

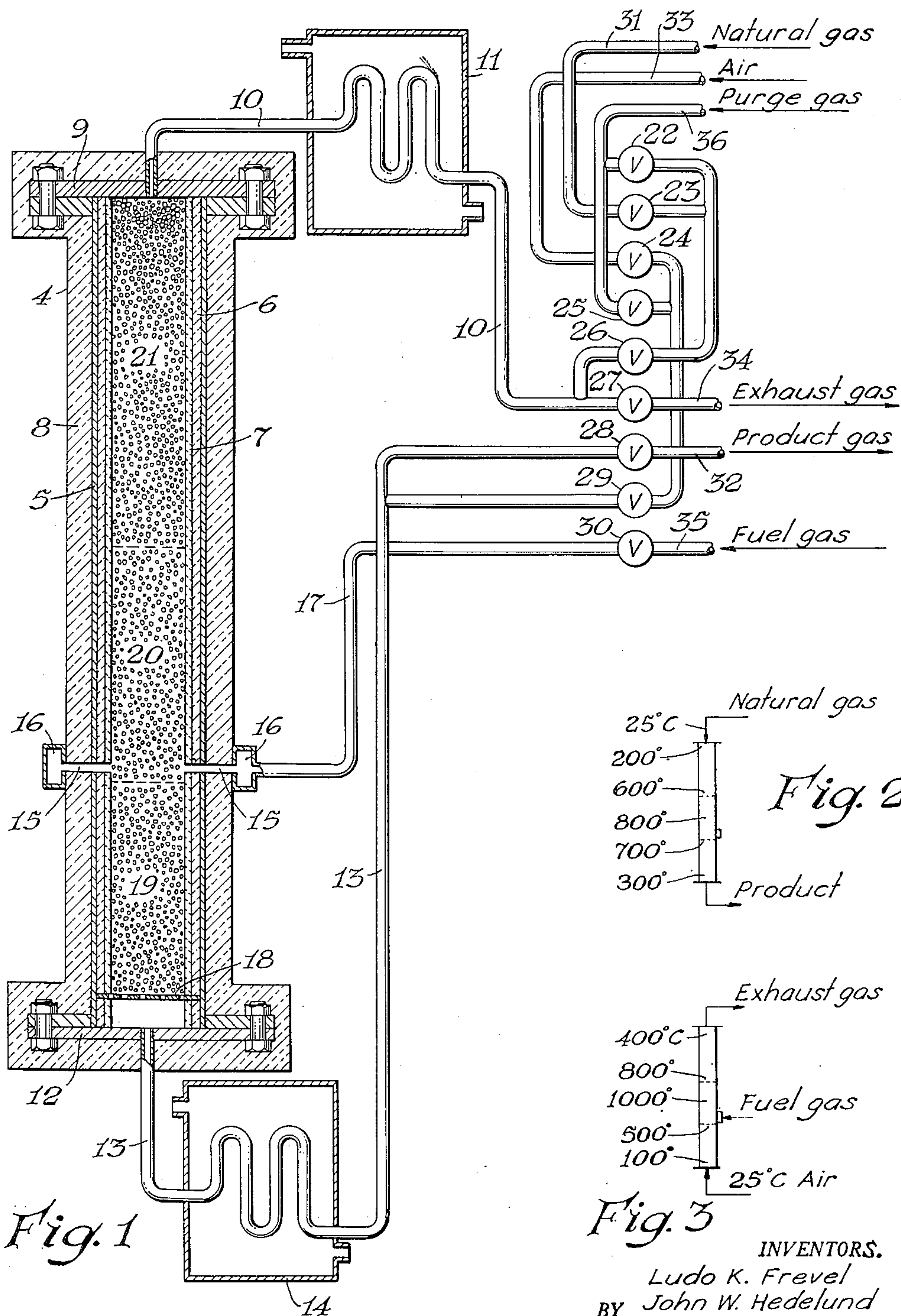
Feb. 24, 1953

L. K. FREVEL ET AL

2,629,753

MAKING ETHYLENE BY CATALYTIC PYROLYSIS

Filed Aug. 26, 1948



INVENTORS.
Ludo K. Frevel
BY John W. Hedelund

Griswold & Burdick
ATTORNEYS

UNITED STATES PATENT OFFICE

2,629,753

MAKING ETHYLENE BY CATALYTIC
PYROLYSIS

Ludo K. Frevel and John W. Hedelund, Midland,
Mich., assignors to The Dow Chemical Com-
pany, Midland, Mich., a corporation of Dela-
ware

Application August 26, 1948, Serial No. 46,328

10 Claims. (Cl. 260—683)

1

This invention relates to an improved method for making ethylene by the catalytic pyrolysis of paraffin hydrocarbons.

In the making of ethylene by the pyrolysis of ethane and heavier paraffin hydrocarbons at temperatures above 750° C. as heretofore carried out, there are produced, in addition to the desired ethylene, significant proportions of acetylene and of non-gaseous hydrocarbons, such as gasolines, tars, and normally solid cyclic hydrocarbons. Not only are these latter formed in part at the expense of the ethylene yield, but their presence also raises serious operating difficulties. Thus, the tars and solid hydrocarbons always tend to foul the cracking equipment and may even plug it, while the acetylene appears as a contaminant of the ethylene and can be separated only by a troublesome purification.

These problems are especially acute when the raw material for making ethylene is the ethane present in most natural gas. When such gas is pyrolyzed above 750° C., the cracked product contains, besides ethylene, several per cent of acetylene and also a heavy brown mist or fog which is extremely hard to deal with. For this reason, the direct pyrolysis of natural gas to make ethylene has been little practiced, and it has been customary first to separate an ethane-rich fraction from the gas by an absorption or other concentrating treatment and then to pyrolyze only this fraction. While effective, this process introduces the expensive complication of another separatory step and hence has found but limited use.

With these considerations in mind, the present invention has for an object the provision of an improved process for making ethylene by the pyrolysis of paraffin hydrocarbons in which the simultaneous production of acetylene and non-gaseous hydrocarbons is largely prevented. A related object is to provide a simple inexpensive method of making ethylene by the direct pyrolysis of ethane-containing natural gas. A further object is to provide a high-temperature regenerative catalytic cracking process in which there is an efficient utilization of heat.

The invention depends on the discovery that there is a small group of catalytic materials which at temperatures of 800° to 1000° C. act selectively to accelerate the cracking of ethane and higher paraffins to ethylene and at the same time to inhibit the formation of acetylene and non-gaseous hydrocarbons, or possibly to destroy these latter as fast as they form. The catalysts found to exhibit this unique behavior

2

consist essentially of refractories which are infusible and irreducible by hydrocarbons at 1000° C. and have a surface area of less than one square meter per gram and which have disposed on their surface a metal of the class consisting of manganese, iron, copper and cobalt in a proportion of from 0.001 to 1.0 per cent by weight of the refractory.

In making ethylene according to the invention, then, ethane or a higher paraffin hydrocarbon is simply passed as a stream over or through a bed of such a catalyst at a temperature of 800° to 1000° C. During contact with the catalyst, the hydrocarbon is pyrolyzed largely to ethylene, with little if any accompanying formation of acetylene and non-gaseous hydrocarbons. The resulting cracked gas is then cooled and may be used as a source of ethylene for chemical reactions or may be treated to separate the ethylene in purified form. Carbon produced during the pyrolysis remains on the catalyst and is later removed by burning it off.

Since the catalysts in the process are refractories, they are well adapted to use as heat-storing media, thus permitting the pyrolysis to be carried out by a cyclic regenerative procedure of high heat economy. In such a case, other catalysts may be employed at other stages of the cycle further to treat the pyrolyzed gas as will be explained in the following detailed description of the invention.

The catalysts of the invention may be regarded as consisting essentially of two components, a refractory base and a metal disposed on it. The refractory appears to be more than a mere support, seeming to exert its own catalytic effect, which is markedly promoted by the metal. The refractory must, of course, be stable under the most extreme conditions of the pyrolysis, and to this end should not fuse at temperatures up to 1000° C. and should likewise not be reduced by hydrocarbons at that temperature.

Aside from these limitations, however, the physical state of the refractory appears to be of more significance than its chemical identity. In particular, it should be relatively dense, i. e. of limited porosity, so that, even when in the form of small pieces, it does not have a catalytic surface area of more than one square meter per gram. The area referred to is not simply the geometric area defined by the outer surfaces of the pieces, but is the total area exposed to the molecules of the gas being pyrolyzed, and thus includes the inner surface of whatever pores there may be in the refractory. This total area

may be determined by any of several known methods, summarized, for example, in the monograph "The Adsorption of Gases and Vapors," vol. I, p. 271-316, by S. Brunauer, Princeton University Press, 1945. Because of its general applicability, the nitrogen adsorption or B. E. T. method (Brunauer, Emmett, Teller, J. Am. Chem. Soc. 60, 309 (1938)) is preferred and was the one employed in arriving at the limiting area value given hereinbefore.

The refractories which most satisfactorily meet the criteria set forth above are in general of the class consisting of metal oxides and metal silicates. Thus, for example, there may be used silica alone, and alumina, beryllia, thoria, magnesia, lime, titania, zirconia, chromia, and hafnia, each of the latter alone or in chemical combination with silica. In general, non-basic refractories are preferred because of their greater resistance to oxides of carbon which may be present in the pyrolysis gases. With certain refractories, such as magnesia and titania, which may in some forms exhibit surface areas over one square meter per gram, care must be taken to secure a non-porous form, as by selecting a dead-burned or even a fused grade. As a practical matter, aluminum silicate refractories, particularly ceramics consisting essentially of sillimanite or mullite, being readily available, are most often used.

The refractory portion of the catalyst may be in any suitable size and shape for contact with the pyrolysis gases, a bed of small pieces being preferred. Sillimanite or mullite pebbles of 0.2 to 1.0 inch diameter are highly satisfactory, as are the corresponding sizes of the porcelain tower packing known as Berl saddles (U. S. Pat. 1,796,501).

The promoter portion of the catalyst is, as stated, made up of one or more of the metals manganese, iron, copper, and cobalt. It should be dispersed over the surface of the refractory in a proportion of from 0.001 to 1.0 per cent by weight. Lesser proportions are too slight to produce a significant effect whereas higher ones may cause serious loss of ethylene. Of the promoters, iron is active in lower concentrations than the others, though a proportion of at least 0.1 per cent is in general preferred for each of the metals. Since copper tends to exert a fluxing action on some silicates, it is essential, with copper as a promoter, to choose the refractory so as to minimize this effect; aluminum silicates are satisfactory. However, maximum activity of copper seems to be realized on a non-silicate refractory, such as alumina.

Inasmuch as the conditions in the pyrolysis zone are highly reducing, the promoter need not be applied to the refractory as the metal itself. It is equally effective to distribute over the refractory any reducible compound of the metal, the latter being then decomposed to free metal in the first minutes of pyrolysis. Consequently, the promoter is most conveniently applied by soaking pieces of the refractory in an aqueous solution of a reducible compound of manganese, iron, copper or cobalt and then drying them. Since the concentration of promoter to be deposited is low, comparatively dilute solutions, e. g. 1 to 5 per cent by weight, of the reducible compound can be used. In general, nitrates or acetates are preferred because of their solubility and ready reducibility.

While deposition of the promoter from aqueous solution is most convenient other methods of

application may be used, as by condensation of the metal on the refractory from the vapor phase. Good results have also been realized simply by passing the gas to be pyrolyzed over unpromoted refractory heated at 800° to 1000° C. and injecting a finely-divided powder of the promoter, either in the metallic state or in the form of an oxide, into the gas stream in the initial stages of pyrolysis.

The catalysts prepared as described are, so far as known, generally effective in accelerating the conversion of paraffin hydrocarbons to ethylene with minimum formation of acetylene and non-gaseous hydrocarbons. They are most useful, however, in the pyrolysis of normally gaseous paraffins, and particularly of ethane. In cracking ethane, best results are obtained when the partial pressure of the ethane in the gas stream undergoing pyrolysis is less than 0.2 atmosphere, either by operating at reduced pressure or in the presence of an inert diluent, such as nitrogen, hydrogen, carbon monoxide, or methane. Steam is also an operable diluent but since its presence makes necessary added equipment and extra heat for vaporization and condensation, it is preferably not used. Methane is perhaps the most practical diluent and has the extreme economic advantage that mixtures of methane with 3 to 15 per cent of ethane are available as natural gas at many fields. In such gas, hydrocarbons other than methane and ethane may also be present, though usually in low concentrations, so that the ethane is ordinarily the major hydrocarbon component having more than one carbon atom per molecule.

In making ethylene according to the invention, maximum temperature in the cracking zone should be in the range 800° to 1000° C. At temperatures much below 800° the yield of ethylene is reduced whereas above 1000° acetylene formation may be encountered. Values of 900° to 950° are most advantageous. Pyrolysis should be rapid, with contact time at the cracking temperature not exceeding 2 seconds, even at 800° C., and preferably being much shorter, e. g. 0.1 second or less, especially at temperatures approaching 1000° C. In operating under these conditions carbon is gradually deposited in the catalyst, reducing its activity. The catalyst may be regenerated and the carbon easily removed by burning it off in air or other oxygen-containing gas.

The cracked gas produced according to the process described ordinarily contains too little acetylene to interfere with most uses to which the gas is put. However, if desired, last traces of acetylene may be removed by passing the gas through a bed of small pieces of a refractory having deposited thereon an oxide of at least one of the metals copper and iron, e. g. copper oxide in a proportion of 0.5 to 2.0 per cent by weight, such bed being at a temperature of 140° to 375° C. at its outlet end. Details of this latter treatment are given in U. S. Patent 2,398,301. The supporting refractory need not meet the surface area limitation which is essential in the cracking catalyst of the present invention.

The new process may be further described with reference to the accompanying drawing, in which

Fig. 1 is a schematic elevation, partly in section, showing one arrangement of apparatus in which the pyrolysis may be carried out in a regenerative cyclic procedure;

Fig. 2 is a flow diagram representative of the

cracking period in the apparatus of Fig. 1, showing the temperatures at the end of the period; and

Fig. 3 is a similar diagram for the regeneration period, showing the temperatures at the end.

In the apparatus of Fig. 1, pyrolysis is carried out in a vertical cylindrical reactor 4 formed of a steel shell 5 lined with courses of insulating brick 6 and refractory silica brick 7 and lagged with heat insulation 8. The top of the reactor is closed by an insulated flanged head 9, from which opens a transfer line 10 provided with a heat exchanger 11. The bottom 12 is similarly flanged to connect to a transfer line 13 also provided with a heat exchanger 14. Part way up the reactor, the wall is penetrated by a number of gas inlets 15 all at the same level and supplied from a common header 16 by a fuel supply line 17.

Fixed transversely within the reactor just above the bottom is a steel grating 18 serving as a support for the packing which fills the tower. The portion of the reactor extending from the grating 18 to just below the inlets 15 functions as a quench zone 19 and is filled with half-inch diameter mullite pebbles having 1.0 per cent by weight of copper oxide on the surface thereof prepared according to U. S. Patent 2,393,301. The central part of the reactor from the fuel inlet level to a level somewhat higher constitutes the cracking zone 20 and is filled with catalyst according to the present invention, e. g. half-inch mullite pebbles having 0.1 per cent by weight of manganese and 0.1 per cent of iron distributed on the surface thereof. The upper part of the reactor forms a preheat zone 21 filled with half-inch untreated mullite pebbles.

The movement of gases through the lines 10, 13, and 17 serving the reactor is controlled by a bank of shut-off valves 22 to 30. These valves are in part interconnected by headers, as shown in the drawing, and can be operated simultaneously by automatic timing mechanism not shown to open or close predetermined gas flow paths through the reactor.

The ethane-containing natural gas used in making ethylene is derived from a source 31 at somewhat above atmospheric pressure. During the cracking period, the natural gas flows in through the valves 23 and 26 and the line 10, passes downwardly through the reactor 4, and leaves through the line 13, and the valve 28, and the product line 32. From the latter it passes to use or to ethylene separation apparatus not shown.

During the regeneration or burn-off cycle, air from a source 33 enters through the valves 24 and 29, passing through the line 13, the reactor 4, the line 10, and the valve 27 to a vent 34. At the same time, fuel gas from a source 35 enters through the valve 30, line 17, and inlets 15, merging with the air stream. Between the cracking and regeneration cycles, the reactor and piping may be purged with inert gas, e. g. steam or nitrogen, from a source 36.

In explaining the operation of the apparatus, it will be assumed that it has been in use for some time and is entering a cracking period. Under these conditions, the valves 23, 26, and 28 are open and natural gas from the source 31 is beginning to flow downwardly through the reactor and out the product line 32. As a result of the regeneration period just completed, the refractory bed in the preheat zone 21 is at a temperature of 400° to 500° C. at the top and nearly

800° C. at the bottom. In the cracking zone 20, the refractory is at 950° to 1000° C. and in the quench zone 19 it is at 400° to 500° C. at the top and 100° to 200° C. at the bottom. As the natural gas, entering at ordinary temperature, flows down through the refractory bed, it is first preheated nearly to 800° C., and then in the cracking zone is raised very rapidly to nearly 950° C. On leaving the latter zone, the cracked gas is quickly chilled in the quench zone, leaving at not over 300° C. It then passes through the heat exchanger 14, surrendering further heat, and flows into the product system 32 at about 100° C.

During passage through the cracking zone where it is in contact with the promoted refractory catalyst of the invention, the ethane in the natural gas is dehydrogenated to ethylene with but very little formation of acetylene or of non-gaseous hydrocarbons. The carbon produced in the pyrolysis remains largely in the cracking zone in the form of luster carbon deposited on the catalyst pebbles. However, a part of the carbon is carried into the quench zone and there retained in a soft, finely-divided, almost pyrophoric form. As the cracked gas goes through the quench zone, remaining traces of acetylene in it are largely decomposed during contact with the copper oxide catalyst, forming cuprene and some additional soft carbon.

Since the refractory body in the preheat and cracking zones gradually cools off during the cracking period, the latter must be terminated when the cracking zone approaches 800° C. Ordinarily this temperature is reached long before carbon is deposited to an extent sufficient to reduce the activity of the cracking catalyst significantly. At this time, the preheat zone will have cooled to around 200° C. at the top and 600° at the bottom, and the quench zone will have risen to nearly 700° C. at the top and 300° C. at the bottom. The cracking cycle is ended by closing the valve 23, and the system is purged by opening the valve 22 for a brief interval, after which all valves are closed.

The regeneration period is next started by opening the valves 24, 27, 29, and 30. Air at ordinary temperature flows upwardly through the reactor; fuel gas enters through the inlets 15, and the gaseous products escape, through the exchanger 11 where their heat is recovered, to the event 34. As the air moves upwardly through the quench zone, it encounters the fine carbon and cuprene in the refractory, very quickly burning the latter clean. The cuprene and copper oxide seem to lower the ignition temperature of the carbon, insuring adequate combustion. Then, as air flow continues, the quench zone is gradually cooled back to the temperatures required for the start of the cracking period.

The fuel gas entering the reactor ignites instantly in the steam of air flowing upwardly, producing combustion gases at high temperature which gradually heat the cracking and quench zones back to the temperatures of the cracking period. The hot air and combustion gas also burn off all carbon in the cracking zone early in the period, leaving the catalyst completely regenerated. When the desired temperatures are attained, the regeneration period is ended by closing the valves 24 and 30, and the valve 25 is opened to allow the purge gas to sweep out the system. All valves are then closed ready for another cracking period.

The ethylene-containing product gas leaving the system through the line 32 may be used di-

rectly as a source of dilute ethylene for chemical processes, or it may be treated in any of several known methods to concentrate the ethylene. In a preferred procedure, the gas is passed to a charcoal hypersorber to separate the ethylene and any uncracked ethane as a concentrated C₂ fraction containing 60 to 90 per cent ethylene.

The following examples will further illustrate the invention but are not to be construed as limiting its scope.

Example 1

In a pilot-plant demonstration of the apparatus of Fig. 1, the reactor was 35 inches long and 3.5 inches inside diameter, lined with fused silica. The quench zone was 12 inches long, the cracking zone 10 inches, and the preheat zone 13 inches, all filled with pebbles of the size and chemical composition explained with reference to Fig. 1. The cracking period was 10 minutes and the regeneration period 20 minutes, with 10 seconds for each purge with nitrogen. Operating temperatures were in the ranges stated, the maximum cracking temperature being 925° C. The pressure was essentially atmospheric. The feed stock and fuel gas were from the same source, a natural gas from the Coldwater field of central Michigan. Feed rate on cracking was 1.35 cubic feet per minute, corresponding to a contact time of about 0.2 second.

Analyses of the feedstock and of a composite sample of the cracked gas taken over 750 consecutive 30-minute process cycles are given below. Analyses were made by the Podbielniak low-temperature distillation procedure.

Component	Natural Gas	Cracked Gas
	Percent by volume	
CH ₄	73.3	65.6
C ₂ H ₆	13.9	4.8
C ₂ H ₄	0	10.5
C ₂ H ₂	0	0.25
C ₃ 's.....	5.9	2.2
C ₄ 's.....	1.7	0.5
C ₅ 's.....	0.6	0.7
H ₂	0	9.6
N ₂	4.6	5.2

The conversion of ethane to ethylene was 51.5 per cent and the chemical efficiency of the conversion was 96.9 per cent. The cracked gas was clear and colorless. No appreciable quantity of tar or liquid condensate was obtained.

and was 11 inches long. The cracking catalyst was a bed of 0.31-inch mullite pebbles which had been coated in place with approximately 0.2 per cent by weight of copper introduced into the gas stream as a dust. The quench zone contained similar pebbles having 1.0 per cent by weight of copper oxide deposited on them by soaking the pebbles in copper nitrate solution and then heating in air to 500° C. Operation was essentially at atmospheric pressure.

The temperature in the cracking zone was 840° to 900° C. while the quench zone ranged from 250° to 590° C. Feed rate was 2.0 cubic feet per minute, corresponding to a catalyst contact time of 0.3 to 0.4 second.

Podbielniak analyses of the natural gas and cracked product were:

Component	Natural Gas	Cracked Gas
	Percent by volume	
CH ₄	71.6	65.0
C ₂ H ₆	14.1	3.5
C ₂ H ₄	0	10.5
C ₂ H ₂	0	0.04
C ₃ 's.....	5.7	1.1
C ₄ 's.....	1.3	0.1
C ₅ 's.....	0.8	0.5
H ₂	0	14.0
N ₂	6.2	5.0

The cracked gas was clear and colorless. No liquid or tarry condensate was produced.

Example 3

In a series of pyrolysis tests, natural gas was passed through an externally-heated 2.5 cm. inside diameter silica tube filled for a length of 57 cm. with small porcelain (quartz-sillimanite) Berl saddles. The effluent gas was immediately quenched in a water-cooled heat-exchanger. In the first test, not in accordance with the invention, the saddles were untreated. In each of the other tests, illustrative of the invention, the saddles were coated with one of the promoter metals iron, manganese, and cobalt applied by soaking the saddles in an aqueous solution of a nitrate of the metal and then drying. Details of the tests are given in accompanying Table A. From the table, the very great reduction in non-gaseous hydrocarbon products (cloudiness) and the significant decrease in acetylene formation occasioned by each promoter are clearly evident.

TABLE A

Promoter—percent by weight.....		None	Fe—0.41	Mn—0.38	Co—0.1
Cracking temperature, °C.....		900.....	920.....	900.....	900.....
Natural gas rate cc./min.....		2,113.....	2,113.....	2,113.....	2,113.....
Appearance of cracked gas.....		very cloudy yellow.	mist-free.....	very slightly cloudy.	slightly cloudy.
Gas Analysis		Natural Gas			
		Vol. percent			
CH ₄	73.5	64.6.....	62.0.....	67.1.....	63.8.....
C ₂ H ₆	13.6	1.9.....	2.2.....	1.5.....	1.8.....
C ₂ H ₄	0	11.1.....	10.2.....	11.4.....	9.8.....
C ₂ H ₂	0	0.64.....	0.38.....	0.27.....	0.41.....
C ₃ 's.....	5.5	0.9.....	0.7.....	0.8.....	2.8.....
C ₄ 's.....	1.9
H ₂	0.1	15.0.....	10.2.....	13.5.....	16.0.....
N ₂	5.4	5.2.....	4.6.....	5.3.....	5.0.....

Example 2

Natural gas was cracked in a regenerative system similar to that of Fig. 1, except that the cracking zone proper had a diameter of 5 inches

What is claimed as the invention is:

1. In a process of pyrolyzing ethane to produce a high yield of ethylene with minimum formation of acetylene and non-gaseous hydrocarbons, the step which comprises passing a stream of

ethane and an inert diluent wherein the proportion of ethane is such that the partial pressure thereof is less than 0.2 atmosphere through a bed of a catalyst at a temperature of 800° to 1000° C. and under reducing conditions such catalyst consisting of small pieces of a refractory of the class consisting of metal oxides and metal silicates which is infusible and irreducible by hydrocarbons at 1000° C. and is of such limited porosity as to have a surface area of less than one square meter per gram, such refractory pieces having deposited on the surface thereof a metal consisting of manganese, iron, copper, and cobalt in a proportion of from 0.001 to 1.0 per cent by weight thereof.

2. In a process of pyrolyzing ethane to produce a high yield of ethylene with minimum formation of acetylene and non-gaseous hydrocarbons, the step which comprises passing a stream of natural gas containing ethane as the major hydrocarbon component having more than one carbon atom per molecule, the proportion of ethane being such that the partial pressure thereof is less than 0.2 atmosphere, through a bed of a catalyst at a temperature of 800° to 1000° C. at a flow rate such that the pyrolysis time is less than 2 seconds and under reducing conditions, such catalyst consisting of small pieces of an aluminum silicate refractory of such limited porosity as to have a surface area of less than one square meter per gram and a metal of the class consisting of manganese, iron, copper, and cobalt deposited on the surface of the refractory pieces in a proportion of from 0.001 to 1.0 per cent by weight thereof.

3. A process according to claim 2 wherein the metal of the catalyst is manganese.

4. A process according to claim 2 wherein the metal of the catalyst is iron.

5. A process according to claim 2 wherein the refractory consists essentially of mullite.

6. A process of making ethylene which comprises passing a stream of natural gas containing ethane as the major hydrocarbon component having more than one carbon atom per molecule, the proportion of ethane being such that the partial pressure thereof is less than 0.2 atmosphere, through a bed of a catalyst at a temperature of 800° to 1000° C. at a flow rate such that the pyrolysis time is less than 2 seconds and under reducing conditions such catalyst consisting essentially of small pieces of a refractory of the class consisting of metal oxides and metal silicates which is infusible and irreducible by hydrocarbons at 1000° C. and is of such limited porosity as to have a surface area of less than one square meter per gram and a metal of the class consisting of manganese, iron, copper, and cobalt deposited on the surface of the refractory pieces in a proportion of from 0.001 to 1.0 per cent by weight thereof, cooling the gas stream after passage through the catalyst bed, and separating ethylene from the cooled gas.

7. In a process of pyrolyzing a paraffin hydrocarbon containing more than one carbon atom per molecule to produce a high yield of ethylene

with minimum formation of acetylene and non-gaseous hydrocarbons, the steps which comprise passing the hydrocarbon as a stream through a bed of a catalyst at a temperature of 800° to 1000° C. and under reducing conditions such catalyst consisting of small pieces of a refractory of the class consisting of metal oxides and metal silicates which is infusible and irreducible by hydrocarbons at 1000° C. and has a surface area less than one square meter per gram and a metal of the class consisting of manganese, iron, copper and cobalt deposited on the surface of the refractory pieces in a proportion of from 0.001 to 1.0 per cent by weight thereof, and cooling the cracked gas stream leaving such catalyst bed by passing it through a bed of small pieces of a refractory having deposited thereon at least one substance of the class consisting of the oxides of copper and iron, such bed being at a temperature of 140° to 375° C. at its outlet end.

8. A process according to claim 7 wherein the refractory in the cooling bed has copper oxide deposited thereon in a proportion of from 0.5 to 2.0 per cent by weight.

9. A process according to claim 8 wherein the feed stock is natural gas containing ethane as the major hydrocarbon component having more than one carbon atom per molecule, the proportion of ethane being such that the partial pressure thereof is less than 0.2 atmosphere.

10. A process of making ethylene which comprises passing a stream of a normally gaseous paraffin hydrocarbon containing more than one carbon atom per molecule through a bed of a catalyst at a temperature of 800° to 1000° C., such catalyst consisting of small pieces of a refractory of the class consisting of metal oxides and metal silicates which is infusible and irreducible by hydrocarbons at 1000° C. and is of such limited porosity as to have a surface area of less than one square meter per gram, such refractory pieces having deposited on the surface thereof a metal consisting of manganese, iron, copper, and cobalt in a proportion of from 0.001 to 1.0 per cent by weight thereof, cooling the gas stream after passage through the catalyst bed, and separating ethylene from the cooled gas.

LUDO K. FREVEL.

JOHN W. HEDELUND.

REFERENCES CITED

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

UNITED STATES PATENTS

Number	Name	Date
1,411,255	Alexander	Apr. 4, 1922
1,973,851	Feiler et al.	Sept. 18, 1934
2,174,196	Rogers	Sept. 26, 1939
2,186,590	Martin et al.	Jan. 9, 1940
2,301,727	Klein et al.	Nov. 10, 1942
2,366,531	Ipatieff et al.	Jan. 2, 1945
2,398,301	Frevel	Apr. 9, 1946