Sept. 15, 1959 J. H. SHAPLEIGH 2,904,502

METHOD OF CRACKING HYDROCARBONS

Filed Feb. 19, 1954 3 Sheets-Sheet 1

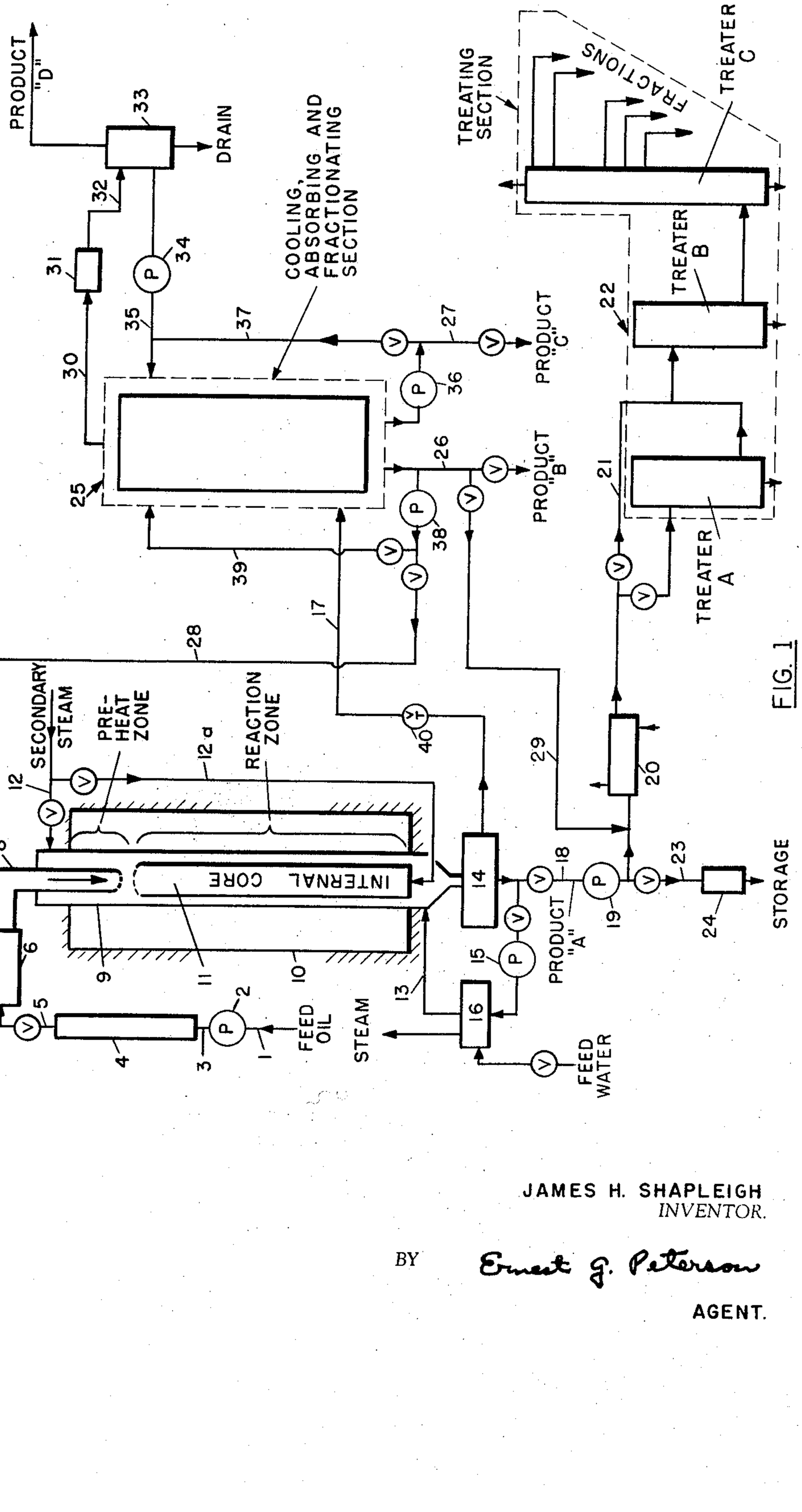

FIG. 1

JAMES H. SHAPLEIGH
INVENTOR.

BY Ernest G. Peterson

AGENT.

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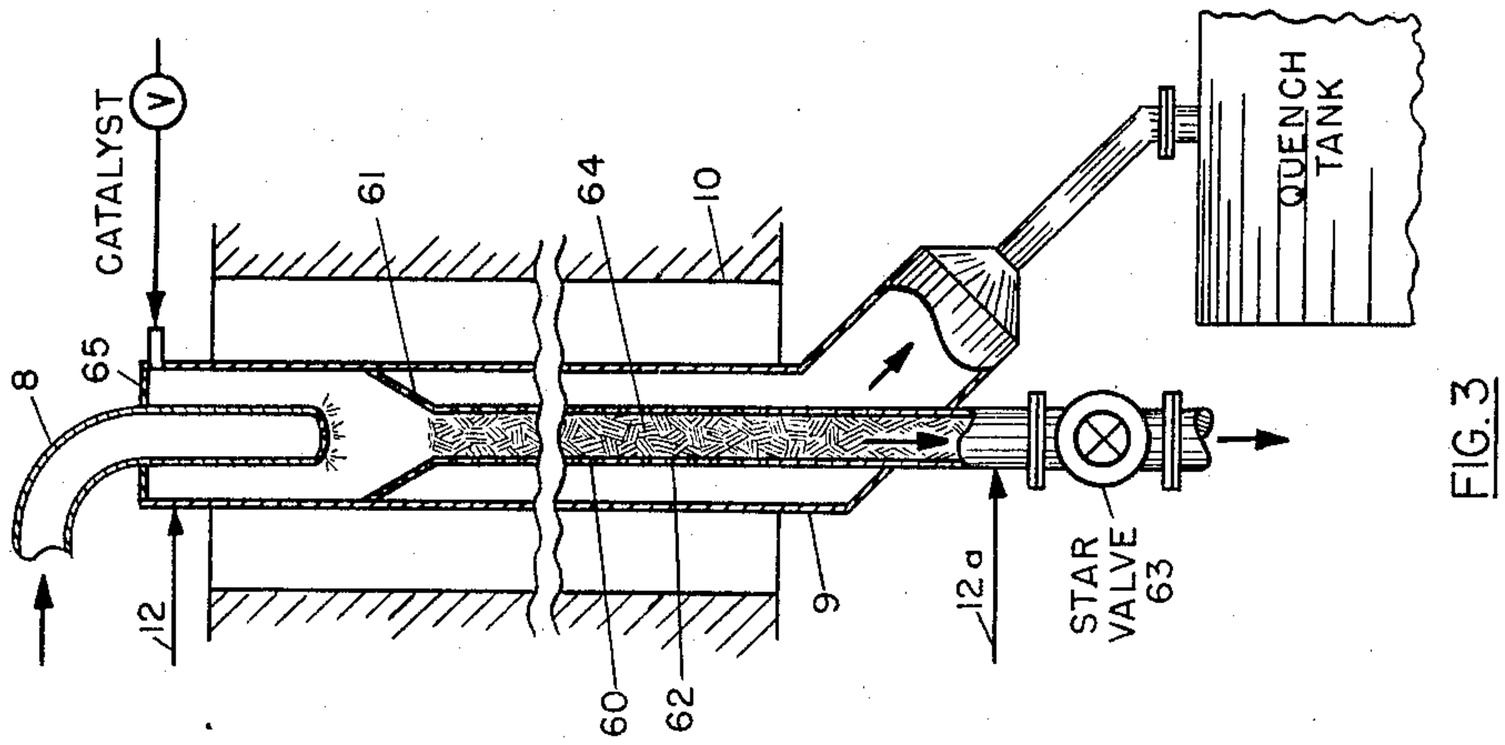

FIG. 3

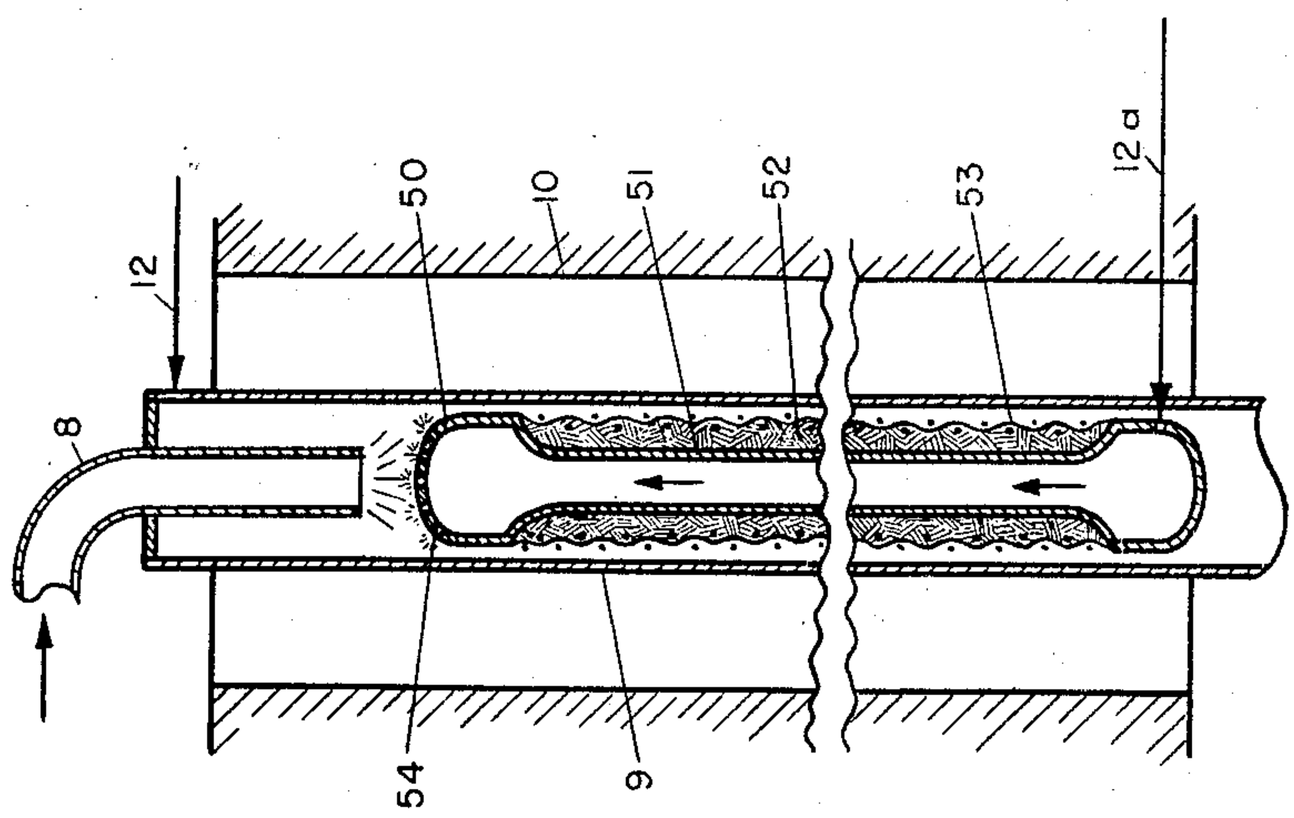

FIG. 2

JAMES H. SHAPLEIGH
INVENTOR.

BY Ernest G. Peterson

AGENT.

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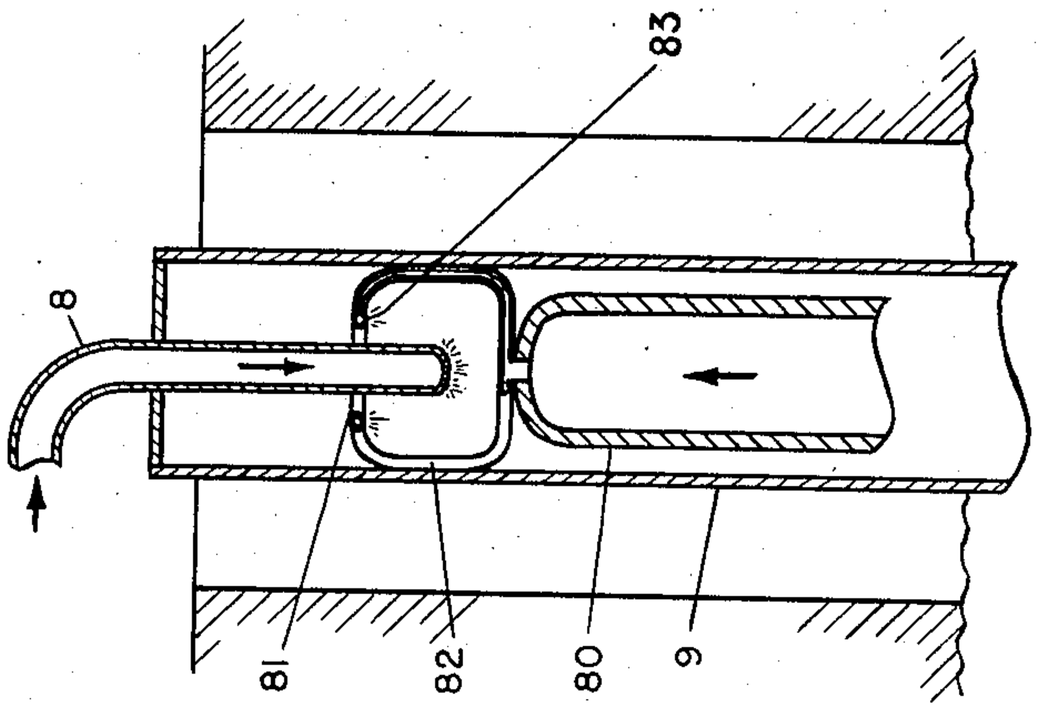

FIG. 5

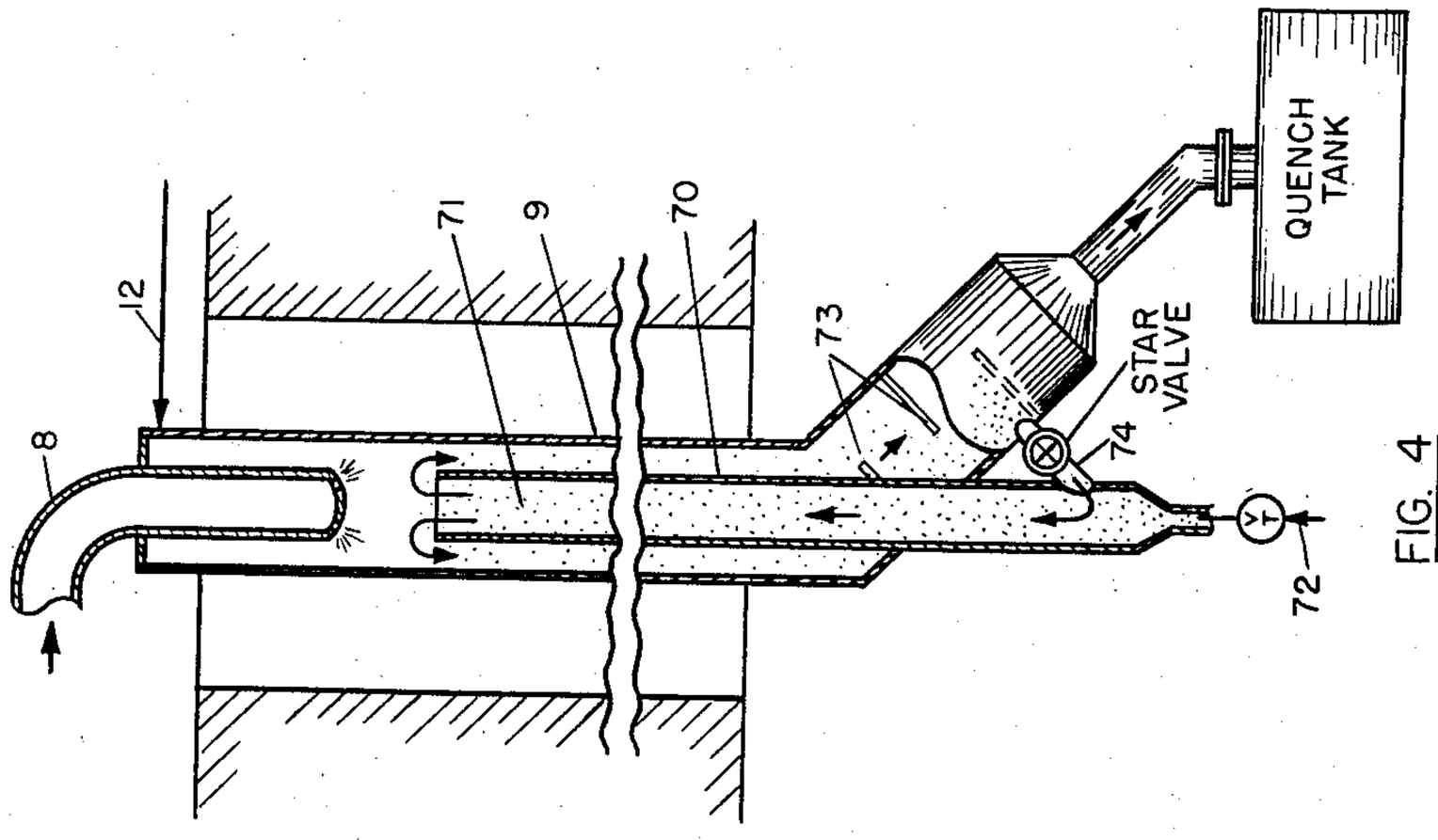

FIG. 4

JAMES H. SHAPLEIGH
INVENTOR.

BY Ernest G. Peterson

AGENT.

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METHOD OF CRACKING HYDROCARBONS

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

Application February 19, 1954, Serial No. 411,378

13 Claims. (Cl. 208—130)

This invention relates to the cracking of hydrocarbons and more particularly to a process for the thermal cracking of normally liquid hydrocarbons in a tubular furnace to produce oils or liquids containing compounds of the same or different chemical series from those treated and more particularly to produce modified mixtures of compounds valuable as intermediate and end products.

In Reissue Patent No. 21,521, there is disclosed a process for treating hydrocarbons in a tubular furnace fired at a plurality of spaced points to give flexible temperature control of the reacting fluids. Additionally, in Patent No. 2,525,276, there is disclosed a process for the cracking of hydrocarbon oils with a minimum of carbon deposition for the substantial production of olefins. These patented processes heretofore set forth have provided practical flexible processes for hydrogen production and the cracking of whole oils to produce valuable liquid components as well as olefins through reaction control. However, in so far as it is known, no process has been developed which utilizes externally heated metal tubes and affords a yield of cracked products and throughput which is attractive to large-scale handling of hydrocarbon stock such as is encountered in the refining of petroleum.

In the art of oil refining, the large plants which now exist are the result of years of progress wherein one of the principal objectives has been economy in the production of refinery products. To achieve this end, extensive processing technique has been employed in the majority of instances to preprocess feed stocks, and to cyclically move large bodies of catalyst. These techniques, though great in undertaking, have certain elemental features. The starting point is an oil which can be principally represented by a carbon-hydrogen relationship. For example, as approximately $CH_{1.85}$ for an East Texas crude, or as $CH_{1.6}$ for another crude; but whether crude, distillate or residue, a single carbon-hydrogen relationship can be used to express the initial stocks, intermediates, and end products notwithstanding that they are mixtures of hydrocarbons.

In the art of oil refining, it is not customary to deal in the foregoing terms, but rather to deal with cuts and distillates, boiling points, and other factors which in general characterize the physical properties of the material.

In contrast, in tubular high temperature cracking it has been discovered that composite products, expressed in terms of carbon and hydrogen, follow a relationship directly influenced by the process conditions peculiar to this invention, and whereby the heat input per tube is brought to a previously thought impossible high value which expressed in refinery terms of throughput is in the order of, for example, for a one-tube unit of 50 to 150 barrels of feed stock per day; or for a nominal size 100 tube installation of 5000 to 15,000 barrels of feed stock per day.

Utilizing the carbon-hydrogen terminology referred to above, the refinery for example may start with a feed stock $CH_{1.8}$. The refinery does two basic things to the stock: (1) applies heat, and (2) provides a residence

time. In the application of heat, one procedure is to utilize substantial sized heat exchangers prior to entering the residence chamber or reactor. Another procedure is to heat large amounts of catalyst while in cyclic movement. In other procedures, noncatalytic type stills are used. The physical aspects are, however, the same, whether catalytic or noncatalytic, i.e., to supply heat and residence time. In the supply of bulk heat according to the procedures heretofore set forth there is a fundamental deficiency in lack of control, regardless of the elaborate instrumentation employed with installations now in existence. For example, the moving bed of catalyst is hottest at its entrance point and follows a descending gradient of temperature during its residence time path. The conditions of limited body temperature and bulk solids movement coat the catalyst with carbon even when handling light distillate, for example, in the form of vaporized gas oil and are prohibitive for heavy stock within reasonable carbon limits. The carbon-coated catalyst must be removed from the reactor, burned free of carbon and recycled.

In contrast, it has been discovered that high throughput is obtainable in tubular cracking in similar terms to those of refinery practice under conditions of much improved control and flexibility. Where catalytic operation is desired, the invention permits carbon formation to be greatly minimized, and permits its relatively easy removal without physical disturbance of the catalytic bed; or if desired, bed movement can still be employed as an alternative while retaining certain advantages. It is preferred, for example, that catalyst, if used, be in a layer parallel to the tube surface, and preferably forming or being part of a radiantly heated internal core within the tube. So used, the catalyst surface is normally at a temperature which promotes reaction to generally cause a decarbonizing state, while at the same time the catalytic action can proceed at an abnormally high rate per unit of surface.

Accordingly, it is a principal object of this invention to secure desired cracked products under conditions of high throughput and under conditions where the fundamental deficiencies heretofore set forth are eliminated. Other objects of the invention will appear hereinafter, the novel features and combinations being set forth in the appended claims.

More specifically, the objects hereinbefore and hereinafter set forth are achieved in accordance with this invention by the improvement which comprises passing hydrocarbon and diluent gas through the reaction zone of an elongated reaction tube for a period of not more than 0.3 second residence time in the reaction zone of the tube, said tube being disposed within a refractory walled furnace having an average surface temperature of at least 1835° F. in the reaction zone and supplying external heat to the tube from the refractory walled furnace to maintain a temperature relationship within the reaction zone between the average surface temperature of the furnace wall and the average temperature of the reaction tube of at least 150° F. and to maintain within said reaction zone a temperature relationship between the average temperature of the said tube and the temperature of the cracked products emerging therefrom of at least 435° F.

Certain embodiments of the invention are presented herein for the purpose of illustration but it will, of course, be understood that the invention is susceptible to different modified embodiments which come within the scope of the appended claims.

In the accompanying drawings:

Fig. 1 represents diagrammatically a flow chart with suitable equipment for carrying the invention into effect;

Fig. 2 is a schematic sectional view showing an alternative embodiment for proving a fixed catalytic surface for the reaction equipment illustrated in Fig. 1; and

Fig. 3 is a schematic sectional view showing still another embodiment for providing a movable catalytic surface for the reaction equipment illustrated in Fig. 1.

Fig. 4 is a schematic sectional view showing still another embodiment for providing a fluidized catalytic body for the reaction equipment illustrated in Fig. 1.

Fig. 5 is a schematic sectional view showing still another embodiment for providing an effective application of countercurrent diluent for the reaction equipment illustrated in Fig. 1.

Referring to Fig. 1, feed oil is passed through a line **1** into and through a pump **2** from which it is passed by a line **3** into a preheater **4**. From the preheater **4**, the oil is passed through a valved line **5** into a mixer **6**. Primary steam from valved line **7** is admitted to the mixer **6** wherein the oil is atomized and partially vaporized and is passed into an injection tube **8**. The injection tube **8** extends into a reaction tube **9** which extends through a refractory walled furnace **10** which is preferably fired at a plurality of spaced points. Within the reaction tube **9** there is disposed an internal core **11** which in combination with the reaction tube **9** defines an annular reaction zone. Similarly, the extension of the injection tube **8** into the reaction tube **9** forms an annular preheat zone. The atomized and partially vaporized mixture of oil and primary steam is injected from the injection tube **8** into a concurrently moving, concentrically disposed body of secondary steam which is fed through valved line **12** into the reaction tube **9**.

The mixer **6** both mixes and atomizes and a preferred embodiment is through use of about 15 p.s.i.g. minimum to force oil through a multihole orifice plate to form jets of oil impinging into similar jets of steam formed by a second multihole orifice plate, the oil-steam mixture issuing from the holes as high velocity jets. After travel through the injection tube for from about 1 to 3 feet, it may be preferred to use a second orifice combination to bring about a finer state of subdivision and to reatomize coalesced oil. It is preferred to use a minimum differential of 15 p.s.i.g. within the mixer atomizer unit regardless of the back pressure against which the mixture is delivered.

The secondary steam flows concurrently, but out of direct contact with the oil-primary steam mixture, the atomized oil-primary steam mixture being within the injection tube **8** and the secondary steam being outside of the injection tube. By this means, 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. Thus, the preheat zone is capable of rapidly and properly conditioning a large volume of charging stock as compared to other prior art methods.

The conditioned oil and steam are quickly passed from the injection tube **8** through the indirectly heated, annular reaction zone formed between the inside wall of the reaction tube **9** and the outside wall of the internal core **11**. In the reaction zone, the reactants are thermally cracked and the cracked products are quenched as they leave the reaction tube **9** by quenching medium. The quenching medium is passed through line **13** and is preferably hydrocarbons produced as the result of quenching in a quench tank **14**; recirculated by means of a pump **15** through a waste-heat boiler **16**. The boiler **16** may produce steam at low pressure for use in the reaction tube **9** as secondary steam or at higher pressure for use as primary steam. It is preferred that boiler **16** produce steam at 50 to 100 p.s.i.g. in which case the quench oil circulated by pump **15** will normally have a temperature entering the quench tank of about 350° F. The quench oil is intimately mixed in substantial quantity with effluent gas from the reaction tube **9**, exiting normally in the range of about 1000° to about 1250° F., to cause about a 50° F. rise in the temperature of the quench oil. Under these conditions, the

diluent passed through the reaction tube **9**, together with hydrocarbons uncondensed in quench tank **14**, pass through line **17** at about 400° to 450° F. minimum.

Additionally, secondary steam is passed or shunted through a valved line **12***a* and into the internal core **11** from which the steam emits from the top thereof through perforations and serves to provide a jet action to dislodge and otherwise remove any carbon tending to deposit on the top of the internal core.

The liquid product "A" is withdrawn from the quench tank **14** through a valved line **18** and passes through a pump **19** to a multipurpose heat exchanger **20** from which the liquid product then passes through a valved line **21** to a treater system represented by **22** wherein the treaters A, B, and C are shown. Alternatively, the liquid product "A" in whole or in part may be passed through a valved line **23** through a cooler **24** from which it passes to storage for use as fuel or as otherwise desired.

The gases and vapors from the quench tank **14** are passed through line **17** to a cooling, absorbing and/or fractionating unit represented by **25**. The unit **25** may consist of one or more fractionating columns provided with suitable condensers, reflux devices, and coolers as well understood in the art. Liquid products designated "B" and "C" are withdrawn from the unit **25** through valved lines **26** and **27**, respectively. The product "B" is an intermediate condensate and may be recycled in whole or in part into the cracking tube **9** by means of a valved line **28** which conducts the condensate from the line **26** into the mixer **6**. Alternatively, product "B" in whole or in part may be passed into a second cracking or treating unit, such as treater A, through a valved line **29** which leads to the exchanger **20**. The vapors and gases which leave the top of the unit **25** pass through a line **30** to a cooler **31** from which gas and condensate are passed through line **32** to a separator **33**. Any light condensate of value is passed from the separator **33** through pump **34** and line **35** to the cooling, absorbing and/or fractionating unit represented by **25**. The valueless condensate is passed from the separator **33** to drain. The product designated "C" is withdrawn from the unit **25** through the valved line **27** and this product is condensed steam and normally portions of light condensate and is decanted or otherwise stripped of hydrocarbons with the residue passed to drain. A pump **36** in the valved line **27** and a valved line **37** connected thereto provides for recycle of product "C" to the unit **25**. In like manner, a pump **38** in the valved line **28** and a valved line **39** connected thereto provides for recycle of product "B" to the unit **25**. The pump **38** further provides for return of product "B" to the mixer **6** through the valved line **28** as hereinbefore described. The product designated "D" is withdrawn from the top of the separator **33**, this product, being, for example, H_2, CH_4, C_2H_2, and olefins, but which may contain aromatics may be passed to pressure-low temperature absorption-liquefaction equipment or to adsorption processes for gas component separation or other processes for recovery of valuable products.

The chemical and physical character of product "A" from quench tank **14** depends upon conditions of the reaction zone. A feed stock of carbon and hydrogen relationship CH_n may be altered to a residual product "A" of relationship CH_{n-r} where r is small, for example, if $n=1.8$ r may only be about 0.1 to 0.4. On the other hand, substantial alteration may be brought about and r may be about 0.6 to about 1.4. The effect of deeper reaction conditions is toward lower and lower values of $(n-r)$ with no appreciable formation of detrimental carbon. Consequently, the condensables from quench tank **14**, i.e., product "A," are subject to a desirable wide and controlled variation, which is related to their field of use and to subsequent further alteration, processing and separation steps. The combined use of the furnacing step, the quenching step and post-treatment steps provides thereby a unique process wherein each step con-

tributes to the alteration of the carbon-hydrogen relationship of the feed stock into liquid products of different carbon-hydrogen relationship under high capacity unit throughput not heretofore achieved. The liquid hydrocarbons, so obtained in altered form, are condensed hydrocarbons or hydrocarbons absorbed in the quenching liquid in contrast to liquids not condensed from a vapor state. Within this limitation, the pressure within the reactor, exclusive of the mixer, is normally the pressure required for motivation of reactants. However, the pressure may be above atmospheric and above that required for motivation, in which case a throttle valve **40** is placed in line **17**; or, if a header is used between the furnace **10** and the quench tank **14**, the throttle valve is used to affect the furnace pressure; or the throttle valve may be so placed as to include the post treaters within the pressure zone.

As previously described, product "A" may be withdrawn from the system through the valved line **23** and the cooler **24** and disposed of as desired. However, in accordance with one preferred embodiment of the invention, product "A" is passed through the valved line **18** and through the pump **19** to the multipurpose heat exchanger **20** from which it passes through the valved line **21** to the treater system represented by **22** wherein the treaters A, B, and C are shown.

The advantages in use of treaters A, B, and C are more clearly understood by again referring to the flexible nature of furnace **10** and product "A." For example, it may be elected to treat an oil of carbon-hydrogen relationship of about $CH_{1.5}$ to $CH_{1.6}$ to the extent of a light depth of cracking to cause a formation of gas exiting through line **17** in an amount of 5% to 20% by weight of feed stock, while subjecting the oil to substantial reaction heat to cause alteration in the chemical composition and arrangement of chemical groups as exemplified by the fact of heat absorption, nominal gas formation, all within a maximum of 0.3 second reaction time, insufficient to cause degrees of polymerization, and complex reformation so attendant with reactions which are permitted to proceed during longer residence time. Having found that an unexpected yield of ethylene can be produced from cuts already heavily cracked by these prior processes (particularly exemplified by U.S. Patent 2,525,276 and application Serial No. 188,567) and decidedly contrary to the teaching of the art, it is deduced that for said ethylene to be produced, it has been preceded in earlier stages of cracking by chemical rearrangement permitting the simple formation of ethylene to occur from what previously was complex hydrocarbon. For example, and in relation to the foregoing, it has been found with both #2 oil and with crude oil that there is an increase of from about 20 lbs. C_2H_4 to about 30 lbs. of C_2H_4 without appreciable change in C_3H_6 production when cracked from around about 45% depth to about 65% to 70% depth. These poundages refer to 100 lbs. of oil feed stock as a unit quantity. The finding of this relationship is new and difficultly believed but proved from results of many runs made under a wide range of conditions. This proof of pretreatment effects brought about with lighter depth of cracking which apply to the condensables is susceptible of wide application. This is more apparent from the following:

Product "A" produced within the scope of this invention at high unit throughput rate as disclosed herein is passed to treaters A, B, and C, exemplifying known methods of treatment, such as thermal or catalytic cracking, distillation, absorption, oxidation, hydrogenation, dehydrogenation, etc., with any such steps singly or in combination. This embodiment of this invention is not concerned with such known steps as such but rather with the combination of pretreatment within the contact time limit and other limits as defined by the appended claims with such known after-treatment step or steps to cause further alteration and/or rearrangement of chemical constituents. Additionally, this invention does not lie in the treatment of hydrocarbons for production of valuable gases, even though these are by-products, but in a new process for producing treated liquids via gas phase reaction, where in combination with the proper post- or after-treatments known in the art, there is provided a novel and efficient overall process for the production of solvents, fuels, high octane hydrocarbons and the like.

It will be apparent that the process and apparatus herein disclosed for diagrammatic presentation of the invention are susceptible to numerous other possible combinations and arrangements for operation of the invention including equipment other than that shown, such as waste heat boilers, heat exchangers, condensers, coolers, multiple fractionating columns with take-off, and the like. However, such means have not been shown or disclosed since they are well within the province of a person skilled in the art. Furthermore, it will be apparent that the process herein disclosed may be operated with or without the use of catalysts. In using catalyst, the catalyst to be employed may be fixed, movable, continuously movable, or fluidized, as hereinafter set forth, and these catalysts may be employed in a simple and expedient manner relative to the preferred embodiment of the invention illustrated in Fig. 1, wherein reference symbols refer to like parts wherever they occur.

Referring now particularly to Fig. 2, a hollow internal core **50** is disposed within the reaction tube **9**. The internal core **50** has a central portion **51** of reduced diameter which supports a catalyst mass **52** held in place by a foraminous member **53** wrapped around the central portion **51** of the internal core **50**. Due to the small annular space provided between the core **50** so equipped and the reaction tube wall, the reactants in considerable measure contact the catalyst to impart catalytic effect as desired for certain end products. In this manner there is provided a fixed catalytic surface which is exposed to the reactants and which does not impede the flow of reactants through the annular reaction zone. Accordingly, extremely high throughput is maintained. Steam from line **12***a* is passed into the hollow internal core **50** from which the steam emits from the top thereof through a plurality of perforations represented by **54**.

In the use of catalysts, as part of this invention, wherein the catalyst is heated by radiation from the tube wall, and wherein the catalyst itself is a heating agent for the reactants, and wherein the catalyst may be disposed around the outer surface of a centrally disposed internal tube or core of metal, ceramic, Carborundum or of other suitable material, said tube may be utilized advantageously, it has been discovered, as a conduit for passage of a diluent material, such as steam, countercurrent to the reactants. The diluent material can be used to control the catalyst temperature by extraction and transfer of heat from and between zones of catalyst. Furthermore, it has been discovered that there is another and very beneficial use for diluent passed through the core, particularly when the diluent is steam, wherein the steam functions as a deterrent to the formation and retention of carbon, particularly at or near the top of the core in the reaction zone. By using perforations, particularly in the top of the core, and/or around the circumference of the core, suitably spaced and sized, it is found that steam, for example, has at least two primary effects relative to carbon deposits. It lifts off and breaks up such deposits, permitting passage into a hotter zone; and provides jet action of hot steam upon carbon so deposited. By these combined effects, continuity of operation is promoted. To the end that maximum temperature of steam is desired for use in openings for passage of steam or other diluent, for beneficial effect upon carbon, or as a deterrent to carbon formation, or as an element of temperature control of reactant mixture, said steam may be passed through a conduit within the core and radiantly heated by the core.

The openings or perforations used for the passage of

diluent from the core to the reactant mixture can be of any shape or size suitable for the purpose, but most conveniently are round holes of small size, for example 1/32" to 1/8" diameter, for maximum beneficial effect upon carbon when utilizing a minimum quantity of steam passed countercurrently to the reactants passing through the reaction zone. For this purpose, there may be used only a small percentage of the total diluent passing from the tube, for example, when a 2 to 1 weight ratio of steam to hydrocarbon is used, the countercurrent steam passing through the core may amount to only about 5%. On the other hand, when the use is primarily as a temperature control element for either the catalyst or the reactant mixture, the steam or other diluent being passed through the core may more substantially replace the other diluent being passed concurrently into the reaction zone, but preferably the countercurrent steam will not exceed 40% of the whole. When diluents other than steam are used, there may be used materials which react with carbon and which are not solely diluents in that sense. In this category, hydrogen, and even air may be used, although with the latter, dilution with nitrogen, flue gas, etc., is safer and preferred. The core may be type 310 stainless steel, stabilized or unstabilized, but type 310 Cb is preferred except where anticatalytic action is highly desirable. In such cases, it is preferred to restrict metal contact through use of a non-metallic exposed core surface, such as ceramic, refractory, or Carborundum types, selected according to the reaction conditions to be employed.

Referring now particularly to Fig. 3, a foraminous core **60** extends into the reaction tube **9** up through the base thereof and has its upper end terminating in the form of a foraminous funnel **61** in juxtaposition to the lower end of the injection tube **8**. The core **60** is hollow and is provided with a plurality of perforations **62** and is provided at its lower end with a valve **63**, such as a star valve. Free-flowing catalyst **64** is supplied around the injection tube **8** at the upper end of the reaction tube **9** through a valved manifold system **65** and flows downwardly within the core **60** and is discharged therefrom through the valve **63** as desired. By control of the valve **63** and valved manifold **65**, the catalyst may be discharged at intervals for reactivation and replenishment or it may be continuously charged and discharged. In this manner, there is provided a movable catalytic surface exposed to the reactants or a continuously movable catalytic surface. Due to the small annular space provided between the core **60** and the reaction tube wall, the reactants in considerable measure contact the catalyst to impart catalytic effect as desired for certain end products. Accordingly, extremely high throughput is maintained with a high level of catalyst contact. Additionally, steam or other diluent may be passed by valved line **12***a* into and through the internal core **60** for the purpose of purging as desired.

Referring now particularly to Fig. 4, a hollow internal core **70** extends into the reaction tube **9** up through the base thereof and extends upwardly into the reaction tube to a point near the injection tube **8**. Suitable catalyst **71** with fluid medium under pressure is injected into the bottom of core **70** through a pressure throttle valve line **72** and carries up through the core **70** countercurrent to the reactant stream. The catalyst emerges from the top of the core **70** into the reactant stream and then passes downwardly therewith as a fluidized catalyst body. Suitable baffles, represented by **73**, are provided for separating the catalyst from the reactant stream which passes on to the quench tank. A conduit **74** is provided for return of catalyst to the core **70**. However, other suitable equipment (not shown) may be used for reactivation, replenishment, or return of catalyst to the system. The fluid medium used as a carrier for the catalyst is preferably steam but other diluent or even reactant medium may be employed for this purpose. The procedure for utilizing fluidized catalyst as set forth herein provides a simple and expedient method for handling catalyst in conjunction with the other objectives of the invention.

Referring now particularly to Fig. 5, still another embodiment is shown for the effective application of countercurrent diluent. In this embodiment steam or other diluent is passed countercurrent to the reactant stream up through a hollow internal core **80**. The internal core **80** has a manifold **81** in communication with the interior of the core through a plurality of pipes represented by **82**. The pipes **82** are preferably arranged in the form of a "spider" utilizing three pipes as support legs to insure rigidity for the manifold **81**. The manifold **81** has a plurality of perforations represented by **83** in the bottom side thereof to project the diluent downwardly around the injection tube **8**. Accordingly, when secondary steam, for example, is passed countercurrent to the reactants through core **80**, the steam issues above the egress point of the injection tube **8**. This causes blanketing of the entering hydrocarbon as it leaves the injection tube but yet provides for intimate mixing in the flash heat zone from which the mixture then passes through the reaction zone. The arrangement of the manifold in this manner is additionally suitable in systems where an annulus is used in lieu of an injection tube for preparing the reactants for passage through the reaction zone. However, regardless of the specific arrangement utilized, an important factor is to obtain flash heating of the reactants prior to passage through the reaction zone.

In accordance with this invention and to illustrate particularly the process for effecting cracking of hydrocarbons in a tubular furnace, the following examples are given. These examples illustrate the results obtained from the use of various type oils. In the examples, the length of the reaction tube within the furnace was approximately 25 feet of which approximately one-third constituted the preheat zone and the remainder the reaction zone. The reaction tube was 8 inches in inside diameter and the internal core was 5 inches in outside diameter and extended substantially throughout the length of the reaction zone. This gave a longitudinal annular space of 1½ inches wide and approximately 17 feet long for the reaction zone.

Example 1

A mixture of #2 Fuel Oil and steam in an amount of 1748 lb. per hour total and in a weight ratio of steam to oil of 1.84 passed into the reaction zone at 580° F. gives a low yield of low molecular weight gas which expressed in terms of C_2H_4 is 10 lb. per 100 lb. of hydrocarbon feed stock when processed under the following conditions:

Average reaction tube temperature	° F.	1704
Average refractory wall temperature	° F.	1868
Residence time of the reactants in the reaction zone	seconds	0.24
Exit temperature of the reactants from the reaction tube	° F.	1125

Example 2

A mixture of #2 Fuel Oil and steam in an amount of 1720 lb. per hour total and in a weight ratio of steam to oil of 1.80 passed into the reaction reaction zone at 623° F. gives a low yield of low molecular weight gas which expressed in terms of C_2H_4 is 7.71 lb. per 100 lb. of hydrocarbon feed stock with depth of cracking 21% when processed under the following conditions:

Average reaction tube temperature	° F.	1691
Average refractory wall temperature	° F.	1837
Residence time of the reactants in the reaction zone	seconds	0.24
Average internal core temperature	° F.	1239
Exit temperature of the reactants from the reaction tube	° F.	1110

Example 3

A preheated mixture of #2 Fuel Oil and steam in an amount of 1720 lb. per hour total and in a weight ratio of steam to oil of 1.80 passed into the reaction zone gives a low yield of low molecular weight gas which expressed in terms of C_2H_4 is 6.45 lb. per 100 lb. of hydrocarbon feed stock with depth of cracking 17% when processed under the following conditions:

Average refractory wall temperature ____° F__	1861
Δt temperature between the average refractory wall temperature and the average reaction tube temperature ____° F__	151
Residence time of the reactants in the reaction zone ____seconds__	0.24
Average internal core temperature ____° F__	1500
Exit temperature of the reactants from the reaction tube ____° F__	1140

Example 4

A mixture of #2 Fuel Oil and steam in an amount of 3050 lb. per hour total and in a weight ratio of steam to oil of 1.49 passed into the reaction zone at 872° F. gives a low yield of low molecular weight gas which expressed in terms of C_2H_4 is 9 lb. per 100 lb of hydrocarbon feed stock with depth of cracking 25% when processed under the following conditions:

Average reaction tube temperature ____° F__	1710
Average refractory wall temperature ____° F__	1958
Residence time of the reactants in the reaction zone ____seconds__	0.16
Exit temperature of the reactants from the reaction tube ____° F__	1070

Example 5

A mixture of #2 Fuel Oil and steam in an amount of 4800 lb. per hour total passed into the reaction zone at 687° F. gives a low yield of low molecular weight gas which expressed in terms of C_2H_4 is 5 lb. per 100 lb. of hydrocarbon feed stock with depth of cracking 14% when processed under the following conditions:

Average reaction tube temperature____° F__	1760
Average refractory wall temperature ____° F__	2060
Residence time of the reactants in the reaction zone ____seconds__	0.10
Exit temperature of the reactants from the reaction tube ____° F__	1050

Example 6

A mixture of East Texas crude oil and steam in an amount of 1590 lb. per hour total and in a weight ratio of steam to oil of 1.84 passed into the reaction zone at 703° F. gives a low yield of low molecular weight gas which expressed in terms of C_2H_4 is 8.08 lb. per 100 lb. of hydrocarbon feed stock with depth of cracking 28% when processed under the following conditions:

Average reaction tube temperature ____° F__	1753
Δt temperature between the average reaction tube temperature and average refractory wall temperature ____° F__	153
Residence time of the reactants in the reaction zone ____seconds__	0.23
Exit temperature of the reactants from the reaction tube ____° F__	1217

Example 7

A mixture of 1408 lb. East Texas crude oil and 2440 lb. steam passed into the reaction zone at 1050° F. gives a low yield of low molecular weight gas which expressed in terms of C_2H_4 is less than 10 lb. per 100 lb. of hydrocarbon feed stock with depth of cracking 40% when processed under the following conditions:

Average reaction tube temperature ____° F__	1730
Δt temperature between the average reaction tube temperature and the average refractory wall temperature ____° F__	250
Residence time of the reactants in the reaction zone ____seconds__	0.11
Exit temperature of the reactants from the reaction tube ____° F__	1040

Example 8

A mixture of 1408 lb. East Texas crude oil and 2440 lb. steam passed into the reaction zone at 1050° F. gives a low yield of low molecular weight gas which expressed in terms of C_2H_4 is less than 18 lb. per 100 lb. of hydrocarbon feed stock with depth of cracking 40% when processed under the following conditions:

	° F.
Average reaction tube temperature ____	2000
Average internal core temperature ____	1690
Δt temperature between the average refractory wall temperature and the average reaction tube temperature ____	200
Exit temperature of the reactants from the reaction tube ____	1235

Example 9

East Texas crude oil, steam and flue gas in equal proportions by weight totalling 4400 lb. per hour total passed into the reaction zone in substantially complete gasified form gives a low yield of low molecular weight gas which expressed in terms of C_2H_4 is less than 10 lb. per 100 lb. of hydrocarbon feed stock with a depth of cracking less than 25% when processed under the following conditions:

	° F.
Average reaction tube temperature ____	1878
Average refractory wall temperature ____	2200
Average internal core temperature ____	1550
Exit temperature of the reactants from the reaction tube ____	1165

With reference to the above examples, it will be noted that high throughput of hydrocarbon stock exclusive of diluent, such as steam or flue gas, is accomplished in accordance with this invention and that the cracked products contain a very small gas yield. In processing according to this invention the formation of C_2's, CH_4 and H_2 is held to a minimum giving a very small gas volume in comparison to the liquid products produced which are represented by the C_5's and higher.

Whereas in the foregoing examples the highest temperature of the hydrocarbon and steam mixture was 1050° F. entering the reaction zone, runs have been made at higher extrant temperature, and in the processing of residual oils, it is advantageous to use temperatures in excess of 1000° F. even with diluent steam. The combination of higher entrant temperature and a diluent to reduce hydrocarbon partial pressure has been found to be particularly advantageous in handling heavy oil. Whether its effectiveness is due to its bringing atomized oil closer to the equilibrium vapor state within the short time interval existent, whether it is due to a more effective production of reactive fog in contrast to droplets, or whether due to some other reason is not definitely known. In such cases, however, it has been found advantageous to enter the reaction zone at, for example, 1100° F., even though the desirable internal disengagement of linkages in the hydrocarbon is associated with the exit temperature which may be the same or lower than the entrant temperature to the reaction zone. Whereas the reaction may have commenced in the mixing zone when the hydrocarbon is suddenly heated to, for example, 1100° F., this zone is so close to the defined reaction

zone and associated such a short time, within it, that the expressions as made will be understood as being reasonably descriptive thereof.

In the practice of this invention, a refractory walled tubular furnace provided with an injection system for liquid hydrocarbon, such as disclosed in Reissue Patent No. 21,521 and Patent No. 2,525,276, respectively, is preferred. This combination gives remarkable flexibility in temperature control with a minimum of carbon deposition. The tubular cracking or reaction tubes are preferably disposed vertically and have a diameter of about 4 to 10 inches. Preferably the tube is in the order of 8 inches in diameter and has about 25 feet of its entire length disposed within the furnace of which about one-third of the tube length is a preheat section and two-thirds a reaction or residence time section. A type 310 stainless steel tube is suitable and this type tube with stabilizing material is preferred. The reaction tube may be lined to repress catalytic effect as desired which has heretofore been discussed in respect to the internal core which extends within the reaction tube substantially the length of the reaction section.

In accordance with this invention the hydrocarbon feed stock may be a liquid product such as a fuel oil or crude oil and may be introduced into the process with or without diluent. With steam, for example, as the diluent the ratio of steam to hydrocarbon can be varied to give either high or low ratios as desired depending on the difficulty encountered in vaporizing the feed stock. Normally, this ratio will be in the order of 1:10 to 5:1 with a preferred steam to hydrocarbon ratio of from about 1:1 to 3:1. The use of a diluent, such as steam, lowers the boiling point of the hydrocarbon and makes possible substantially complete vaporization of certain stocks, such as crude or topped crude, which are heavier than gas-oil, for example. Additionally, the diluent, such as steam, can be used to assist in control of the residence time which in conjunction with the control of the reaction tube wall temperature makes it possible to control the effluent temperature of the reactants within a considerable range as desired.

In the reaction section of the reaction tube the average metal wall temperature will be maintained at a temperature of at least 1685° F. with the average surface temperature of the refractory walled furnace maintained at a temperature of at least 1835° F. Under such conditions, the temperature relationship (Δt) between the average temperature of the reaction tube and the average surface temperature of the core will be maintained at from about 300° F. to about 600° F. while maintaining the temperature relationship (Δt) between the average temperature of the tube and the temperature of the cracked products emerging therefrom of at least 435° F. Higher temperatures may be employed with the upper limit primarily dictated by the materials of construction involved. Generally, it has been found that an average metal wall temperature of from about 1700° to about 2000° F. for the reaction section of the reaction tube gives very satisfactory results.

Although it is not intended that the invention shall be limited to any particular theory of operation, it appears that the components of the gaseous reactants passing through the reaction zone make multiple very short contacts with the high temperature walls of the reaction tube and the core, which contacts are believed to influence the end result in obtaining a low gas yield. This also applies to the effectiveness of the catalyst bodies disclosed herein. Thus, whereas the average temperature of the gaseous reactants may be 500° F. or more below the average tube wall temperature, it is believed that the multiplicity of these short high temperature contacts affects the end result to the extent that a certain amount of deep cracking occurs without appreciable increase in yield of gaseous end product. In other words, in refinery practice with increased depth of cracking there is almost a continuous increase of hydrogen to carbon ratio as the quantity of gas thus produced increases. This increase of hydrogen to carbon ratio is directly related to increased amounts of coke formed. According to the conditions of this invention and in marked contrast to the foregoing, the hydrogen-carbon ratio of the effluent gas is nearly constant even over a substantial range of cracking depth. Furthermore, the absence of substantial carbon formation according to this invention is established by lack of equivalent oxides formation in the presence of steam.

The core in its relationship to the annulus and to size of tube is a process variable. It is a factor to regulate time and plays an important part because of its own temperature, controlled on the one hand by radiant heat and on the other by extraction of heat by the reactants. Under normal operating conditions, the high surface temperatures of the reaction tube and internal core are not found to be conducive to formation of carbon or to the retention of carbon to any detrimental degree. The preferred vertical tube arrangement disclosed herein is conducive to cleanliness and freedom from operating trouble.

Whereas it has been customary in vapor phase cracking to use residence times of 1 to 10 seconds, and even with the use of diluent steam to limit the feed stock to light distillates because of coke formation, it has been found that at residence times of not more than 0.3 second the heat that normally goes into deep cracking with large yield of low molecular weight gas can be made to go into an overall much lighter depth of cracking with low yield of such gas and yet with substantial change in composition of the condensables. Under these conditions, the yield of C_2H_4 may be less than 10% by weight of the hydrocarbon feed stock with an increased gain in C_4's and materials of higher carbon content. This type of cracking is particularly adaptable to structural change of liquids at low gas yield preparatory to subsequent processing of the liquids formed. Another point of contrast is in the rate of heat input per square foot of tube surface. In refinery practice, a range of from 4000 to about 20,000 B.t.u. per square foot is used wherein the latter represents very high and somewhat unusual conditions. However, in accordance with this invention, there is used from about 20,000 to about 50,000 B.t.u. per square foot in the reaction zone under which condition cracking results are quite different as has been herein set forth. Referring again to an initial feed stock represented by a carbon to hydrogen relationship as $CH_{1.8}$, in accordance with the process of this invention the condensable portion of the effluent can be made to have successively lower hydrogen content substantially at will, while maintaining high throughput low residence time values. For example, reduction of the hydrogen by 10% conforms to a definite depth of cracking, 5% would be another, 15% another, and so on. Yet under each condition the vapor body would have been subjected to a temperature normally in excess of 900° F., and the compounds present would all have been subjected to a modifying temperature level. Furthermore, the depth of cracking, in terms of percent of the feed stock by weight to be converted to gas, can vary from less than 17% to over 40% while still maintaining high throughput and with effluent gas in the range of 900° F. to 1250° F.

The use of catalysts to influence the purity or the composition of ultimate end products is within the scope of this invention and includes the preferred arrangements set forth herein along with such catalysts as pumice, clays, aluminum silicates, hydrosilicates, chromium, molybdenum, vanadium oxides, ferric oxides, magnesia, cupric oxide, zinc oxide, potassium oxide, plus other materials and modifiers therefor as are well known in the art. Dehydrogenation is one type of reaction taking place while cracking, and butadiene is a normal constituent of the product gas. Butadiene, however, can be produced by the well-known dehydrogenation of butane or butene

using well-known catalysts, and such a reaction is illustrative of the known use of catalysts and of diluents other than steam such as flue gas, nitrogen, etc., where, for example, catalyst activity might be impaired by the presence of steam.

It will be understood that this invention is not limited to normally liquid feed stock and that regardless of whether the feed stock is normally liquid or normally gaseous, the reactants entering the reaction zone are intended to be gaseous, as effectively as practically possible within the objectives of the invention. Once in the gaseous state, the reaction zone processing is unresponsive to any characterization of the original feed stock state as it may have existed in storage. Butane, butene, propane, and hexane are examples of feed stocks differing from oils. Such stocks are processable to utilize the high capacity features of this invention. In such cases, the liquid product "A" will be small in proportion to the gaseous product, thereby illustrating a process advantage which is different from the application to oil cracking per se, but which is very advantageous for the processing of blended feed stocks which heretofore have been limited in respect to capacity and performance due to processing deficiencies.

It is evident that there are numerous factors which will influence conditions for the most satisfactory operation of this invention, the actual limitation of which can be determined only by consideration of the starting materials and the intermediate and the finished products desired. For example, the extremely high heat inputs associated with this invention are the result of complex action. First, it demands the use of high average refractory temperatures normally above 1835° F. and for high capacity throughputs in the order of 2200° to 2250° F. Second, the average metal wall temperatures for the reaction zone are normally above 1685° F. and for optimum results from about 1900° to 2100° F. Third, the heat of the reacting mixture is a combination of internal radiant and convection heat under unusual temperature level relationships involving heat passage to the core, and to the gas, and from the core to the gas, all simultaneously. Fourth, the complex heat input mechanisms function simultaneously with the progressive reaction heat mechanisms. Fifth, the variants, such as preheat, dilution ratio, reactant velocity, temperature levels, core size and material, the feed stock itself, equilibrium and side reactions, catalytic effects, the diluent itself, completeness of vaporization, mixing, flash heating of hydrocarbon, surface conditions, etc., have direct bearing upon the high unit surface heat input of the invention. The trend in the refinery field over the years has been from lower temperature ranges upward, and with the time-temperature relationships used, the limitation of vapor phase cracking to light distillates with high hydrogen yield has given rise to the production of substantial quantities of coke which have acted to restrain progress, particularly in the field of tubular cracking. This has been contributed to by processes used in refinery practice when employing tubular furnaces and by the limitations placed upon the maximum temperatures permissible in these furnaces. In recent nontubular refining practice, the trend has been to promote better methods of utilizing coke rather than to develop processes which avoid or greatly minimize its production.

It will be seen therefore that this invention may be carried out by the use of various modifications and changes without departing from its spirit and scope.

The advantages of the invention are as follows: a minimum of C_2's, CH_4 and H_2 is obtained; a smaller gas yield richer in C_4's and higher is obtained; a larger condensable portion which has undergone modification compared to the feed stock is obtained; and the compounds present in the liquid portion are represented in part by the aromatic and olefin series and some are, of course, naphthenic, and valuable antiknock compounds are obtained therewith.

This application is a continuation-in-part of my copending application for United States Letters Patent, Serial No. 188,567, filed October 5, 1950, now abandoned.

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

1. In the process of converting hydrocarbons to obtain high capacity throughput per unit of transverse cross-sectional gas passage area with high yield of liquid products and low yield of gaseous products containing less than 18 pounds of ethylene per 100 pounds of hydrocarbon feed stock in a tubular furnace whereby the converted end products are recovered therefrom and separated, the improvement which comprises passing a reactant mixture comprising heated diluent gas and gaseous hydrocarbon through the reaction zone of an elongated metallic reaction tube for a period of not more than 0.3 second residence time in said zone and at high capacity throughput of the reactants while supplying external heat to the reaction zone at an average rate of more than about 20,000 B.t.u. per square foot of reaction tube surface to maintain an average temperature of the tube at the reaction zone of from about 1335° to about 2100° F., and controlling the relationship between said throughput and said average temperature of the tube to maintain a temperature differential (Δt) of at least 435° F. between the said average temperature of the tube and the reacted products immediately emerging from the reaction zone thereof and to maintain said reacted products at a temperature of from about 900° to about 1665° F. upon emergence from said reaction zone, whereby there is obtained after recovery and separation of the said reacted products the aforesaid high yield of liquid products and low yield of gaseous products.

2. In the process of converting hydrocarbons to obtain high capacity throughput per unit of transverse cross-sectional gas passage area with high yield of liquid products and low yield of gaseous products containing less than 18 pounds of ethylene per 100 pounds of hydrocarbon feed stock in a tubular furnace whereby the converted end products are recovered therefrom and separated, the improvement which comprises passing a reactant mixture comprising heated diluent gas and gaseous hydrocarbon through the reaction zone of an elongated metallic reaction tube for a period of not more than 0.3 second residence time in said zone and at high capacity throughput of the reactants while supplying external heat to the reaction zone at an average rate of more than about 20,000 B.t.u. per square foot of reaction tube surface to maintain an average temperature of the tube at the reaction zone of from about 1335° to about 2100° F., the said reaction zone being formed by an elongated core disposed within the elongated reaction tube to form a narrow substantially annular passageway for the reactants between said core and said tube, and controlling the relationship between said throughput and said average temperature of the tube to maintain a temperature differential (Δt) of at least 435° F. between the said average temperature of the tube and the reacted products immediately emerging from the reaction zone thereof and to maintain said reacted products at a temperature of from about 900° to about 1665° F. upon emergence from said reaction zone, whereby there is obtained after recovery and separation of the said reacted products the aforesaid high yield of liquid products and low yield of gaseous products.

3. The process of claim 2 wherein the diluent gas and the gaseous hydrocarbon are passed through the reaction zone as a mixture comprising steam and vaporized hydrocarbon oil, respectively.

4. The process of claim 2 wherein the reactants comprise steam, vaporized hydrocarbon oil and catalyst.

5. The process of claim 2 wherein diluent gas is passed through the elongated core countercurrent to the reactant

mixture and emerges therefrom and is then passed concurrent with said mixture.

6. The process of claim 2 wherein diluent gas is passed through the elongated core countercurrent to the gaseous hydrocarbon and is emerged beyond the entrance of said gaseous hydrocarbon into the reaction zone and is then passed concurrent with the said gaseous hydrocarbon.

7. The process of claim 2 wherein the average surface temperature of the core is maintained at a temperature of from about 300° to about 600° F. below the average temperature of the tube at the reaction zone.

8. In the process of converting hydrocarbons to obtain high capacity throughput per unit of transverse cross-sectional gas passage area with high yield of liquid products and low yield of gaseous products containing less than 18 pounds of ethylene per 100 pounds of hydrocarbon feed stock in a tubular furnace whereby the converted end products are recovered therefrom and separated, the improvement which comprises passing a reactant mixture comprising heated diluent gas and gaseous hydrocarbon through the reaction zone of an elongated metallic reaction tube for a period of not more than 0.3 second residence time in said zone and at high capacity throughput of the reactants while supplying external heat to the reaction zone at an average rate of more than about 20,000 B.t.u. per square foot of reaction tube surface to maintain an average temperature of the tube at the reaction zone of from about 1335° to about 2100° F., the said reaction zone being formed by an elongated tubular core disposed within the elongated reaction tube to form a narrow substantially annular passageway for the reactants between said core and said tube and said core containing catalyst for contact of the reactants therewith, and controlling the relationship between said throughput and said average temperature of the tube to maintain a temperature differential (Δt) of at least 435° F. between the said average temperature of the tube and the reacted products immediately emerging from the reaction zone thereof and to maintain said reacted products at a temperature of from about 900° to about 1665° F. upon emergence from said reaction zone, whereby there is obtained after recovery and separation of the said reacted products the aforesaid high yield of liquid products and low yield of gaseous products.

9. The process of claim 8 wherein the elongated tubular core contains an external catalyst mass exposed to the reactants.

10. The process of claim 8 wherein fluidized catalyst is passed through the elongated tubular core countercurrent to the reactants and emerges therefrom and is then passed concurrent with said reactants through the reaction zone.

11. The process of claim 8 wherein the elongated tubular core is perforated and has a catalytic body therein exposed to the reactants.

12. The process of claim 8 wherein the elongated tubular core is perforated and has a movable catalytic body therein exposed to the reactants.

13. The process of claim 8 wherein the elongated tubular core is perforated and has a continuously movable catalytic body therein exposed to the reactants.

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