Oct. 10, 1950 J. H. SHAPLEIGH 2,525,276

METHOD OF CRACKING HYDROCARBONS

Filed Aug. 22, 1946

Fig. 1

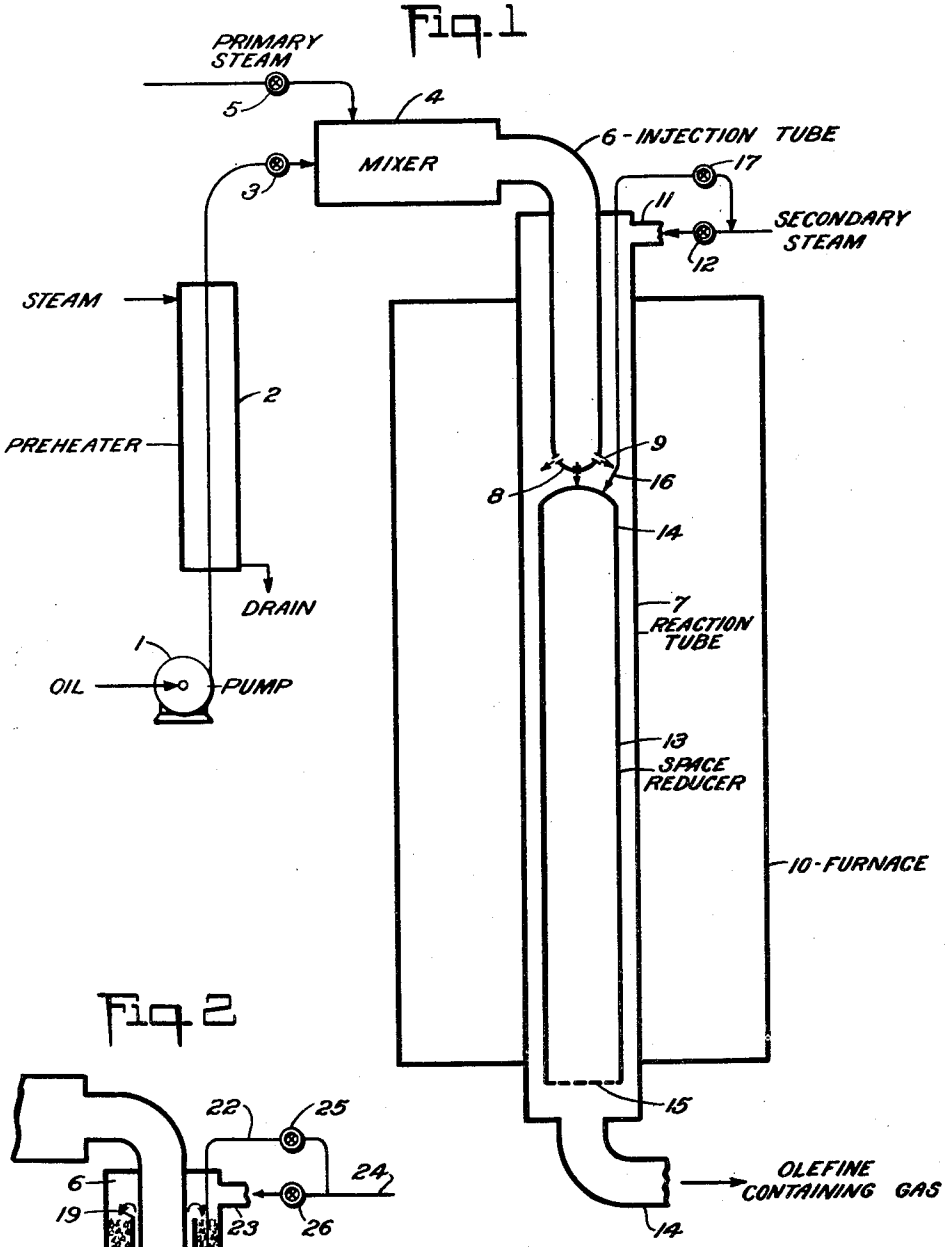
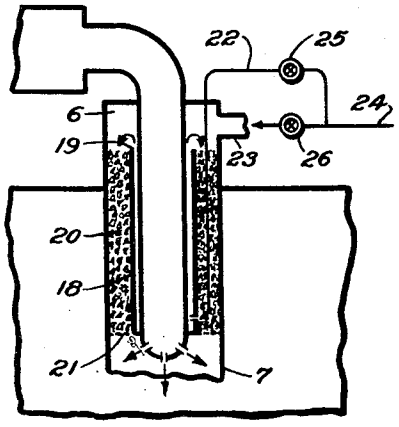


Fig. 2



INVENTOR
JAMES H. SHAPLEIGH.
BY Ernest G. Peterson
AGENT

Patented Oct. 10, 1950

2,525,276

UNITED STATES PATENT OFFICE

2,525,276

METHOD OF CRACKING HYDROCARBONS

James H. Shapleigh, Wilmington, Del., assignor to Hercules Powder Company, Wilmington, Del., a corporation of Delaware

Application August 22, 1946, Serial No. 692,345

13 Claims. (Cl. 196—63)

1

This invention relates to the cracking of hydrocarbons and more particularly to a novel process and apparatus for the thermal cracking of normally liquid, as well as normally gaseous, hydrocarbons.

In the art of cracking hydrocarbons with one objective the substantial production of olefines, the fear of serious carbon deposition together with a fear of ethylene polymerization, has resulted in a retardation of improvement whereby the state of the art is substantially behind the somewhat related art of cracking hydrocarbons for hydrogen production. The processes for ethylene production are actually pointed toward use of only the most highly favorable raw materials, usually propane, kerosene and gas oil or at the most, steam distillates from heavier oils. Processes using whole oils are singularly lacking and the facilities of reaction control existing in the art of hydrogen production are absent in the majority of processes for ethylene production, due probably to the assumption, perhaps unwarranted, that ethylene is more difficult to produce. The art is therefore in need of a practical flexible process, similar to that used in hydrogen production and adaptable to the cracking of whole oils to produce valuable liquid components as well as olefines through reaction control.

In the art of producing ethylene representative processes are those of Nagel (U. S. Patent No. 2,111,899) and Grebe (U. S. Patent No. 2,176,962) who use the principle of flash mixing and reacting separate streams of hydrocarbon and steam highly preheated so as to be self-sufficient as to total heat requirement. Another representative process for the production of ethylene is carried out in a refractory regenerative type of apparatus such as shown, for example, in U. S. Patent No. 2,208,123 to Duncan.

In contrast to the flash heat method of Nagel and Grebe or the regenerative type of Duncan are the tubular-type processes in which olefines are produced from sulfur-containing hydrocarbons and steam in chrome-nickel alloy tubes under controlled temperature conditions. The patents to Wietzel (1,934,836) and Balcar (2,218,495) and Reissue Patent No. 21,521 to J. H. Shapleigh disclose representative processes of this type. Wietzel discloses the use of chrome-nickel alloy in the catalytic cracking of hydrocarbons with

2

steam in an art utilizing sulfur-containing gases within the limits allowed by catalysts in use. Shapleigh discloses a process for treating fluid reactants in a tubular furnace fired at a plurality of spaced points to produce countercurrent firing and flexible temperature control of the reacting fluids. Balcar discloses a way of preparing a steam distillate, but fails to describe all important details of how to furnace process to avoid carbon deposition or to control reaction.

The tubular-tyle process has been highly developed in the field particularly applied to hydrogen, and it is known to the few skilled in its use how successful it is in controlling temperature of the reacting fluids. Even so, it is recognized that in treating hydrocarbons, particularly in preheating them in the temperature zone a few hundred degrees short of that necessary for a good reaction velocity, there is a great tendency for carbon deposition to take place, the seriousness depending upon the feed stock used. It is also possible to prolong contact of hydrocarbons with excessively heated surfaces to the detriment of economic oil cracking, if operated by unskilled hands. This lack of familiarity with tubular furnace operation has contributed much to a fear of carbon deposition, excess cracking, polymerization and general mechanical difficulty such as short tube life. It may account for the less flexible flash heat-type process.

Now in accordance with the present invention it has been discovered that if atomized oil or oil vapor mixtures at noncondensing temperatures and at substantially atmospheric pressure, are injected suddenly into a stream of steam within an externally heated alloy tube, the mixture can be supplied with heat during its further passage through the remainder of the tube to bring about satisfactory cracking of oils with a minimum of carbon deposition and a maximum of flexibility of temperature, time and pressure control. The process of this invention provides an improvement not only in olefine production but in the cracking of oils and gaseous hydrocarbons to produce maximum value of total products, and in selective production of particular products. Whole oils, i. e., those containing asphalt and the heavy hydrocarbons, as well as the lighter hydrocarbons and the normally gaseous hydrocarbons, may be used without substantial car-

bon deposition. In fact, no serious carbon deposition whatsoever has been found to occur within the cracking tube in commercial size application. This constitutes an established successful improvement not heretofore possible without the hazards of carbon build-up.

In practice hydrocarbons, such as liquid petroleum hydrocarbons including deasphalted oils and crude stocks, for example East Texas crudes, are atomized with steam (or other suitable gas) without heating to a thermal decomposition temperature, and then injected in a novel manner into a stream of superheated steam (or other suitable gaseous medium containing the required amount of sensible heat) at one end of an externally heated alloy tube to substantially completely vaporize the oil and form a gaseous mixture of hydrocarbons and steam and immediately thereafter passing the mixture through the remainder of the tube which is maintained at the desired temperature by direct heating. The hydrocarbons are thereby cracked into a mixture of constituents including olefines, which may then be treated in any suitable manner to retard polymerization, to separate normally liquid from the normally gaseous components and/or to separate liquid and/or gaseous streams into components. The process is continuous and results in a product high in olefine content.

Having now indicated in general the nature and purpose of the present invention, there follows a more detailed description of the invention with reference to the accompanying drawing in which Figure 1 represents, diagrammatically, a flow sheet indicating the production of olefines and other products by the thermal cracking of a petroleum oil in the presence of steam, and Figure 2 is a modification of the novel injection and mixing means of this invention.

Referring now to Figure 1 of the drawing the petroleum oil is delivered by means of a pump 1 from any suitable oil reservoir to a preheater 2 where it may be heated with steam by indirect heat exchange to a predetermined temperature depending upon the raw material used. The preheated oil is passed through a measuring valve 3, and delivered to a mixer 4 where it is atomized and partially vaporized with a primary stream of saturated or superheated steam (called primary steam) which is delivered to the mixer through a measuring valve 5. The atomized and partially vaporized mixture of oil and primary steam is then injected into a concurrently moving, concentrically disposed, body of a secondary stream of steam (called secondary steam) by means of an injection tube 6. The injection tube 6 extends a predetermined distance into the entrance end of a reaction tube 7, heated externally by a furnace 10, and is provided with a rounded end 8 having perforations 9. The atomized and partially vaporized mixture of oil and primary steam is confined within the injection tube until it reaches the exit end 8 thereof when it passes through the perforations 9 in a plurality of streams. Thus, it is heated to a predetermined temperature by indirect heat transfer from the furnace.

The secondary steam is delivered to the reaction tube 7 by means of a conduit 11 controlled by a measuring valve 12. It flows concurrently, but out of direct contact, with the oil-primary steam mixture, the atomized oil-primary steam mixture being within, and the secondary steam being outside of, the injection tube. The oil-

primary steam mixture exits from the injection tube through the perforations 9 and into the annular stream of secondary steam. By this procedure, the atomized oil-primary steam mixture is intimately and quickly admixed with the secondary steam, and quickly heated by direct heat exchange of sensible heat of the secondary steam, which has been heated in the upper portion of the reaction tube.

The atomized and previously partially vaporized oil is further vaporized and the intimate gaseous admixture of hydrocarbons and steam is passed quickly through the indirectly heated, annular, reaction space between the walls of the reaction tube and a tubular space reducer 13 disposed axially within the reaction tube.

The tubular space reducer 13 is provided at its upper end with a closure 14 and at its lower end with a perforated plate 15. Steam may be introduced to the space reducer 13 by a pipe 16 controlled by a valve 17. In operation a small amount of steam is admitted to the space reducer 13 to maintain complete displacement of any hydrocarbons which would otherwise enter the interior thereof through the perforated plate 15. Regulation of the steam passing into the member 13 additionally aids in controlling the temperature of the steam-hydrocarbon mixture passing through the reaction tube.

The reaction product containing olefines is withdrawn from the reaction tube through a conduit 14, quenched by liquid hydrocarbons and the mixture passed to a plate column for separation and recovery of the normally gaseous and normally liquid products. Quenching, separation and recovery of products may be accomplished by means well known in the art. Products from the plate column may then be disposed of as such or mixed with feed stock or otherwise recycled through the process.

In the modification of the device shown in Figure 2 a portion of the injection tube 6 is surrounded by a concentric tube or jacket 18 having its upper end open as at 19. The space between the reaction tube 7 and the tube or jacket 18 is filled with ring packings or other suitable material 20 to promote heat transfer to the secondary steam and/or to reduce the radiation of heat to the injection tube The packing material 20 is suitably supported on a perforated plate or screen 21 mounted adjacent the exit end of the injection tube. Steam pipes 22 and 23 are connected to a steam header 24 and serve to introduce the secondary superheated steam to the lower portion of the tube 18 and to the upper portion of the reaction tube 7, respectively. Suitable measuring valves 25 and 26 selectively control the flow of steam through the pipes 22 and 23.

In the operation of this form of the device all or a portion of the secondary steam may be introduced into the lower portion of the tube or jacket 18 and passed countercurrent to the flow within the injection tube prior to entering the outer concentric space. Steam passing through the tube 18 exits therefrom through the open end 19 and mixes with any secondary steam introduced through the pipe 23. The mixture then passes downwardly through the packing material 20 and mixes with the hydrocarbon-steam mixture as it exits from the injection tube. This arrangement provides a very effective temperature control of the steam-hydrocarbon mixture flowing through the injection tube while at the same time permitting the secondary steam pass-

tube the more B. t. u. input to the primary steam is required. This is favored by oil preheat, by the use of superheated steam and by injection tube conditions conducive to high heat tranfer, such as high velocity, use of fins, etc., for increasing surface and turbulence. The steam-oil ratio can also be varied to assist attainment of the best conditions. The exact conditions of temperature of oil and steam, manner of mixing and ratio in which they are mixed in order to obtain an atomized and partially vaporized oil-primary steam mixture, will depend upon the characteristics of the given hydrocarbon and the conditions of treatment as will be understood in the art.

The atomized and partially vaporized mixture of hydrocarbon and primary steam is then passed through the injection tube where it is heated by the superheated steam flowing on the exterior of the tube and by indirect heat from the wall of the reaction tube. The temperature of the mixture as it exits from the injection tube may vary from about 250° F. to about 800° F. but preferably does not exceed about 600 to 650° F. The temperature selected depends upon the volatility of the hydrocarbon, its stability to heat, the ratio of hydrocarbon to steam and the time in transit. A temperature is selected which results in partial vaporization of the hydrocarbon by the time it leaves the injection tube but which does not result in substantial thermal decomposition of the hydrocarbon constituents within the injection tube. It will be understood that the hydrocarbons of the petroleum fractions with a low boiling range are more easily volatilized but, at the same time, are more stable at elevated temperature than are those with a higher boiling range.

The heated mixture of oil and primary steam, in which the oil has been partially vaporized, is then injected into a concurrently moving, superheated body of secondary steam confined within the reaction tube. The objective, at this point, is to flash heat and mix the hydrocarbon vapor and particles by quickly injecting the hydrocarbon into the hot secondary steam with minimum or no impingement on the high temperature cracking tube wall which, in this zone, is at a temperature of about 1500 to 1900° F. The stream of secondary steam acts to cushion the projected vapors and particles and to turn the hydrocarbon trajectories into axially promoted, turbulent flow into a zone at reaction temperature. In this manner, the vaporization of the oil is quickly completed, while at the same time, the hydrocarbons are flash heated to substantially reaction temperature and the mixture supplied with reaction heat from the furnace along its reaction path. These conditions minimize the carbon-producing type of thermal decomposition of the hydrocarbons and are conducive to elimination of any carbon formed.

There is considerable latitude as to the method of injecting the primary steam-hydrocarbon mixture into the stream of secondary steam. The mixture may be injected at any angle to the secondary stream. It may be injected at multiple points laterally and/or axially. It may be injected tangentially or by any other means suitable to the objective. Angular injection at about 60° away from the axis with a small amount at 0° along the axis and from a conical or spherical end, is preferred.

The position of the injection point axially along the cracking tube can be varied. For instance, with a heavy oil it is preferred to utilize a point about 6 feet from the furnace arch, wall or hearth nearest the gas entrance end of the furnace. However, for an oil of Diesel grade, good results are obtained, utilizing about 3 feet.

The injection tube may be jacketed or unjacketed depending upon other factors. For example, when packing is not used in the secondary steam space, it may be desirable to reduce the radiation effect between the cracking tube and the injection tube walls to promote control of injection temperature. This can be done by use of a jacket on the injection tube and with all or a part of the secondary steam passed through the jacket countercurrently to the primary steam-hydrocarbon mixture flow and subsequently into the secondary steam channel. In other cases it may be desirable to utilize both the jacket and packing material as shown in Figure 2 of the drawing.

The secondary steam is supplied to the reaction tube in the manner shown in either Figure 1 or Figure 2, one objective being to prepare a secondary stream of steam at temperatures preferably ranging from about 1000° F. to about 1600° F. at the point of mixing with the primary steam-hydrocarbon mixture exiting from the injection tube. The temperature to be attained in any particular case depends upon the relative amounts of secondary steam and oil-primary steam mixture, the temperature of the oil-primary steam mixture just prior to mixing with the secondary steam, the thermal stability of the hydrocarbons, and the like. The above objective may be realized by utilizing superheated steam and by further heating the steam as it passes through the reaction tube. Various methods may be used, if desired, to promote and/or accelerate heat transfer from the reaction or cracking tube. One method involves the use within the cracking tube of surface exposed to radiant heat. Another method involves the use of heat-resistant metallic packing supported on a perforated plate attached to the injection tube as shown in Figure 2. If desired the packing may be confined within a containing metal tube concentric with the cracking tube and suitably suspended from an end plate of the same or otherwise mounted on the injection tube and/or perforated plate to form a removable packing assembly.

On mixing of the oil-primary steam and the secondary steam a flash lowering of hydrocarbon partial pressure takes place simultaneously with flash heating and with further heating from the wall of the cracking tube, and soon thereafter from the wall of the inner spacer tube. The combination of low partial pressure and temperature immediately or quickly thereafter creates a condition whereunder all hydrocarbons except extremely small amounts of high boilers must be in the vapor state and undergoing reaction. The higher the temperature at the time of mixing the oil-primary steam and the secondary steam, the more complete the hydrocarbon vaporization on flash mixing.

The most satisfactory conditions as to temperatures, ratio of primary steam to oil, ratio of secondary to primary steam, etc., will be determined by experiment for each particular oil or set of other conditions such as feed rate, type of oil, etc.

The total amount of steam used, primary plus secondary, will depend upon a number of considerations. Since in the process of this invention the steam serves essentially as a bulk heat me-

ing through the packing material to be quickly heated to the desired degree.

In accordance with this invention and to illustrate in more particular the method of producing olefines and other products by the thermal cracking of hydrocarbons in the presence of steam, several examples in tabular form are given below. These examples illustrate the results obtained from the use of various type oils when feeding each oil in its entirety, i. e., without any prior separation of favorable from unfavorable components, to the cracking tube. Asphalt and all components of each oil entered the cracking tube.

to obtain maximum values for industrial use and particularly for use in the chemical industry.

The successful cracking of hydrocarbons with attendant production of olefines and other products by the thermal cracking of hydrocarbons in a tubular cracking furnace in the presence of steam primarily depends (1) on the proper preparation and introduction of the steam-hydrocarbon mixture into the alloy cracking tube and (2) passing the mixture through the remainder of the tube under controlled conditions of temperature, reaction time and pressure to produce the desired result.

The novel method of properly preparing and

TABLE

Results of tests on various oils

	#2 Fuel		Deasphalted Residual			E. Texas Crude	
	(a)	(b)	(a)	(b)	(c)	(a)	(b)
Cu. Ft. Exit Gas per 100 lbs. Oil Cracked. S. T. P. and Dry Basis	1,820	1,965	1,395	1,500	1,785	1,530	2,240
Per Cent Olefines	46.3	41.7	61.7	57.4	46.0	53.3	41.0
Steam-Oil Wt. Ratio:							
Primary	1.0	.9	.6	.6	.6	.9	.9
Secondary	.9	1.0	2.0	1.4	1.9	2.0	2.1
Total	1.9	1.9	2.6	2.0	2.5	2.9	3.0
Temperatures °F.:							
Injection Tube Exit degrees	255	260	260	300	300	290	310
Sec. Steam at Inj. Pt do	1,150	1,090	1,270	1,285	1,310	1,310	1,380
Avg. Tube-Metal Wall do	1,650	1,650	1,585	1,610	1,640	1,600	1,650
Lbs. Oil Feed Per Tube/Hr	124	155	146	154	154	102	102
Type Injection	Angular penetration of secondary steam						
Per Cent Feed Cracked	54	48	47	49	51	64	73

The foregoing examples do not represent maximums nor optimums. The process is flexible whereby feed rates can be substantially increased, the per cent oil cracked varied up or down, and the gas produced per 100 pounds of oil increased or decreased. Gas rates of 3940 cubic feet per 100 pounds of oil have been obtained containing 18% olefines with a good percentage of C_2H_2, and 3690 cubic feet with 20% C_2H_2 plus C_2H_4. This represents a rate of gas production of the order of 12,000 cubic feet per barrel. The figures in the table above represent a rate of gas production of the order of 4000 to 7500 cubic feet per barrel of oil fed.

Likewise it has been found that some oils can beneficially be cracked substantially 100%, obtaining, for example, 30% or better total olefines and eliminating the step of fractionation separation of gas from uncracked oil. Thus, for instance, the product from the reaction column can be quenched with intermediate hydrocarbon fractions, or with water, and the gas passed direct to pressure-low temperature absorption-liquifaction equipment or to adsorption processes for gas component separation.

Depending upon the oil cracked and upon the precise process conditions used, there is obtained, under conditions of partial cracking and after quenching and condensation, a liquid product which may be lighter than water, whereas under other conditions the unfractionated condensate may be a creamy liquid heavier than water. The components of the uncracked oil vary but conditions under which the cracking takes place affect the percentage of any group of components and of any one in particular.

The liquid portion may contain for instance, butadiene, isoprene, styrene, indene, naphthalene and resins aside from more normally expected cuts. This invention, therefore, comprises not only an advantageous process for economically producing olefines but a process for cracking oils

introducing the steam-hydrocarbon mixture according to the present invention consists in atomizing and partially vaporizing the hydrocarbon preferably with steam, passing the atomized and partially vaporized mixture of hydrocarbon and steam through an injection nozzle extending into the cracking tube and quickly injecting the atomized and partially vaporized mixture into a stream of superheated steam. Optional preheating of hydrocarbons is accomplished by any suitable type of device such as an indirect heat exchanger, the degree of desired heat varying with the type of raw material and being supplied in insufficient amount to cause any appreciable decomposition of the hydrocarbon. Desirable hydrocarbon preheat temperatures at this point are in the order of about 250° F. but may be varied from about 200° F. to about 500° F. under different operating conditions and when treating different kinds of hydrocarbons. No preheat need be used with light hydrocarbons or gaseous hydrocarbons and dependence is placed on the heat in the secondary steam plus indirect heat to the injection tube.

The hydrocarbon, when in liquid form, is atomized and partially vaporized with high pressure primary steam, the objective being to put the hydrocarbon into either the vapor state or a fine state of subdivision. Hydrocarbons readily volatilized, such as ethane and propane, can be fed to the injection tube wholly in the vapor state. With oils the primary steam functions to prepare the oil in a fine state of subdivision by means of a mixer or atomizer, to retard coalescence prior to injection into the secondary steam and to promote partial vaporization. Tthe lowering of the partial pressure of the oil by the steam within the injection tube lowers the boiling point and assists vaporization. To the extent that vaporization can occur without carbon deposition, it is favorable to the process.

The higher the vaporization in the injection

a vertical or horizontal furnace with any combination of injection tube and exit flue gas location, with or without multiple chambers along the axis of the tube, and with ascending or descending tube temperature gradients or combinations thereof. This flexibility in conjunction with others such as temperature level, diluent gas and oil ratio, or steam-oil ratio, time of contact and pressure makes possible a marked improvement in the control of output of desired products. An important control is obtained through the use of the multiple point firing plan of Reissue Patent No. 21,521 to James H. Shapleigh which may be modified in this process to either countercurrent or parallel flow of process and combustion gases.

The reaction tube of the present invention preferably consists of an inner spacer tube and an outer cracking tube concentrically arranged, as shown in Figure 1, and made from a chrome-steel alloy containing about 25% chromium, 20% nickel, 1% columbium and the remainder substantially iron. These specific proportions are merely given for purposes of illustration, however, and it will be realized that other suitable alloys may be used. The reaction tube may be vertical, horizontal or inclined depending on the conditions of use, space available, etc. Very effective temperature control is afforded by direct heat applied to the exterior of the outer tube in the manner heretofore stated, and by the added surface provided by the spacer tube.

If desired, the inner spacer tube may be replaced by packing rings or other suitable material or the spacer tube removed and the empty reaction tube utilized. However, in each case, conditions must be such as to give the required heat transfer and time of passage within the reaction zone.

The steam-hydrocarbon mixture may be injected into the reaction tube at either end, i. e., at the end from which combustion gases exit or at the opposite end. As applied to Figure 1, for example, injection may take place either near the top of the tube as shown, or near the bottom of the tube, combustion gases flowing countercurrent or parallel to the steam-hydrocarbon mixture, and being discharged adjacent either end of the tube as desired.

Although it is desirable in most instances to obtain a high percentage of cracking of the hydrocarbons it is possible and sometimes desirable to obtain a partial cracking, i. e., from about 50% to 75% cracking, and to recycle portions of the uncracked products for mixture with feed stock, thus resulting in a favorable lower viscosity net feed. A further advantage of this procedure lies in the effective use of recycle stocks for quenching the reaction products from the cracking tube.

The present process is advantageously carried out at substantially atmospheric pressure although pressures somewhat above or below atmospheric can be used with satisfactory results. In addition, pressure of 25 to 100 pounds per square inch can be used successfully to regulate types and proportions of products obtained. Operating pressures of this order may be obtained by providing a regulating valve at the end of the cracking system.

By the process of injecting and flash heating, in accordance with this invention, it will be noted that the liquid hydrocarbons containing sulfur do not come in contact with the metal wall in any case except possibly with traces of very high boilers and then not to any appreciable or serious extent. The hydrocarbons within the cracking tube proper, are above the dew-point. Further, the sulfur containing hydrocarbon vapors are out of contact with the metal wall at the temperatures whereunder carbide precipitation and any coincident sulfur attack normally occurs to any serious extent. Under the conditions of injection the mercaptans present are converted to H_2S and cause no difficulty under the temperature and hydrocarbon dew-points prevailing.

The process of this invention is adaptable to the injection of emulsions, oils containing catalysts, and oils containing anti-carbon forming materials. It is applicable to the treatment of normally gaseous as well as normally liquid hydrocarbons. Although preferred apparatus and procedure have been set forth, it will be realized that many changes may be made without departing from the scope of the invention.

A particular advantage of the present invention resides in the fact that higher yields of olefines and valuable liquid products are obtained with less carbon trouble than has hitherto been possible in the cracking of hydrocarbons in tubular furnaces. A further advantage resides in the successful and economical treatment of whole oils, the heavier liquid petroleum hydrocarbons, deasphalted oils and crude stocks containing asphalt. This makes it possible to take advantage of the availability and economy of such raw materials and without limitation on the geographical location of plants hitherto considered necessary.

This application is a continuation-in-part of my copending application for United States Letters Patent, Serial No. 576,481, filed February 6, 1945.

The words "concurrent" and "parallel," as used in the specification and claims, apply to the flow of fluids and mean parallel flow in the same direction as contrasted to countercurrent, meaning parallel flow in opposite directions.

What I claim and desire to protect by Letters Patent is:

1. A process of cracking hydrocarbons which comprises flowing a finely-diffused hydrocarbon along an inner path in a cracking tube, flowing steam concurrent therewith along an outer path concentric with the inner path and in contact with the cracking tube, applying heat to the cracking tube to superheat the steam, causing the hydrocarbon flowing from the inner path to mix directly with the steam flowing along the outer path in contact with the cracking tube, and immediately passing the mixture of steam and hydrocarbon through the cracking tube while applying heat to bring about satisfactory cracking of the hydrocarbon without appreciable carbon deposition.

2. A process of cracking hydrocarbons which comprises flowing a finely-diffused hydrocarbon along an inner path in a cracking tube, flowing steam concurrent therewith along an outer path concentric with the inner path and in contact with the cracking tube, applying heat to the cracking tube to superheat the steam to a temperature above about 1000° F., causing the hydrocarbon flowing from the inner path to mix directly with the steam flowing along the outer path in contact with the cracking tube at a temperature above about 800° F., and immediately passing the mixture of steam and hydrocarbon through the cracking tube while applying heat to bring about satisfactory cracking of the hydrocarbon without appreciable carbon deposition.

dium, a partial pressure reducer for hydrocarbons and as an anticarbon deposit material, it can be varied in relation to the quantity of oil fed to vary conditions of time of contact or temperature, to regulate temperature conditions of injection, and temperature gradients along the reaction path both radially and axially. The steam-hydrocarbon ratio can be varied to give either high or low ratios as desired for less difficult or more difficult feed stocks, but normally will be in the range of ratio of .1 to 1 to 5 to 1. It is preferred to use steam-hydrocarbon ratios varying from about 1 to 1 to 3 to 1.

The exact manner in which the steam is proportioned between primary and secondary depends upon a number of factors as already indicated. In some cases it may be desirable to atomize the hydrocarbon with some other medium than steam, such as for example hydrogen, nitrogen, combustion gases, etc., under pressure. In such cases all of the steam is furnished as secondary steam. On the other hand, all of the steam may be introduced in the atomization, and some other heated gaseous medium besides steam may be used for the heating and diluting in the secondary stream of gas. Hot combustion gases, heated hydrogen or nitrogen, etc., may be used.

An important part of the present invention and one which aids greatly in attaining the objective of efficiently cracking hydrocarbons in the presence of steam is the formation of an atomized and/or vaporized mixture of the higher hydrocarbons with steam, maintaining the material in a state such that there is minimum coalescence of the hydrocarbons, and flash heating the mixture to a cracking temperature without appreciable carbon deposition.

Although it is preferred to form the desired mixture of steam and vaporized hydrocarbons within the cracking tube, as illustrated and described, it may under some circumstances be desirable and satisfactory to form the mixture separately and then pass it to and through the reaction tube. This may be accomplished by providing a separate injection and mixing means, embodying the principles already described, and connecting it to the reaction tube by a flanged coupling, pipe or other suitable connecting means.

The thing of importance is to obtain a gaseous mixture comprising steam and vaporized hydrocarbons from higher petroleum hydrocarbons, particularly normally liquid petroleum oils, containing about .1 to 5 parts by weight of steam for each part by weight of oil, at a temperature of from about 1000° F. to about 1600° F., substantially free of free carbon.

The gaseous mixture of steam and vaporized hydrocarbons which should be at a temperature of at least about 700° F. and preferably from about 1000° F. to about 1600° F. is immediately passed through the remainder of the cracking tube. Factors which are of primary importance in this phase of the process are temperature of the steam-hydrocarbon gas, metal wall temperature in its relation to temperature gradient, and contact or reaction time. These factors depend on the characteristics of the hydrocarbon being cracked, the ratio of quantity of oil to quantity of steam and/or other gas, percentage cracking desired, etc. In general, steam-hydrocarbon temperatures varying from about 1100° F. to about 1700° F. give the gest results and are preferred. Such temperatures are not, however, critical and may be extended to provide conditions most favorable to the specific oil and products sought. Metal wall temperatures are regulated in relation to the other conditions of treatment to give the desired temperature and temperature gradient within the reaction zone.

Reaction time under given conditions of treatment will depend on the selected temperature and hydrocarbon partial pressure. When the temperature is increased the reaction time will be correspondingly decreased and vice versa. Generally it has been found that comparatively short reaction times varying from about .1 to 5 seconds and preferably from about .1 to 1 second are most effective.

Reaction products from the cracking tube are preferably quenched by the use of liquid hydrocarbons and the quenched gas stream passed to a fractionating tower system to separate the normally liquid and gaseous products.

The flexibility of the process of the present invention is partly obtained through the ability to control temperature gradients and temperature itself both axially and radially in the cracking tube.

Radially it is obtained with respect to a point or zone on the tube wall by firing the furnace to give a specific tube wall temperature, and by controlling the transfer of heat to the gas stream, for example, by changing the gas velocity, by changing the area for gas passage or by increasing the throughput, by changing the ratio of outer and inner tube surface, by the use of fins, deflectors, etc., to increase turbulence, by changing the steam-oil ratio or the diluent-oil ratio generally, and by the use of packing material.

Axially, control may be obtained in a number of ways. One procedure involves the use of a furnace in which heat is selectively applied at spaced points along the periphery of the reaction tube, the hot combustion gases flowing upwardly along the tube countercurrent to the flow of steam-hydrocarbon mixture therethrough, and passing off through a flue exit adjacent the end at which the steam hydrocarbon mixture is injected into the secondary steam. By this procedure furnace zone temperatures can be adjusted at will, but a high downward gradient, i. e., high temperature at the injection zone and low temperature at the gas exit becomes increasingly difficult to obtain, the greater the desired gradient.

In a slightly different procedure hot combustion gases are passed downwardly around the reaction tube, parallel to and concurrent with the flow of steam-hydrocarbon mixture therethrough, and are discharged through a flue exit adjacent the end of the tube opposite that in which the steam-hydrocarbon mixture is mixed with the secondary steam, heat being applied at spaced points along the tube as before. This procedure gives good control, particularly where high temperature is required in the injection zone and low temperature is required in the reaction zone. Either of the above procedures may be modified by firing adjacent the end of the tube rather than at spaced points along the tube.

In a still different procedure cross radiation can be materially lessened and full benefit from a selected firing plan realized when utilizing a single chamber furnace. In this case, by the use of one or more partition walls along the axis of the tube, zones are formed which contribute to finer points of gradient control. Tubes and combustion products pass through said partition walls by means of proper openings.

These procedures may be carried out in either

3. A process of cracking hydrocarbons which comprises flowing a finely-diffused hydrocarbon containing more than two carbon atoms per molecule and heated to a temperature below about 800° F. along an inner path in a cracking tube, flowing steam concurrent therewith along an outer path concentric with the inner path and in contact with the cracking tube, applying heat to the cracking tube to superheat the steam to a temperature above about 1000° F., causing the hydrocarbon flowing from the inner path to mix directly with the gaseous medium flowing along the outer path in contact with the cracking tube at a temperature above about 800° F., and immediately passing the mixture of steam and hydrocarbon through the cracking tube while applying heat to bring about satisfactory cracking of the hydrocarbon without appreciable carbon deposition.

4. A process of cracking hydrocarbons which comprises flowing a gaseous hydrocarbon along an inner path in a cracking tube, flowing gaseous medium concurrent therewith along an outer path concentric with the inner path and in contact with the cracking tube, applying heat to the cracking tube to superheat the gaseous medium, causing the hydrocarbon flowing from the inner path to mix directly with the gaseous medium flowing along the outer path in contact with the cracking tube, and immediately passing the mixture of gaseous medium and hydrocarbon through the tube while applying heat to bring about satisfactory cracking of the hydrocarbon without appreciable carbon deposition.

5. A process of cracking hydrocarbons which comprises flowing gaseous hydrocarbon along an inner path in a cracking tube, flowing gaseous medium concurrent therewith along an outer path in the cracking tube and in contact with the cracking tube wall, applying heat to the cracking tube, causing the hydrocarbon flowing from the inner path to mix directly with the gaseous medium flowing along the outer path in contact with the cracking tube, and immediately passing the mixture of gaseous medium and hydrocarbon through the tube while applying heat to bring about satisfactory cracking of the hydrocarbon without appreciable carbon deposition.

6. A process of cracking hydrocarbons which comprises flowing finely-diffused hydrocarbon along an inner path in a cracking tube, flowing gaseous medium concurrent therewith along an outer path in the cracking tube and in contact with the cracking tube wall, applying heat to the cracking tube, causing the hydrocarbon flowing from the inner path to mix directly with the gaseous medium flowing along the outer path in contact with the cracking tube, and immediately passing the mixture of gaseous medium and hydrocarbon through the tube while applying heat to bring about satisfactory cracking of the hydrocarbon without appreciable carbon deposition.

7. A process of cracking hydrocarbons which comprises flowing a finely diffused hydrocarbon along one path, flowing steam countercurrent thereto along a second path concentric therewith, flowing the same steam along a third path concentric with and countercurrent to the flow of steam in the second path, applying indirect heat to the third path to superheat the steam, causing the finely diffused hydrocarbon to mix with the steam flowing through the third path, and immediately passing the mixture of steam and hydrocarbon through a cracking tube while supplying heat thereto to bring about satisfactory cracking of the hydrocarbon without appreciable carbon deposition.

8. A process of cracking hydrocarbons which comprises flowing a finely diffused hydrocarbon along one path, flowing steam countercurrent thereto along a second path concentric therewith, admixing additional steam with the steam flowing from the second path, flowing the resulting steam mixture along a third path concentric with and countercurrent to the flow of steam in the second path, applying indirect heat to the third path to superheat the steam, causing the finely diffused hydrocarbon to mix with the steam flowing through the third path, and immediately passing the mixture of steam and hydrocarbon through a cracking tube while supplying heat thereto to bring about satisfactory cracking of the hydrocarbon without appreciable carbon deposition.

9. In a device for the cracking of hydrocarbons in a furnace the improvement comprising a cracking tube, spacer means in the cracking tube forming an annular passage, injector means extending into the cracking tube, means for flowing gaseous medium along the injector means exteriorly thereof, means for heating the gaseous medium as it flows along the injector means, and means for passing a partially vaporized hydrocarbon through the injector means and injecting it into the flow of gaseous medium to form a mixture of hydrocarbon and gaseous medium.

10. In a device for the cracking of hydrocarbons in a furnace, the improvement comprising an exteriorly-heated cracking tube, spacer means in the cracking tube forming an annular passage, injector means extending into the cracking tube, means for flowing gaseous medium along the injector means exteriorly thereof and in contact with the cracking tube, means for passing a gaseous hydrocarbon through the injector means and injecting it into the flow of gaseous medium to form a mixture of hydrocarbon and gaseous medium, and means for passing gaseous medium through the spacer means.

11. In a device for the cracking of hydrocarbons in a furnace the improvement comprising injector means, means for passing a finely diffused hydrocarbon through the injector means, means for flowing steam through a confined path concentric with the injector means, means for flowing the same steam through a second confined path concentric with the first-mentioned path, the flow of steam in the first path being countercurrent to and the flow of steam in the second path being in the same direction as the flow of finely diffused hydrocarbon through the injector means, and means for injecting the finely diffused hydrocarbon into the stream of steam flowing through the second path to form a gaseous mixture of hydrocarbon and steam.

12. A device according to claim 11 including means for mixing additional steam with the steam passing from the first path to the second path.

13. A device according to claim 11 including a cracking tube into which the injector means extends, spacer means in the cracking tube, means for passing steam through the spacer means, and means for passing the gaseous mixture of hydrocarbon and steam through the cracking tube.

JAMES H. SHAPLEIGH.

(References on following page)

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,445,040	Read	Feb. 13, 1923
1,477,860	Adams	Dec. 18, 1923
1,613,010	Armstrong	Jan. 4, 1927
1,621,652	Bean	Mar. 22, 1927
1,627,937	Tingley	May 10, 1927
1,628,532	Coultas, Jr.	May 10, 1927
1,698,811	Forward	Jan. 15, 1929
1,792,912	Landes	Feb. 17, 1931
1,944,483	Zieley	Jan. 23, 1934
2,176,962	Grebe	Oct. 24, 1939
2,377,847	Allen	June 12, 1945