Feb. 24, 1959 R. C. SCOFIELD 2,875,148

REGENERATIVE HYDROCARBON CRACKING PROCESS IN SERIES

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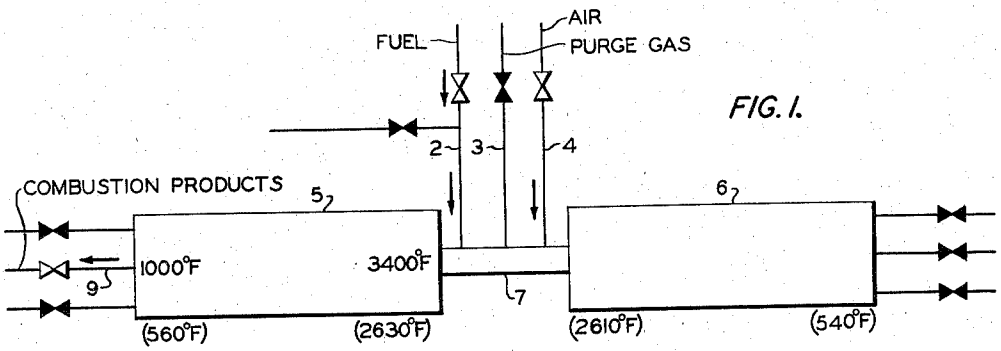


FIG. 1.

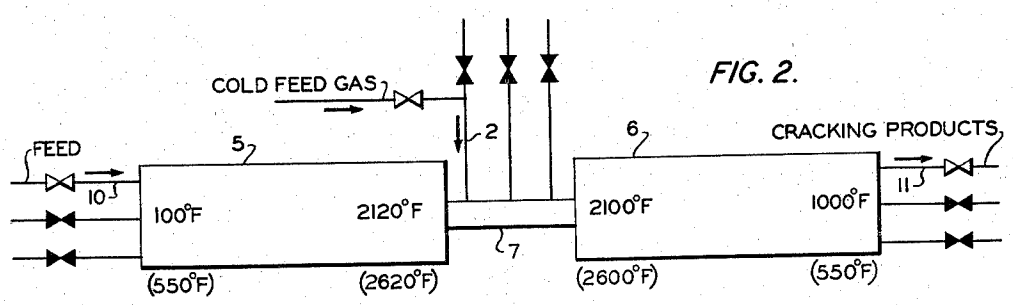


FIG. 2.

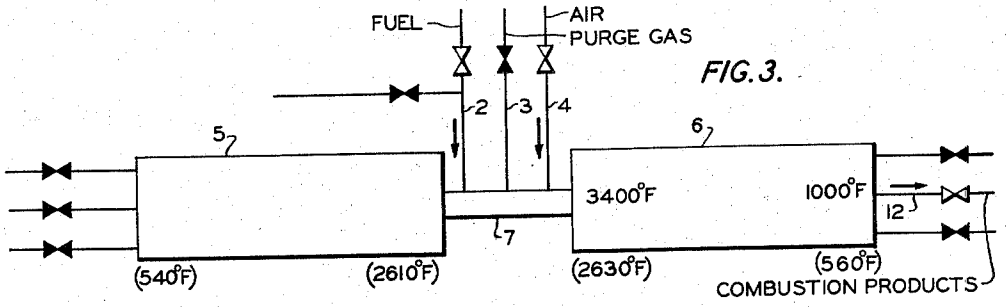


FIG. 3.

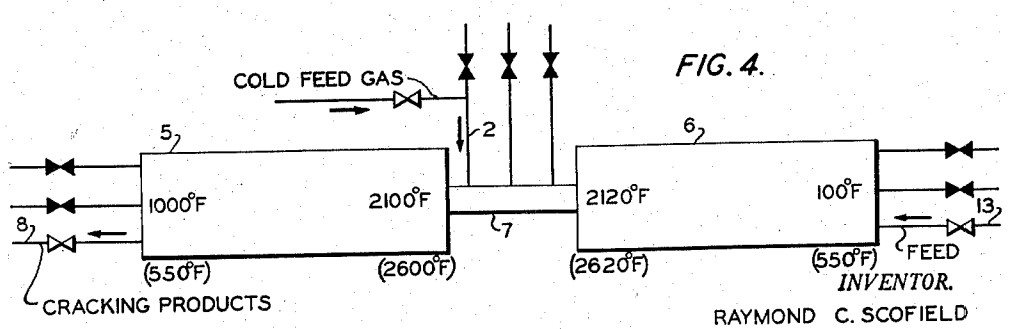


FIG. 4.

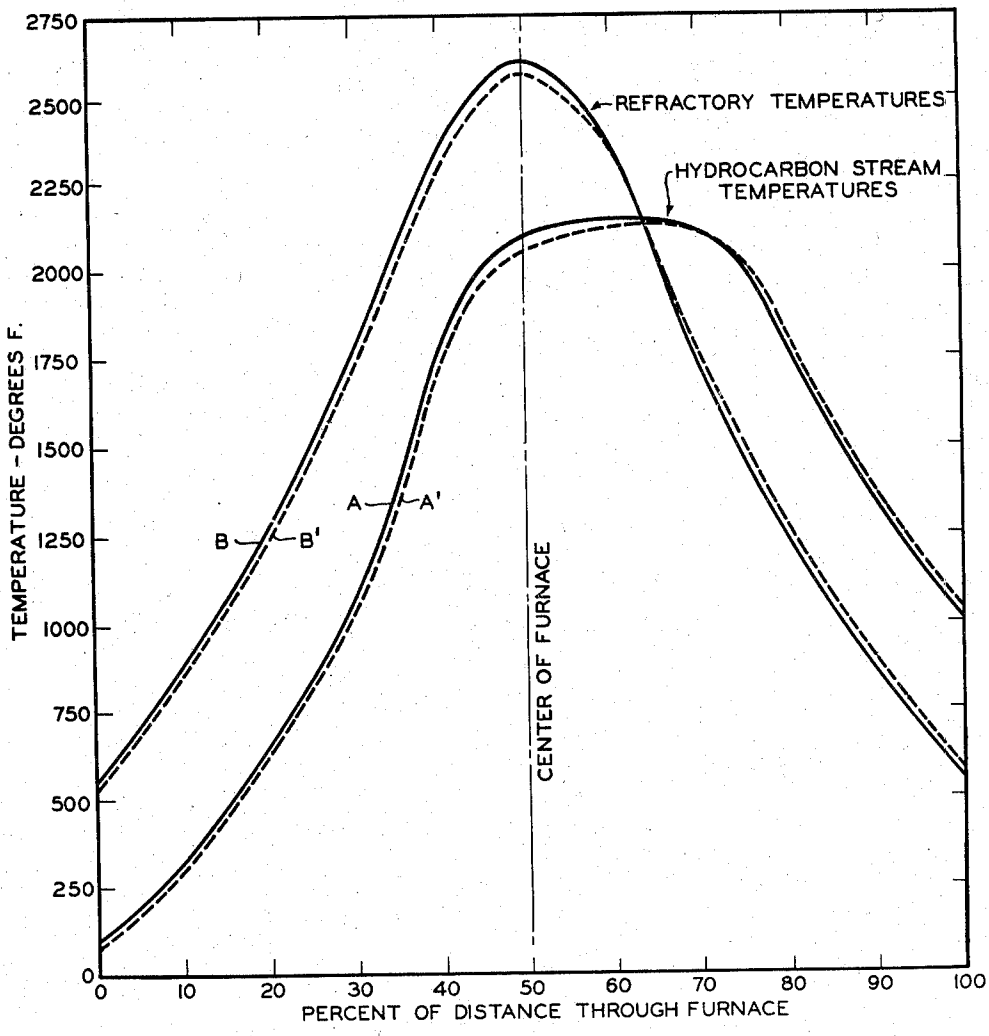
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REGENERATIVE HYDROCARBON CRACKING PROCESS IN SERIES

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FIG. 5.



TEMPERATURE PROFILE DURING CRACKING PERIOD

——— START OF CRACKING PERIOD

– – – – END OF CRACKING PERIOD

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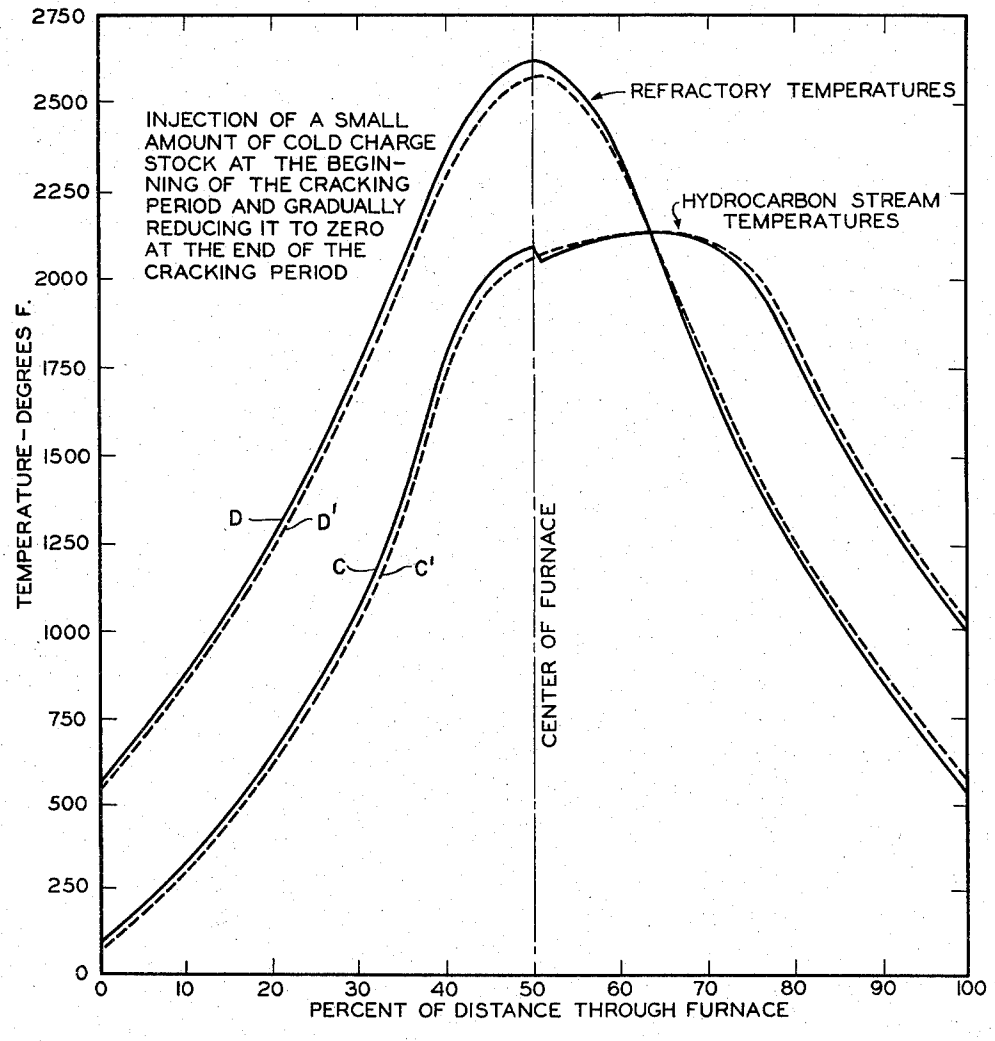
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REGENERATIVE HYDROCARBON CRACKING PROCESS IN SERIES

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FIG. 6.



TEMPERATURE PROFILE DURING CRACKING PERIOD

——— START OF CRACKING PERIOD

---- END OF CRACKING PERIOD

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REGENERATIVE HYDROCARBON CRACKING PROCESS IN SERIES

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Application January 11, 1952, Serial No. 265,987

13 Claims. (Cl. 208—64)

This invention relates to the cracking of hydrocarbons. In one aspect, it relates to the pyrolysis or thermal cracking of hydrocarbons. In another aspect, it relates to the catalytic cracking of hydrocarbons. In another aspect, it relates to the conversion of methane to benzene in a regenerative furnace.

The regenerative furnace is one of the few forms of commercial equipment that are satisfactory for extremely high-temperature pyrolysis. Whereas regenerative furnaces have appeared to be attractive because of low cost, their use has been discouraged by their limitations, namely, low thermal efficiences, fluctuating severity of pyrolytic conditions, high maintenance cost of high-temperature valves, and low conversions.

At least two methods have been suggested for obviating the above-mentioned disadvantages: (1) gradually decreasing the flow rate of the reactants; and (2) diluting the reactants with inert gases. The first method results in low throughputs. The second results in undesirable dilution of products. For these reasons, the proposed methods are unsatisfactory.

The present invention solves the problems of low thermal efficiencies, low conversions, and fluctuating severity, and obviates the necesity for using special valves which must be adapted to high-temperature usage.

According to this invention, overcracking is avoided by adding a small amount of cold feed hydrocarbon to a stream of hydrocarbon undergoing cracking, the cold feed being added at a point at which cracking begins. Since the added feed is chemically similar to or even identical with the stream being cracked, no dilution occurs. Furthermore, since cracking is endothermic, the heat of reaction of the added cold feed, as well as the sensible heat thereof, is utilized to remove heat from the hydrocarbon being cracked. Overcracking and consequent loss occasioned by formation of undesired by-products, such as coke, are minimized or prevented.

By "cold" feed, is meant feed at a temperature substantially below the cracking temperature used in the process. Since the feed in the process of this invention need not be preheated before entering the system, the "cold" feed added can also be unpreheated.

Further, in accordance with the invention, as the cracking period proceds, the amount of added cold feed is gradually decreased. This results in increased uniformity of cracking conditions throughout the cracking period and in a high throughput.

In one modification of the invention, two regenerative furnaces are connected in series, one being maintained at a higher temperature than the other. One furnace is heated to a high temperature by means of a fuel-oxygen mixture and is later purged to remove any remaining oxygen or other oxidizing gas. The feed passes through the furnace thus heated to cracking temperature and subsequently through the low-temperature furnace. In passing through the low-temperature furnace, the hot, cracked hydrocarbon transfers heat to the low-temperature furnace. The flow of hydrocarbon is then discontinued, and the low-temperature furnace is heated to cracking temperature and purged as previously described. Hydrocarbon feed then passes through the furnaces, but in a direction opposite to that previously specified. During the passage of hydrocarbon through the furnaces in each direction, a small amount of cold hydrocarbon feed is added preferably at, or upstream from the mid-point between the two furnaces, so as to maintain nearly constant depth of cracking. The point of injection of cold feed is preferably upstream from the mid-point by a distance not greater than 20 percent of the length of the upstream furnace. The amount of cold feed added is in the range of 1 to 5 percent of the total hydrocarbon feed passing through the furnaces, preferably from 2 to 4 percent, and more desirably about 3 percent. The amount of added cold feed is gradually decreased during the cracking cycle, preferably being decreased to zero at the end of the cycle. The location of the point of injection of cold feed is preferably such that the main hydrocarbon fed stream will have reached the desired cracking temperature, but, because of the injection of cold feed at this location, will not be permitted to exceed the desired temperature range even during the first part of the cracking cycle. The gradual reduction in the amount of cold feed added, as the cycle progresses, results in a more nearly constant cracking temperature throughout the cycle and hence in nearly constant depth of cracking. The products are then rapidly quenched to below reaction temperatures in passing through the low temperature furnace.

The term "cracking," as used herein, is considered generic to catalytic and pyrolytic cracking. It includes such processes as pyrolysis of methane to carbon black and hydrogen, pyrolysis of methane to benzene or acetylene and of ethane to ethlene, pyrolysis of naphtha to butadiene, thermal reforming of naphtha, catalytic cracking of gas oil, catalytic reforming of gasoline or of naphtha, and the like.

One embodiment of the invention is diagrammatically illustrated in Figures 1 to 4. In these figures, the heavy arrows indicate the flow of materials during the cycle illustrated. The temperatures not enclosed in parentheses are the average stream temperatures. Those enclosed in parentheses are average furnace refractory temperatures.

Figure 1.—First heating and purge cycle

Fuel gas, such as natural gas, producer gas, hydrogen, or the like passes through inlet **2**, together with air or oxygen admitted through inlet **4**, and thence through furnace **5**. The combustion of the fuel gas heats the furnace refractory to the required temperature.

After the furnace has been heated to cracking temperature, the flow of fuel and air is discontinued and a purge gas, such as steam, nitrogen, or other inert gas is passed through inlet **3** and through the furnace to remove any residual oxygen.

Combustion gases and purge gas are removed through outlet **9**.

Figure 2.—First cracking cycle

Hydrocarbon gas, such as natural gas or methane, enters furnace **5** through inlet **10** and is rapidly heated to cracking temperature by contact with the furnace refractory. It continues through conduit **7** and furnace **6**, imparting heat to the refractory therein. Cracking products are removed through outlet **11** and passed to means, not shown, for recovery of products, such as benzene.

A small amount of cold feed gas is introduced through inlet **2** at the beginning of the cracking cycle, and is gradually reduced to zero as the end of the cycle is reached.

Figure 3.—Second heating and purge cycle

Fuel gas and air are introduced through inlets 2 and 4, respectively, and heat furnace 6 to cracking temperature, as described in connection with furnace 5 and Figure 1. Combustion products are withdrawn through outlet 12.

Figure 4.—Second cracking cycle

Natural gas or methane feed enters furnace 6 through inlet 13 and is rapidly heated to cracking temperature. The gas being cracked passes through conduit 7 and through furnace 5, imparting heat to the refractory therein, which has previously been cooled by the endothermic cracking reaction. Cracking products are withdrawn through outlet 8 and passed to a recovery system not shown.

As described in connection with Figure 2, a small amount of cold feed gas is added through inlet 2 to prevent overcracking, and is gradually decreased to zero as the end of the cracking cycle is reached. While inlet 2 is shown, for simplicity in the drawings, as located adjacent furnace 5, in both Figures 2 and 4, it should be understood that the exact location of the point of injection of cold feed will depend on the direction of flow of the main body of feed.

It will be noted from the drawings, that one advantage of this invention is that the cracking products are withdrawn from the cooler furnace at a temperature of the order of 1000° F. Heat previously imparted to the stream in the hotter furnace is retained in the cooler furnace for the next cracking cycle. A desirable heat economy, hitherto unrealized, is thus effected by the invention.

It is in the interest of heat economy to maintain a low temperature at the furnace outlet. On the other hand, raising the outlet temperature reduces the amount of heavy hydrocarbons, tar and coke which deposits on the refractory. Also, increasing the outlet temperature favors the kinetics of combustion during the regeneration cycle. The amount of heavy hydrocarbons, tars and coke produced in cracking operation and, therefore, the fouling tendency, will vary widely depending on the hydrocarbon charge depth of cracking and cracking conditions. Consequently, for reasons of economy, it is preferred to operate at the lowest outlet temperature consistent with an adequate burning of the deposits on the refractory.

As has been indicated, the extent of refractory fouling can vary considerably depending on the conditions of operation. In many instances, it is possible to maintain an outlet temperature materially below 1000° F. without sacrificing continuity of operation.

Furnaces 5 and 6 are regenerative furnaces containing refractory heat-transfer members made of materials such as fire brick, silicon carbide, zirconia, Alundum, and the like. The refractory may be in shapes characterized as slabs, plates, bricks, and balls or pebbles. For purpose of illustration, the application of silicon carbide in slabs is considered in more detail.

When regenerative furnaces utilizing slab silicon carbide refractory are employed in accordance with this invention, the mass velocity of the hydrocarbon charged during the cracking cycle is in the range from 1.2 to 2.5 pounds per square foot of heating surface per hour, preferably 1.7 to 2.1 pounds per square foot of heating surface per hour. During the heating cycle a fuel gas is charged to provide a heat release of from 3,500 to 7,000 B. t. u. per square foot of heating surface per hour. The duration of the cracking cycle is in the range of 0.5 to 2 minutes, and preferably 1 minute. Alternation from the cracking to the heating cycle and vice versa, can be accomplished by the use of automatic valves, which need not be designed with water cooling or for extreme operating temperatures.

When so desired, the furnaces can contain known cracking catalysts, such as silica-alumina, bauxite, silica-zirconia, magnesia-zirconia, and the like. These catalysts are, of course, used at lower temperatures than those indicated in the drawing. Also reforming catalysts such as alumina-molybdena, alumina-chromia, and the like, can be used when naphtha or gasoline is reformed.

High-temperature thermal cracking, e. g., of methane for the production of benzene may be conducted at temperatures in the range 1900 to 2500° F., preferably 2100 to 2250° F. Pressures may be selected from a wide range but preferably 15 to 35 p. s. i. a. Thermal cracking of methane for the production of acetylene may be conducted in the range of 2100 to 2500° F., preferably 2200 to 2300° F. Preferred pressures are between 2 and 25 p. s. i. a.

High-temperature thermal cracking of ethane for the production of ethylene may be carried out at 1300 to 1700° F., preferably 1400 to 1600° F. Operating pressures may be chosen between 15 and 60 p. s. i. a, preferably between 15 and 30 p. s. i. a. The pyrolysis of ethane to produce benzene may be performed over a wide range of temperatures from 1400 to 1800° F., preferably 1500 to 1600° F. The pyrolysis of ethane to produce acetylene may be conducted in the range 2000 to 2400° F., preferably 2100 to 2250° F. The preferred operating pressures are in the range 2 to 30 p. s. i. a.

The pyrolysis of propane to produce ethylene can be performed in the range 1200 to 1800° F., preferably 1450 to 1600° F. The preferred pressure range is 15 to 35 p. s. i. a. Benzene can be produced by thermal cracking of propane in the range of 1300 to 1600° F., preferably in the range of 1450 to 1550° F. and preferably at pressures in the range of 15 to 35 p. s. i. a. Acetylene can be produced in the range from 1900 to 2300° F., preferably at 2100 to 2250° F. and at preferred pressures from 2 to 30 p. s. i. a.

Heavy oils and residuum stocks may be thermally cracked in regenerative furnaces to produce a variety of products including heavy oils, light oils, benzene, toluene, xylenes and heavier aromatics, ethylene, propylene, diolefins, cyclic diolefins, and light hydrocarbons. The provision for constant depth of cracking is especially helpful with this class of hydrocarbons as a means of limiting fouling of the refractory while maintaining high conversions. The preferred operating temperatures with this class of chargestock is in the range 900 to 1300° F. and the corresponding pressures lie in the range from 0.5 to 25 p. s. i. a.

When catalytic cracking or reforming is practiced according to this invention, the temperature is from 850 to 1200° F., preferably 900 to 1100° F. The space velocity is from 0.5 to 10 liquid volumes per volume of catalyst per hour.

In Figures 5 and 6 are curves obtained by plotting temperature against percentage of distance between the inlet of one regenerative furnace and the outlet of another such furnace, said furnaces being connected in series, in accordance with this invention when operated to produce benzene by pyrolysis of methane. The solid curves represent temperatures at the beginning of the cracking cycle. The broken curves represent temperatures at the end of the cracking cycle.

Figure 5 shows temperatures obtained when no cold natural gas feed is added at the point where cracking begins. Curves A and A′ represent temperatures of the hydrocarbon stream at the beginning and at the end, respectively, of the cracking cycle. Curves B and B′ represent refractory temperatures at the beginning and at the end, respectively, of the cracking cycle.

Figure 6 shows temperatures obtained when 3 percent of cold natural gas feed is added, at the mid-point of the furnace, to the natural gas undergoing cracking. Curves C and C′ represent natural gas stream temperatures at the beginning and at the end, respectively, of the cracking cycle. Curves D and D′, respectively, represent the corresponding refractory temperatures.

Comparison of curves A and A′ with curves C and C′

shows that the temperature level in the high temperature zone dropped as much as 50° F. between the beginning and end of the cracking cycle, whereas, when cold feed is introduced, in accordance with this invention, at the point where cracking begins, the high temperature zone remained for the most part at substantially constant temperature levels.

The variation in temperatures through the high temperature zone during the cracking cycle frequently results in variations in depth of cracking. The serious nature of this problem is made evident by Bureau of Mines data[1] on the pyrolysis of methane in a quartz tube at constant flow rates.

Reaction Temperature, ° C.	Expansion Volume Percent	Yield, Weight Percent	
		Acetylene	Coke
1,200	14.5	3.70	0.20
1,220	22.6	5.42	0.91
1,240	23.5	5.74	2.01

The higher temperatures at the start of the cracking cycle normally results in deep cracking and high coke production. Towards the end of the cycle the temperature is lower, with the result that cracking is less deep and acetylene production is considerably reduced.

As a result of this invention, a substantially constant depth of cracking can be maintained and the reaction can be carried out at optimum conditions of yield.

Variation and modification are possible within the specification and claims to this invention, the essence of which is that overcracking of a hydrocarbon stream is prevented and increased uniformity of cracking conditions is obtained by introducing into a stream of hydrocarbon being cracked a small proportion of cold hydrocarbon feed at a point at which cracking begins.

I claim:

1. In a cracking process in which a hydrocarbon feed stream is cracked by passing it through a first regenerative zone maintained at cracking temperature and then through a second regenerative zone maintained at a lower temperature, the improvement which comprises adding to said stream, at a locus of incipient cracking, a small proportion of said feed, uncracked, and at a temperature below cracking temperature, gradually decreasing said proportion of added hydrocarbon, and recovering cracking products.

2. The process of claim 1 in which said point is located at a locus intermediate said zones.

3. The process of claim 1 in which said cracking is continued for a predetermined period of time, and said proportion of added hydrocarbon is decreased to zero at the end of said period.

4. The process of claim 1 in which a feed selected from the group consisting of naphtha and gasoline is reformed in the presence of a catalyst selected from the group consisting of alumina-chromia and alumina-molybdena.

5. The process of claim 1 in which said zones contain a cracking catalyst and said cracking temperature is in the range 850 to 1200° F.

6. The process of claim 5 in which said catalyst is selected from the group consisting of silica-alumina, bauxite, silica-zirconia, and magnesia-zirconia, the temperature is from 900 to 1100° F., the space velocity is in the range 0.5 to 10 liquid volumes of feed per volume of catalyst per hour, and the feed is selected from the group consisting of gas oil and naphtha.

7. A process which comprises maintaining two regenerative furnaces in series; passing a fuel-oxygen mixture through only one of said furnaces while burning said fuel to heat said furnace; purging said furnace to remove residual oxidizing gas; passing a hydrocarbon feed through the furnace so heated; cracking said feed at a temperature in the range 1900 to 2500° F., imparted by the furnace heated as described, a pressure in the range 15 to 35 p. s. i. a., a mass velocity in the range 1.2 to 2.5 pounds of feed per square foot of heating surface per hour, for a cracking period in the range 0.5 to 2 minutes; adding to said feed, when it reaches incipient cracking temperature, uncracked hydrocarbon feed at a temperature below said cracking temperature, the proportion of added feed being in the range 1 to 5 percent of the total feed; passing said total feed through the other of said furnaces, thereby imparting heat to the other furnace; gradually decreasing the proportion of uncracked feed added during said cracking period; after said cracking period, heating said other furnace by burning fuel and purging as aforesaid; cracking said feed in said other furnace under cracking conditions described above; adding uncracked feed as aforesaid; passing total feed through the first-mentioned furnace to impart heat thereto; gradually decreasing the amount of added feed as aforesaid; and recovering cracking products.

8. The process of claim 7 in which the hydrocarbon feed comprises methane, the temperature is in the range 2100 to 2250 F., the mass velocity is from 1.7 to 2.1 pounds per square foot per hour, the proportion of uncracked feed added is from 2 to 4 percent, said proportion being decreased to zero at the end of the cracking period, and one of said cracking products is benzene.

9. The process of claim 8 in which the feed is natural gas, the pressure is atmospheric, the proportion of uncracked feed added is 3 percent, and the duration of said cracking period is 1 minute.

10. The process of claim 9 in which said uncracked feed is unpreheated prior to addition.

11. A process which comprises maintaining two regenerative furnaces in series, passing a fuel-oxygen mixture through only one of said furnaces while burning said fuel to heat said furnace, purging said furnace to remove residual oxidizing gas; passing hydrocarbon feed through the furnace so heated, cracking said feed at cracking conditions of temperature, pressure and mass velocity for a predetermined cracking period; adding to said feed at a locus intermediate said furnaces, a small amount of uncracked hydrocarbon feed at a temperature below said cracking temperature; passing the combined feed through the other of said furnaces; gradually decreasing the proportion of uncracked feed added during said cracking period; after said cracking period, heating said other furnace by burning fuel and purging as aforesaid; cracking said feed in said other furnace under cracking conditions of temperature, pressure and mass velocity; adding uncracked feed as aforesaid; passing combined feed through the first-mentioned furnace to impart heat thereto; gradually decreasing the amount of added feed as aforesaid; and recovering cracking products.

12. The process of claim 11 in which the hydrocarbon feed is a normally gaseous hydrocarbon.

13. In a process carried out in a pair of regenerative furnaces maintained in series, the improvement which comprises passing a fuel-oxygen mixture through one only of said furnaces while burning said fuel to heat said furnace; purging said furnace to remove residual oxidizing gas; passing a hydrocarbon feed through said furnace so as to heat said feed to a desired cracking temperature; adding to said feed, when it reaches incipient cracking temperature, uncracked hydrocarbon feed at a temperature below said cracking temperature; passing said total feed through the other of said furnaces, thereby imparting heat to said other furnace; gradually decreasing the proportion of uncracked feed added during a desired

[1] H. M. Smith, P. Grandone and H. T. Rall, U. S. Bureau of Mines R. I. 3143 (October 1931).

cracking period; and recovering from said other furnace cracking products.

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