows therein and inlet and outlet conduits leading to the apparatus.

7. Apparatus for heating materials to high temperatures, which comprises a furnace having a heating chamber, a vertical-refractory pyrolysis tube extending through the chamber and at least partially through the furnace walls, means associated with both the furnace and tube for holding the tube in a firm but non-rigid manner, said means including a double wall construction having a flexible bellows in the inside wall and a metal seal on the outside wall.

8. Apparatus for thermal treatment at temperatures in excess of 800° C., which comprises a furnace having a heating chamber with exit passages therefrom, a preheater in an exit passage connected through a trap with at least one vertically extending refractory pyrolysis unit having a diameter greater than two inches in said heating chamber, the preheater and pyrolysis unit being positioned out of substantially radiative

contact with one another, means associated with the pyrolysis unit for fastening it to the furnace and to other conduits in a gas-tight, non-rigid manner whereby temperatures in excess of 1000° C. may be applied thereto, said means comprising a cooled spherical seat and a double wall construction having a flexible member therein.

9. Apparatus which comprises a furnace having heating chamber with exit passages therefrom, a preheater in an exit passage connected with at least one vertically-extending refractory pyrolysis unit in said heating chamber, a plurality of feed conduits connected to the preheater, means associated with the pyrolysis unit for fastening it to the furnace and to other conduits in a gas-tight, non-rigid manner whereby temperatures in excess of 800° C. may be applied thereto, said means comprising a seat to receive the lower end of the pyrolysis unit, a hollow ring adapted for cooling the seat, a flange associated with the hollow ring for the connection thereof with the seat and furnace, a metal conduit which terminates in a shoulder and flange, said shoulder and flange abutting and embracing the upper end of the pyrolysis unit, a gland containing packing between the pyrolysis unit and flange, concentric collar means for exerting pressure on the packing and connecting the unit with a furnace, said conduit comprising a chamber in which cooling fluid may be circulated, another metal conduit connecting the first-mentioned metal conduit and leading to a quencher unit for treating the products produced in the apparatus, and at least one return conduit leading to the feed conduits.

10. Apparatus for high temperature use, which comprises a furnace having a heating chamber with at least one exit passage therefrom, a preheater in an exit passage, connected with at least one horizontally extending refractory pyrolysis tube in the heating chamber, means associated with the pyrolysis tube for fastening it to the furnace and to other elements in a substantially gas-tight, non-rigid manner, said means including a flexible double wall construction attached to the tube, thereby forming a chamber in which cooling water may be circulated, which construction is free to move with respect to the furnace, conduits associated with said construction for supplying the water, and conduits leading to a plurality of units for treating the products produced in the apparatus.

11. Apparatus for heating materials to high temperatures, which comprises a vertical furnace having a heating chamber, a vertical pyrolysis tube extending through the chamber, a spider member positioned in the lower portion of said tube, the pyrolysis tube including a refractory corebuster having protrusions thereon for positioning the corebuster in spaced relation from the chamber supported on the spider, means associated with both the furnace and pyrolysis chamber for holding it in a firm but non-rigid manner so that high heat may be applied thereto, said means including a non-rigid double wall construction in which fluid may be circulated and conduits connected therewith for supplying and withdrawing said fluid.

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