

Oct. 19, 1965

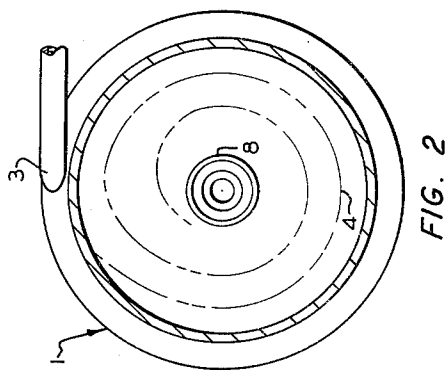
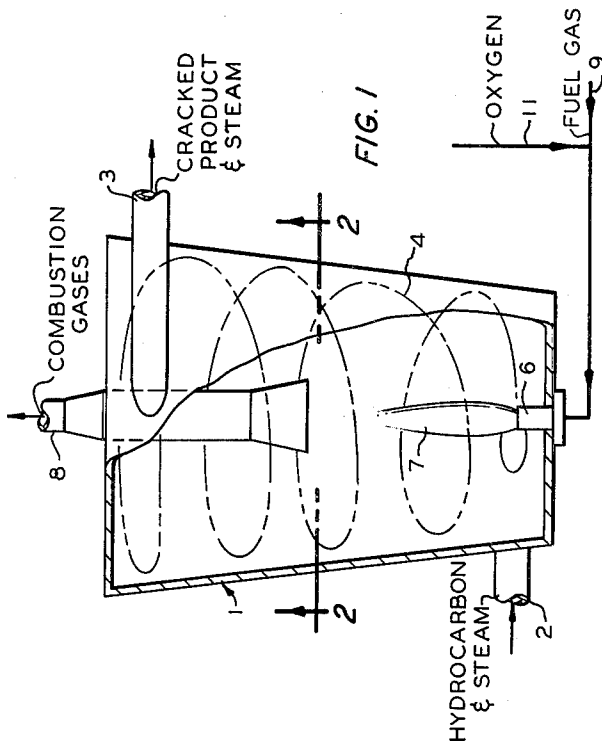
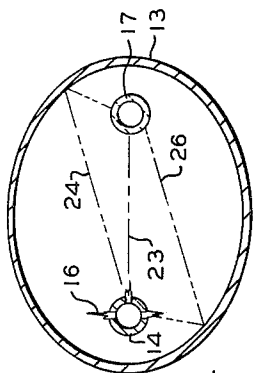
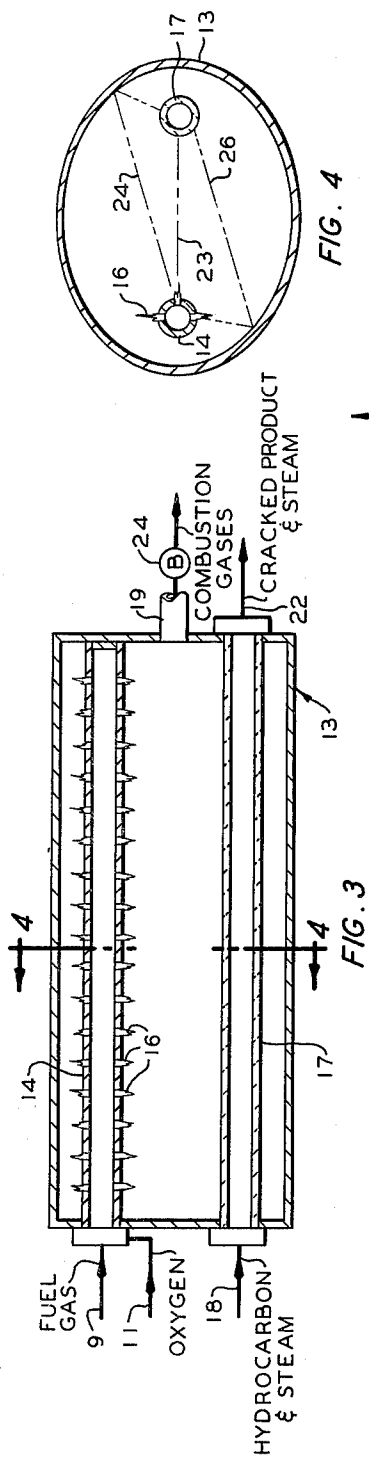
R. G. ATKINSON ETAL

3,213,015

CRACKING OF HYDROCARBONS WITH STEAM OR CARBON DIOXIDE

Filed Feb. 25, 1963

2 Sheets-Sheet 1



INVENTORS
R.G. ATKINSON
R.L. ARNETT
BY
Young & Quigg
ATTORNEYS

Oct. 19, 1965

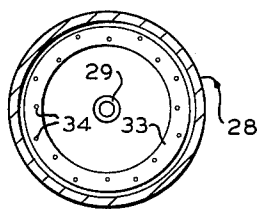
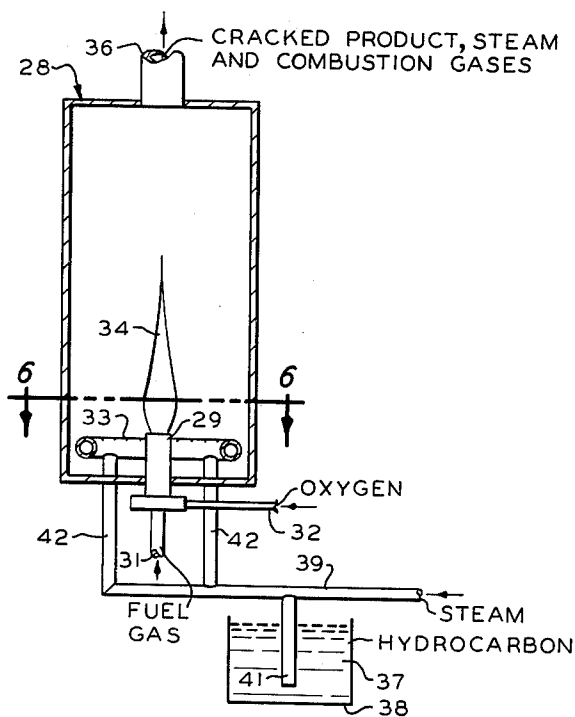
R. G. ATKINSON ETAL

3,213,015

CRACKING OF HYDROCARBONS WITH STEAM OR CARBON DIOXIDE

Filed Feb. 25, 1963

2 Sheets-Sheet 2



INVENTORS
R.G. ATKINSON
R.L. ARNETT

BY *Young & Quigg*
ATTORNEYS

1

3,213,015

CRACKING OF HYDROCARBONS WITH STEAM OR CARBON DIOXIDE

Robert G. Atkinson, Idaho Falls, Idaho, and Raymond L. Arnett, Bartlesville, Okla., assignors to Phillips Petroleum Company, a corporation of Delaware
Filed Feb. 25, 1963, Ser. No. 260,532
9 Claims. (Cl. 208—130)

This invention relates to the cracking of hydrocarbons. In another aspect, it relates to a process and apparatus for cracking hydrocarbons in the presence of steam, utilizing infrared radiation.

In the art of petroleum refining, it is a common practice to crack hydrocarbons by subjecting them to various thermal processes. For example, cracking stills or furnaces are used in which coils containing the hydrocarbon are externally heated, or the hydrocarbon is sprayed on a bed of coke which is heated to incandescence. Other methods employ checker-brick regenerative furnaces or a moving or stationary bed of solid contact material such as pebbles or catalyst-impregnated bases. These thermal processes rely primarily upon the heating effects of conduction and/or convection. While many of such processes do enjoy commercial exploitation, the many problems encountered, such as coking, burn-out of tubes, the necessity for regenerating contact materials, etc., leave room for improvement. Also, such processes, particularly where black body radiation is generated, are not generally selective in the cracking they cause to take place, the hydrocarbon molecules being split in a random nature, often at the end of chains, usually with the production of large amounts of methane and other low molecular weight products.

Accordingly, an object of this invention is to improve the cracking of hydrocarbons. Another object is to provide an improved process and apparatus for cracking hydrocarbons in the presence of steam, utilizing infrared radiation. Another object is to provide an improved process and apparatus for converting hydrocarbons to certain cracked hydrocarbons in high yields without relying in the first instance on conduction and convection, and in the absence of solid contact material, and with a minimum, if any, of black body radiation. Further objects and advantages of this invention will become apparent to those skilled in the art from the following discussion, appended claims and accompanying drawing in which:

FIGURE 1 is an elevational view in cross section of one embodiment of the improved apparatus of this invention;

FIGURE 2 is a cross sectional view of FIGURE 1 taken along the plane indicated; and

FIGURES 3 and 5 are elevational views in cross section of other embodiments of the improved apparatus of this invention, with FIGURES 4 and 6 being cross sectional views thereof, respectively, taken along the planes indicated.

In the improved cracking process of this invention, the hydrocarbon feed to be cracked is admixed with a fluid which will absorb infrared radiation of select wavelength and the mixture is subjected to intense infrared radiation of said select wavelength emitted by the combustion product generated by a fuel gas-oxygen burner. The infrared absorber used preferably will be of the same chemical constituency as that of the combustion product generated by the burner; for example, where the fuel gas is hydrogen, the combustion product generated will be water, and thus the infrared absorber to be admixed with the hydrocarbon feed will be water, or if the fuel gas is a hydrocarbon, such as methane, in which case the combustion product will comprise both water and

2

carbon dioxide infrared emitters, the infrared absorber to be admixed with the hydrocarbon feed will be water and/or carbon dioxide.

Several different furnaces or reactor configurations can be used to bring about the intense infrared radiation of the hydrocarbon-infrared absorber mixture, such furnaces being constructed so as to avoid the black body radiation of the prior art and foster the selective cracking of the hydrocarbon feed. For example, the cracking of straight chain paraffins, such as those present in paraffin wax, is effected according to this invention by splitting the hydrocarbon molecules near the center of the chains to form 1-olefins (which can be converted to primary alcohols, useful in the manufacture of biodegradable detergents) together with low molecular weight normal paraffins, with minimum formation of undesirable products, such as dienes, tar, methane, coke, etc.

The hydrocarbon-infrared absorber mixture is introduced into the furnaces of this invention in such a manner that it immediately "sees" the infrared radiation source provided by the fuel gas-oxygen burner; that is, the hydrocarbon-infrared absorber mixture is brought into the furnace in such a manner that it does not first pass through combustion gases, heated product, or other foreign gases which would present a barrier between the infrared radiation source and the hydrocarbon-infrared absorber mixture.

The hydrocarbon in the hydrocarbon-infrared absorber mixture is preferably in the gaseous or vaporous state, or in the form of a mist, and it is preferred to preheat the feed mixture before introducing the same into the furnace. Such preheating can be accomplished in any conventional preheater, by passing the hydrocarbon in indirect heat exchange with the products of conversion, or by circulating the hydrocarbon feed in a jacket surrounding the furnace, etc. The amount of infrared absorber employed can vary; generally the mole ratio of infrared absorber to hydrocarbon will be in the range of 0.001/1 to 1/1, preferably in the range of 0.01/1 to 0.1/1.

The infrared absorber molecules in the hydrocarbon-infrared absorber mixture introduced into the furnace readily absorb the infrared radiation emitted by the molecules of the infrared emitter formed in combustion of the fuel gas with oxygen. In the case of water, infrared radiation having wavelengths of about 2.7 and 6.2 microns will be emitted and absorbed; in the case of carbon dioxide, infrared radiation having wavelengths of about 4.3 and 15.0 microns will be emitted and absorbed. Such infrared radiation is not absorbed to any significant extent by hydrocarbon molecules of the feed. The infrared absorber molecules (e.g., water and/or carbon dioxide) are activated to high energy levels, e.g., 1000° F., by absorbing said infrared radiation and transfer this high energy immediately to the hydrocarbon molecules of the feed by conduction, causing the high molecular weight hydrocarbon molecules to undergo a selective cracking reaction (with a minimum of pyrolysis) which results in the splitting of hydrocarbon molecules at carbon-carbon bonds near the center of the molecules to produce 1-olefins ($RCH=CH_2$) and straight chain paraffins ($R'CH_3$) of about the same molecular weight. In order to foster this selective cracking, the process is carried out in the absence of a luminous flame (which contains soot or carbon particles, i.e., black body radiators), solid contact material, firebrick, catalyst impregnated supports, or other black body radiators, and by using highly reflective material, such as stainless steel, chromium plated alloys, metallized quartz, etc., in construction of the furnaces of this invention.

Referring now to the drawing, in which like parts have been designated with like reference numbers, and initially to FIGURES 1 and 2, there is illustrated one embodiment

of the furnace of this invention. This furnace comprises a shell 1 having a highly reflective inner surface to prevent or minimize black body radiation. Shell 1 preferably has a conical shape as shown to minimize the mixing of combustion gases with cracked products, with the diameter of the shell increasing uniformly from the bottom to the top. The rate of diameter increase in this design is correlated with the square root of the volume increase in cracked products. For example, if the volume of cracked products is twice the volume of the feed, the diameter of the top of the furnace will be $\sqrt{2}$ or about 1.4 times that of the bottom. This furnace, preferably made from or lined with stainless steel, has an inlet tube 2 near the lower end for the introduction of the hydrocarbon-infrared absorber feed mixture and an outlet tube 3 near the upper end of the shell for the withdrawal of cracked products and combustion products. Inlet 2 and outlet 3 are preferably disposed tangentially with respect to the periphery of shell 1, so that the feed mixture flows through the furnace in the form of an ascending helical stream adjacent the inner wall of the shell, as indicated by reference number 4. Axially disposed in the lower end of the furnace is a fuel gas-oxygen burner 6 which provides a non-luminous flame 7 that emits the infrared radiation of the selective wave length mentioned above. Flame 7 is disposed axially within the helically swirling hydrocarbon-infrared absorber mixture 4, and the combustion gases from the burner can be removed via axial pipe 8 in the top of the furnace, which pipe can depend some distance within the furnace, as shown, with the lower end thereof flared out, so as to further minimize admixture of the combustion gases with the gaseous cracked product and thus simplify to some extent the separation and recovery of desired components from the furnace effluent. Note especially that the hydrocarbon-infrared absorber feed mixture introduced via pipe 2 immediately "sees" the infrared radiation source—there is no substantial foreign gaseous barrier obstructing the transmission of this radiation to the introduced feedstock.

Fuel gas is supplied to burner 6 by line 9. Almost any type of fuel gas can be employed which will not give rise to a luminous flame, though it is preferred that the fuel gas be relatively rich in hydrogen. The ideal fuel gas is hydrogen itself, but because of economical considerations hydrocarbon fuels such as natural gas, liquid petroleum gas, or the like, will often be advantageous to use, these latter fuels generating water and carbon dioxide as combustion products which serve to emit the infrared radiation and transfer energy to the corresponding infrared absorber present in the feed, which energy is thence transferred to the hydrocarbon molecules causing the same to crack. The oxygen employed by the burner 6 is supplied by line 11 and it should be relatively pure to provide intense infrared radiation of the desired wave length and minimize the presence of fixed gases, such as nitrogen. Air itself will not be satisfactory because of the presence of nitrogen in the air, which nitrogen will cool the combustion flame and thus decrease the intensity of infrared radiation that is generated. The energy used to heat such nitrogen is lost to the cracking process. While combustion of the fuel gas with the oxygen will produce at least one species of infrared emitter as a combustion product, the fuel gas can be mixed with the same material that is mixed with the hydrocarbon cracking feed as an infrared absorber to augment the amount of infrared emitter generated by the burner as a combustion product. For example, water (e.g., 0 to 79 percent) can be admixed with the hydrocarbon fuel gas-oxygen mixture, the amount of such water being sufficient to enhance the intensity of the infrared radiation generated.

The products of the cracking process, withdrawn from the furnace via tube 3, can be condensed in any suitable cooler and the desired cracked products, such as 1-olefins, can be separated from non-condensed gases and recovered

by suitable conventional recovery equipment, such as distillation, etc.

Looking now at the embodiment shown in FIGURES 3 and 4, the furnace there comprises a shell 13 which is an elliptical cylinder, and again is made of a highly reflective material, such as stainless steel. Extending along part or all of one focus of the elliptical furnace 13 is a burner tube 14 having a plurality of spaced ports to provide sites for flames 16, the infrared radiation emitters. Like FIGURE 1, burner 14 can be provided with fuel gas 9 and oxygen 11. Disposed along the other focus of the elliptical furnace 13 is a tube 17 to which hydrocarbon-infrared absorber feedstock is supplied via line 18. The feedstock tube 17 is made of a material which is transparent, i.e., which transmits radiation preferably through the wavelength the range of 2.7 to 15.0 microns, for example, mica, quartz or such synthetic materials like Irtan. In this embodiment of the furnace of this invention, all contact between the combustion gases formed with the feedstock and cracked product are avoided, the combustion gases being withdrawn via outlet pipe 19 (preferably with the aid of a blower 24 or the like) and the product of the process being withdrawn via line 22.

The elliptical nature of the embodiment of FIGURE 3 is such as to enhance the intensity of the infrared radiation received by the hydrocarbon-infrared absorber mixture, in that the infrared radiation is received by the mixture by direct wave paths, such as path 23, and reflected wave paths 24, 26. No foreign gaseous barrier is disposed between flames 16 and the feed in tube 17.

In the embodiment of the furnace shown in FIGURES 5 and 6, the cylindrical shell 28, again made of a highly reflective material such as stainless steel, is provided with an axial burner 29, like that of FIGURE 1, again with suitable fuel gas being supplied via line 31 and oxygen supplied via line 32. Surrounding burner 29 is a tubular ring 33 for introduction into the furnace of the hydrocarbon-infrared absorber mixture, the ring 33 being provided with a plurality of apertures 34 to permit injection of the mixture as a gaseous cylinder. As in the case of the embodiment for FIGURE 1, the introduced hydrocarbon-infrared absorber mixture immediately "sees" the infrared source 34. The products of combustion and products of hydrocarbon conversion can be removed from the shell 28 by means of a common axial outlet pipe 36 in the upper end of the furnace. Alternatively, pipe 36 can depend within shell 28 in the manner shown in FIGURE 1, and another outlet pipe provided in the top of the shell 28 for withdrawal of the products of cracking, so as to minimize mixture of the two and simplify the separation and recovery of desired cracked components.

FIGURE 5 also illustrates a scheme for mixing the hydrocarbon with the infrared absorber, e.g., water, namely by aspiration of hydrocarbon 37 from a tank 38 into a line 39 by means of an aspirator pipe 41. (This technique can be employed in any of the embodiments of this invention.) The resulting mixture of the infrared absorber and hydrocarbon is then passed via one or more supply lines 42 to the injection ring 33.

As an example of this invention, referring to FIGURES 1 and 2, n-hexadecane at the rate of one gallon per minute (6.9 lbs./min.) is preheated and vaporized to yield 11.6 s.c.f. per min. of hexadecane vapor at 700° F. This vaporous hydrocarbon is mixed with steam and passed at 5 p.s.i.g. via line 2 into the shell 1 of the furnace, which is 3 ft. in height with bottom diameter of 1 ft. and a top diameter of 2 ft. A combustible mixture comprising 7% methane, 14% oxygen and 79% steam, is burned by burner 6 to produce a flame 7 having a temperature of 1100° F. Such combustion produces infrared radiation of 2.7, 4.3, 6.2 and 15.0 microns. This radiation is absorbed by the steam in the hydrocarbon-steam feed and the energy from these irradiated molecules is transferred to the hydrocarbon withdrawn from the shell 1 of the furnace via outlet pipe 3 and passed to a cooler. The

cooled effluent is then passed to a gas-liquid separator, from which is recovered 3900 cc. of liquid product (comprising 1900 cc. of C₆ to C₁₀ 1-olefins), and uncondensed gases (2% of feed).

As a comparison, the same hydrocarbon-steam mixture described in the example above is passed to a single tube heater measuring 4 in. inner diameter and 10 ft. in length, where the mixture is heated to 1100° F. The gaseous effluent therefrom is similarly cooled and condensed, yielding a gaseous product amounting to 25 weight percent of the feed (comprising 17% hydrogen, 20% methane, 21% C₂ and saturates and 42% olefins) and 2900 cc. of liquid product (comprising 1800 cc. of uncracked hexadecane, 500 cc. of C₄ to C₁₂ paraffins, 500 cc. of C₄ to C₁₂ olefins, and 100 cc. of diolefins and tar).

Various modifications and alterations of this invention will become apparent to those skilled in the art from the foregoing discussion and accompanying drawing without departing from the scope and spirit of this invention, and it should be understood that this invention is not to be limited unduly to that set forth herein for illustrative purposes.

We claim:

1. A process for cracking hydrocarbons which comprises mixing said hydrocarbons with a compound selected from the group consisting of steam, carbon dioxide and mixtures thereof;

passing a combustible fuel and oxygen in admixture which forms combustion products comprising the chemical composition of said selected compound into a conversion zone;

combusting said fuel in said conversion zone to produce an infrared radiation source;

passing said hydrocarbons in admixture with said selected compounds into said conversion zone in unobstructed communication with said infrared radiation source whereby the infrared radiation emitted by said source is absorbed unaltered in wavelengths by said selected compounds;

withdrawing the resulting gaseous effluent from said zone; and

separating the desired cracked hydrocarbon products from said effluent.

2. The process of claim 1 wherein said hydrocarbons-selected compound admixture is introduced into said conversion zone tangentially to said fuel-oxygen admixture.

3. The process of claim 2 wherein said selected compound is steam and said fuel is hydrogen.

4. The process of claim 2 wherein said selected compound is a mixture of steam and carbon dioxide and said fuel is a hydrocarbon gas.

5. The process of claim 1 wherein said fuel-oxygen admixture is introduced axially into the lower portion of said conversion zone and said hydrocarbons-selected compound admixture is introduced axially into the lower portion of said conversion zone and circumscribing said fuel-oxygen admixture.

6. Apparatus for cracking hydrocarbons, which comprises a frusto conical reaction chamber formed of highly

reflective materials, a fuel gas-oxygen burner axially disposed in the bottom of said chamber, the diameter of said chamber increasing from bottom to top, means to tangentially introduce a hydrocarbon-steam mixture into the lower end of said chamber whereby unobstructed communication is provided between said burner and said mixture, means to axially remove combustion gases from the top of said chamber, and means to tangentially remove gaseous cracked product from the upper end of said chamber.

7. A hydrocarbon cracking furnace which comprises an inverted truncated cone housing, a burner axially positioned at the base of said housing, a first conduit communicating with said burner for passing fuel and oxygen thereto which produces infrared rays, a second conduit tangentially communicating with the lower portion of said housing for introducing hydrocarbon feed material, whereby unobstructed communication is provided between said burner and said hydrocarbon feed, a cylindrical hood depending axially from the top of said housing and communicating with a third conduit extending therefrom for removing combustion gases from said housing, and a fourth conduit tangentially communicating with the upper portion of said housing for removing cracked feed therefrom.

8. Apparatus for cracking hydrocarbon which comprises a horizontal elliptical shaped housing, a burner longitudinally disposed along one focus of the housing, a plurality of openings in said burner, a first conduit communicating with said burner for introducing fuel and oxygen which produces infrared rays, an infrared transparent chamber disposed longitudinally along the other focus of said housing, a second conduit communicating with said chamber for introducing hydrocarbon feed material, a third conduit communicating with the opposite end of said chamber for removing cracked product therefrom, and a fourth conduit communicating with said housing for removing combustion gases therefrom, the communication between said burner and said hydrocarbon feed being otherwise unobstructed.

9. Apparatus for cracking hydrocarbons which comprises a housing, a burner axially positioned in the base of said housing, means for introducing fuel and oxygen to said burner which produces infrared rays, manifold ring having a plurality of openings therein disposed about said burner within said housing, means for introducing hydrocarbon feed material to said manifold whereby unobstructed communication is provided between said burner and said hydrocarbon feed, and means axially positioned at the top of said housing for removing cracked product and combustion gases.

References Cited by the Examiner

UNITED STATES PATENTS

2,172,228	9/39	Van Peski	208—106
2,397,899	4/46	Witkiewicz	23—288.9
3,018,309	1/62	Krejci	260—679

ALPHONSO D. SULLIVAN, *Primary Examiner.*