Feb. 13, 1951 L. K. FREVEL ET AL 2,541,693

PRODUCTION OF LOWER OLEFINS

Filed July 28, 1947 2 Sheets-Sheet 1

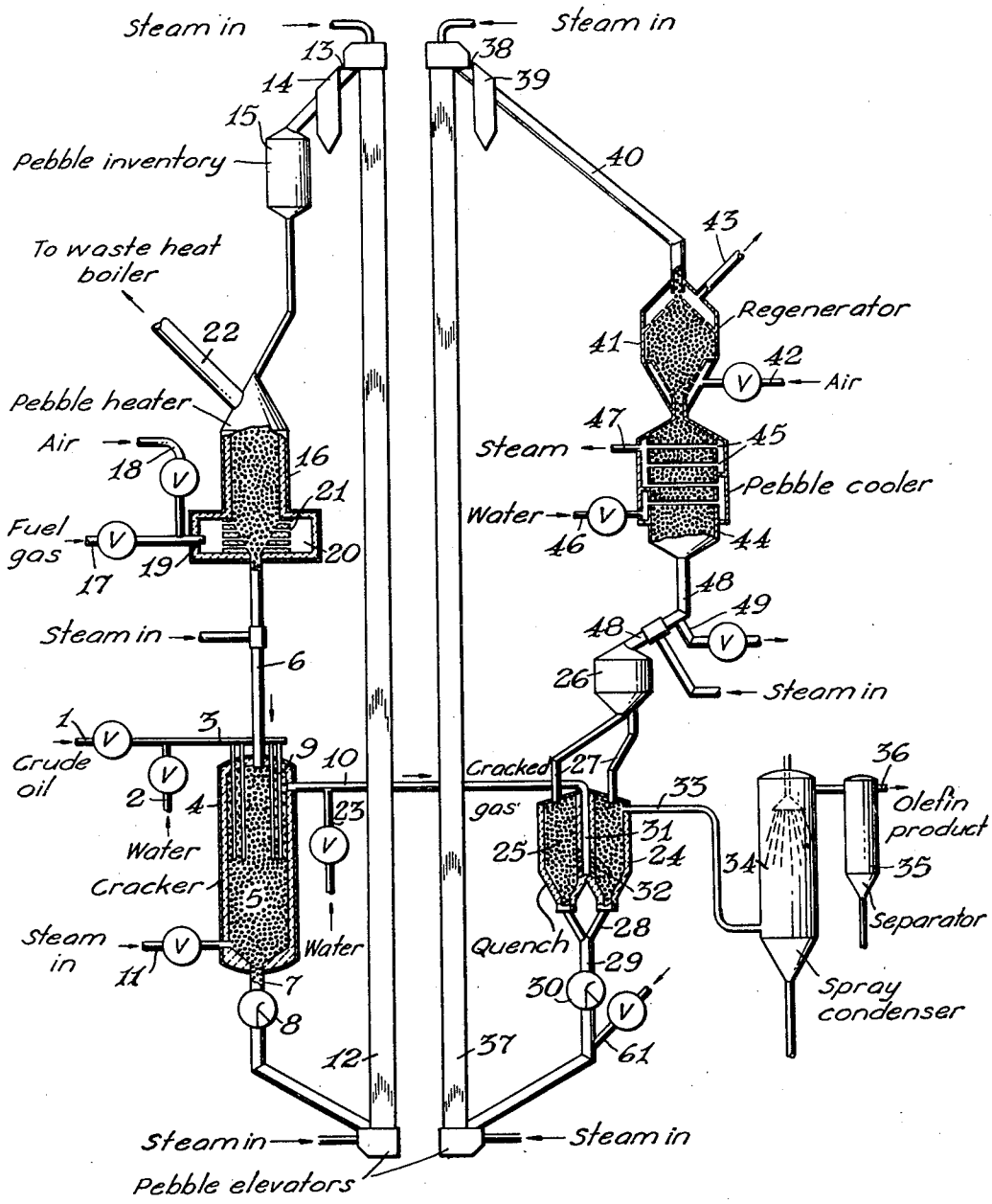


Fig. 1

INVENTORS.
Ludo K. Frevel
Wilson W. Hunt
John J. Grebe
BY Griswold & Burdick
ATTORNEYS

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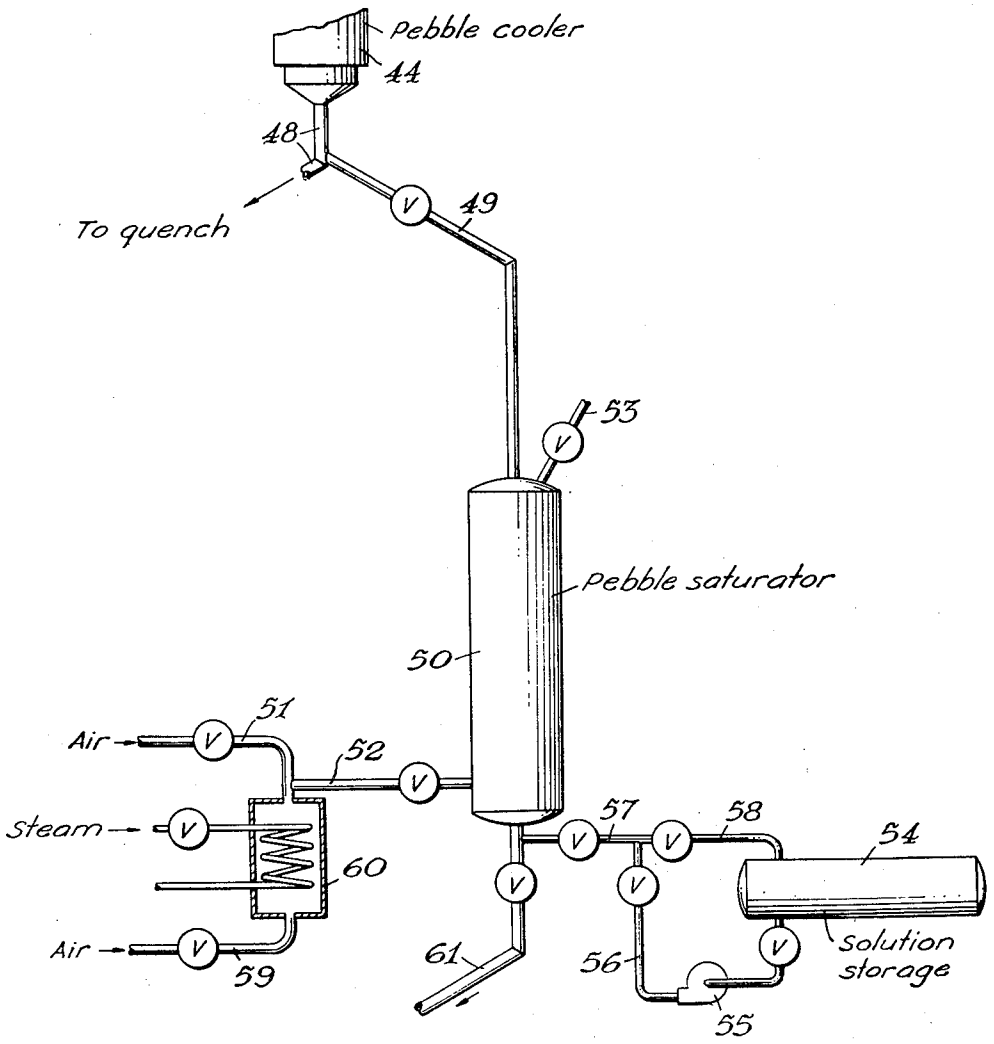


Fig. 2

INVENTORS.
Ludo K. Frevel
Wilson W. Hunt
John J. Grebe
BY Griswold & Burdick
ATTORNEYS

Patented Feb. 13, 1951

2,541,693

UNITED STATES PATENT OFFICE

2,541,693

PRODUCTION OF LOWER OLEFINS

Ludo K. Frevel, Wilson W. Hunt, and John J. Grebe, Midland, Mich., assignors to The Dow Chemical Company, Midland, Mich., a corporation of Delaware

Application July 28, 1947, Serial No. 764,140

7 Claims. (Cl. 260—683)

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This invention relates to process improvements in the manufacture of lower olefins by the pyrolysis of hydrocarbons.

An established method of making ethylene and other olefins for use in chemical manufacturing involves pyrolyzing a hydrocarbon feed stock, such as gas oil, at temperatures above 1300° F. This operation produces a cracked gas rich in olefins which is quenched and then treated to separate the olefins from the accompanying heavier pyrolysis products.

In carrying out this process, practical difficulties arise because of the fact that tar and carbon are usually formed in the pyrolysis and tend to separate from the gas stream during the quenching step. When the cracked gas is quenched directly in a shower of water, tar emulsions are formed which present a serious disposal problem. On the other hand, when quenching is carried out in tubular heat exchangers, the tubes foul rapidly, losing efficiency and necessitating frequent shutdowns for cleaning. These procedures, besides being troublesome, are also somewhat wasteful in that none or only part of the heat energy of the cracked gas is recovered and in that the tar and carbon formed are for the most part discarded, no attempt being made to recover even the fuel value in them.

In the pyrolysis process, a further problem exists in that the cracked gas usually contains appreciable proportions of acetylenic hydrocarbons, hydrogen, and, with certain feedstocks, also hydrogen sulfide and related sulfur compounds. Since the presence of these impurities is undesirable in many of the uses to which lower olefins are placed, the cracked gas, after quenching, must be subjected to purification steps to remove these materials.

With these factors in mind, it is a principal object of the present invention to provide an improved process for making lower olefins in which the quench step is carried out without encountering the difficulties of water-sprays and tube-coolers as heretofore used and in which acetylenes, sulfur compounds, and hydrogen are in large part removed from the cracked gas during the quenching operation. Another object is to provide a process in which much of the heat energy in the cracked gas is recovered in useful form and in which the tar and coke deposited during quenching are burned under controlled conditions to produce additional heat. Still another object is to provide a process in which a wide variety of hydrocarbon feed stocks, including crude oil, may be pyrolyzed successfully.

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These and related objects are realized in the process hereinafter described in detail with reference to the accompanying drawings, in which

Fig. 1 is a schematic flowsheet showing in elevation one arrangement of equipment for carrying out the manufacture of olefins; and

Fig. 2 is another elevation illustrating auxiliary equipment used periodically in connection with that of Fig. 1.

In the process of the invention, the stream of hot olefinic gas produced by cracking a hydrocarbon feed above 1300° F. is quenched by passing it into contact with a mass of relatively cool refractory particles having deposited thereon at least one catalyst of the class consisting of the oxides of copper and iron. During the quenching, the particles absorb and store the heat from the gas stream and may later be transferred to another zone in which the heat is recovered. At the same time, the catalyst causes removal of most of any acetylenic hydrocarbons and sulfur compounds, and at least part of any hydrogen, present in the gas being quenched. Further, the tar and coke usually formed in quenching are caught by the particles and remain deposited on them, being later burned off under conditions such that the heat of combustion is also recovered.

According to the specific form of the process illustrated in Fig. 1, a stream of crude oil at ordinary temperature from a valved line 1 is mixed with steam or water from a valved line 2 and the mixture is then injected through an inlet manifold 3 into a brick-lined cracking chamber 4. In this chamber, cracking is carried out by countercurrent contact of the injected stream and a compact mass of downwardly moving highly heated refractory pebbles 5 which fills the chamber. A constant flow of these pebbles, supplied through a line 6 at a temperature above 1300° F., enters the chamber 4 at the top, passes down the inside, and leaves at the bottom through an outlet line 7. The rate at which the pebbles move through the cracker may be regulated by an adjustable gate 8 in the line 7.

The crude oil feed mixture from the manifold 3 is introduced into the chamber 4 at points roughly halfway to the bottom by means of dip pipes 9 which are thermally insulated to prevent premature cracking of the oil within the pipes. As the oil issues from the dip pipes it impinges on the bed of moving hot pebbles and is almost instantly vaporized. The vapors pass upwardly, being cracked largely to olefins by contact with the descending hot pebbles, and leave the cham-

ber at a temperature of at least 1300° F. through a transfer line 10 leading to the quench system. Coke and tar formed during this pyrolysis become deposited on the pebbles and ultimately move out of the chamber with them. A small flow of steam from a line 11 is injected into the bottom of the chamber 4 to strip residual volatiles from the pebbles.

The carbon-coated pebbles leaving the cracking chamber through the outlet 7 at a temperature of 900° to 1000° F. move to a high-temperature bucket elevator 12 where they are lifted to the top of the system and dropped into a feeder 13 from which they flow by gravity through the process. The pebbles first pass through a classifier 14 in which any fine particles are screened out and thence to an inventory tank 15.

From this tank 15, the pebbles move downwardly into a heating chamber 16 where they are raised back to a cracking temperature by countercurrent contact with hot combustion gas. As shown, fuel gas from a valved line 17 and an excess of preheated air from a valved line 18 are passed through a burner 19 into an annular combustion chamber 20. The resulting combustion gas, at a temperature of at least 2000° F. passes through horizontal ports 21 into the bottom of the heating chamber 16. It then flows upwardly, transferring its heat to the bed of descending pebbles. In addition, the excess air present in the gas burns off carbon deposited on the pebbles, thus regenerating them and at the same time recovering the heat of combustion of the carbon. After passage through the pebble bed, the gas leaves through a flue 22 at a temperature of at least 1000° F. It may be passed to a waste-heat boiler, not shown, to recover its residual heat content.

The hot olefinic gas leaving the cracker 4 through the transfer line 10 is preferably chilled slightly to terminate thermal cracking, e. g. to a temperature of 1100° to 1200° F., by injecting a small proportion of water or other cooling fluid from a line 23 entering the transfer line at a point near the cracker. The stabilized gas then passes to the quench system.

The quenching operation is carried out in a brick-lined chamber 24 by countercurrent contact of the olefinic gas and a compact mass of downwardly moving relatively cool refractory pebbles 25 which fills the chamber. A constant flow of these pebbles, which are impregnated with from 0.5 to 2.0 percent by weight of copper oxide, is supplied from an inventory tank 26 at a temperature of 500° to 600° F., and moves through branching feeders 27, entering the quench chamber 24 at the top. The pebbles then pass slowly down inside the chamber and leave at the bottom through a collector 28 leading to a discharge leg 29. The rate at which the pebbles move through the system under the action of gravity may be regulated by an adjustable gate 30 in the leg.

The hot olefinic gas stream entering the quench system from the transfer line 10 is introduced into the bottom of the pebble body within the chamber 24 by means of a distributor 31. This distributor is a vertical cylindrical brick conduit extending centrally the full depth of the chamber and provided at its lower end with gas ports 32 which open into the annular pebble space. The stream of hot gas enters the pebble bed through these ports and flows upwardly into countercurrent contact with the relatively cool pebbles, being quenched thereby. At the same time, acetylene, sulfur compounds, and some hydrogen are removed from the gas by the action of the copper oxide in the pebbles. The quenched purified gas finally leaves the chamber 24 through an outlet line 33. Any tar or coke formed during the quenching step becomes deposited on the pebbles and ultimately moves out of the chamber with them.

The pebble quench system is preferably operated to remove and recover most of the heat in the olefinic gas stream without cooling it to such an extent that the gasoline-like condensable cracked hydrocarbons and steam in the gas are themselves condensed within the chamber 24. An exit gas temperature of 500° to 600° F. is preferred. The condensables are later removed from the quenched gas in a separate water spray condenser 34 to which the outlet line 33 leads. The resulting fully cooled gas, after passing through a separator 35 to eliminate entrained water, leaves by a product line 36. The gas may be used as such for processes in which mixed lower olefins are required, or may be subjected to known separatory processes to isolate the individual lower olefins.

The hot carbon-coated pebbles leaving the quench chamber through the leg 29 at a temperature of about 1050° F. pass to a high-temperature bucket elevator 37 where they are lifted to the top of the system and dropped into a feeder 38 from which they flow by gravity through the process. The pebbles first pass through a classifier 39, in which any fine particles are screened out, and thence through a transfer line 40. From this latter, they move downwardly through a brick-lined regenerator 41 in direct countercurrent contact with a flow of air injected into the chamber at its bottom from a valved line 42. The air is admitted at ordinary temperatures in a proportion sufficient to burn substantially all of the carbonaceous deposit out of the hot pebbles and to regenerate the copper oxide present but insufficient to cool the pebbles appreciably. The quantity of air is preferably limited so that the pebbles are actually heated by the combustion to 1050° to 1100° F. The resulting combustion gas escapes through a vent 43.

From the regenerator 41, the hot pebbles pass to a cooler 44 where they are reduced back to the desired quenching temperature under conditions such as to recover the heat stored in them. As shown, the cooler 44 consists of a brick-lined chamber in which are positioned a number of horizontal boiler tubes 45 through which boiler feed water from a valved line 46 may be circulated. The hot pebbles move downwardly in contact with the outside walls of the tubes, transferring heat to the latter. This heat is absorbed by the water inside the tubes, forming steam which escapes through a header 47 leading to a system, not shown, where the steam may be utilized. The rate of flow of the feed water is controlled so that the pebbles, during passage through the chamber 44, are cooled back to the initial quenching temperature of 500° to 600° F. The pebbles then proceed through a line 48 to the cool pebble inventory tank 26 and thence into the quench chamber 24.

In the apparatus of Fig. 1, the various pieces of equipment are provided with thermal insulation, not illustrated, to reduce heat loss. The atmospheres within the various chambers through which the pebbles pass are maintained independ-

ent of one another by the continuous injection of steam into the various pebble transfer lines 6, 7, 13, 29, 38, and 48 at rates sufficient to prevent diffusion of process gases through these lines.

Over a prolonged period, the copper oxide content of the pebbles circulating in the quench system tends to decrease due to reaction with trace impurities in the gas and to attrition of the pebbles. It is necessary, therefore, occasionally to withdraw a portion of the pebbles and treat them to replenish the copper oxide. Equipment for this purpose is illustrated in Fig. 2.

As there shown, the pebbles leaving the cooler 44 may be diverted through a valved line 49 to a saturator tank 50 until the latter is filled. The pebbles in the tank are then cooled, preferably to below 250° F., by allowing cooling air from a source 51 to enter through a valved side inlet 52, pass upwardly through the pebble body, and escape through a vent 53. After the pebbles are cool, the air flow is turned off and the saturator tank is filled with ammoniacal copper acetate solution from storage 54 by pump 55 and lines 56 and 57 leading into the bottom of the tank. Following a period of soaking the pebbles, the solution in the saturator tank is returned to storage 54 through lines 57 and 58. The saturated pebbles in the tank are then dried by a flow of hot air entering from a source 59 through a steam heater 60 and the side inlet 52 and leaving through the vent 53. The pebbles may then be returned to the circulating system by a line 61 leading into the quench leg 29.

The process of the invention is applicable to the pyrolysis of any hydrocarbon or hydrocarbon mixture which can be cracked at elevated temperatures to form olefins. Ethane, propane, refinery gas, and liquid fractions such as kerosene, gas oil, and fuel oil may all be used. However, as previously explained, the process is especially advantageous in that it can successfully utilize as feedstocks the heavier residual oils and also ordinary crude oil. These latter stocks are preferably sweetened and desalted before introducing them into the cracker. They may be introduced as liquid streams, or in partially vaporized or atomized form.

In order to secure acceptable yields of lower olefins, i. e. olefins containing four or less carbon atoms per molecule, the temperature in the cracking zone should be at least 1300° F. Temperatures above 1400° F. are more satisfactory, with 1500° to 1600° F. being preferred when ethylene is the desired major product. Since heat transfer conditions between hot pebbles and hydrocarbon vapor in the cracking zone are excellent, the cracked gas ordinarily leaves the zone at a temperature closely approximating the temperature of the entering pebbles. Consequently, in ordinary practice, the temperature of the cracking zone is controlled at the desired value simply by providing an adequate rate of flow of the pebbles and regulating the pebble heater 16 to maintain the appropriate pebble inlet temperature. The pebble flow rate is preferably sufficient that the outlet temperature of the pebbles is above 750° F., to avoid tarring the pebbles. Countercurrent flow of feed and pebbles is most satisfactory, though concurrent flow may be used.

Although a pebble cracker as illustrated is preferred, pyrolysis of the feedstock may also be carried out in a tube furnace or other manner.

While the pyrolysis may be carried out on undiluted hydrocarbon, it is preferable to employ an inert carrier gas, as by adding steam or water to the feed, to lower the partial pressure of the hydrocarbon in the cracking zone and to improve heat transfer. In general, from 0.05 to 3.0 parts by weight of carrier gas per part of vaporized hydrocarbon is used. Rapid pyrolysis is most effective, the rate of flow through the cracking zone being preferably controlled so that the heating time is not over one second, advantageously 0.2 second or less.

In the pebble quench chamber 24, the hot cracked gas entering from the transfer line 10 is cooled to as low a temperature as possible in order to recover the maximum amount of heat energy from the gas. In any event, the gas should be cooled to an outlet temperature below that at which most of the tars present in the cracked gas are condensed, i. e. to well below 850° F. and preferably below 600° F., so that deposition of tar and coke takes place largely within the pebble bed and not at some later stage of the process. However, as previously explained, it is also most satisfactory to avoid chilling the quenched gas to such a temperature that the volatile liquid products of cracking are condensed within the pebble bed, as may occur at 300° to 500° F. For these reasons, pebble inlet temperatures of 500° to 600° F. are in general most satisfactory. The pebble flow rate is preferably controlled so that the outlet temperature of the pebbles is in the range of 900° to 1100° F. Contact times in the pebble quench are short, being of the order of 0.2 to 2.0 seconds.

After the olefinic gas leaves the pebble quench, it is further cooled, e. g. to 100° to 200° F. or lower, to condense the liquefiable products present, chiefly hydrocarbons boiling in the gasoline range. This cooling may be carried out in surface condensers, by a cold oil wash, or by the use of a water spray condenser as illustrated. The liquid products so condensed and separated from the gas may be disposed of as such or may be recycled to the hydrocarbon feed to the cracker. The uncondensed gas surviving this step is rich in lower olefins and constitutes the final product of the process.

The pebbles leaving the quench chamber contain carbon and tar, which is removed in the regenerator by combustion in air or other non-combustible oxygen-containing gas, the catalyst on the pebbles being simultaneously reactivated. Maximum heat economy of the process is realized when the proportion of air used in regeneration is limited to the amount just necessary to burn off the carbonaceous deposit and to reactivate the catalyst, since in this way the pebbles may be heated, rather than cooled, during regeneration. Following regeneration, the pebbles are cooled back to a quenching temperature in any desired manner, either by direct heat-transfer to a fluid to be heated, or by indirect heat-transfer as illustrated. Alternatively, regeneration and cooling may be carried out in the same zone by blowing sufficient air through the pebble body to regenerate the pebbles and cool them to a quenching temperature. The resulting heated air may then be used in other processes.

The process illustrated requires two separate bodies of pebbles, which may be of the same or different composition. The pebbles should be formed of abrasion-resistant refractory material which is also resistant to thermal shock. Somewhat porous refractory materials, such as mullite or alpha-alumina, are perhaps most satisfactory for the quenching cycle since they retain the catalyst better, these latter having the fur-

ther advantage that they are chemically inert to the olefins formed. However, for the pebble bed used in the cracking cycle, the severity of the service requires pebbles of maximum resistance to spalling, high alumina-aluminum silicate or zirconia-base refractories being preferred. Pebble size is not critical, though fairly large pebbles, of 0.2 to 0.7 inch in diameter, are advantageous in that they present a minimum resistance to the flowing gas stream and do not tend to become fluidized.

As stated, the catalyst used in the pebbles in the quenching cycle is an oxide of one of the transition elements copper and iron, or a mixture of such oxides. Cupric oxide is preferred. A discussion of these catalysts, and of the conditions under which they act to remove acetylene and higher acetylenic hydrocarbons from a cracked-oil gas without affecting its olefinic content, appears in U. S. Patent 2,398,301.

In general, in the process of the invention, the copper or iron oxide absorbed in or contained on the pebbles selectively decomposes acetylene and higher acetylenes in the cracked gas under quench conditions, converting them largely to carbon and hydrogen. The carbon remains with the pebbles and is burned off when the pebbles are regenerated. The hydrogen liberated, together with part of the hydrogen previously present in the gas, tends to react with the copper or iron oxide catalyst, reducing it in part to a lower oxide and to the free metal. In addition, with cupric oxide as the catalyst, at least part of the acetylene reacts to form the substance cuprene which remains in the pebbles. When the cracked gas contains hydrogen sulfide or sulfur compounds, these latter also are removed by reaction with the copper or iron oxide catalyst. Since the catalyst is selective, however, the olefins, diolefins, and saturated hydrocarbons in the cracked gas are largely unaffected.

The proportion of catalyst is preferably controlled to a concentration between about 0.5 and about 2 percent by weight of the pebbles, about 1 percent being most satisfactory in the case of cupric oxide. With proportions much below 0.5 percent, there is insufficient catalyst to remove all the acetylenes and sulfur compounds in the cracked gas, whereas with quantities much over 2 percent, some attack on olefins and diolefins may take place. The catalyst may be introduced into the pebbles in any desired manner, soaking the pebbles in an aqueous solution being most convenient. The solute in such a solution may be any salt of copper or iron which is converted to an oxide on heating in air at the temperatures in the regenerator, e. g. an acetate or nitrate. The concentration of the solute should be such as to leave a deposit on the pebbles in which the catalyst is in the desired concentration. In impregnating alumina pebbles with copper oxide, it is most satisfactory to soak them for half a day in a solution of aqueous ammoniacal cupric acetate containing about 7.5 percent total copper by weight. After drying and heating at 900° F. or more, the pebbles contain about 1.0 percent cupric oxide.

As previously explained, during the step of regenerating the quench pebbles, not only are the tar and carbon burned out but the copper or iron catalyst is reoxidized to the higher oxide form. In the case of cupric oxide which has been converted to cuprene in the quench, the cuprene is decomposed, reforming cupric oxide. The presence of this cuprene, and also of finely-divided copper formed by reduction of the copper oxide, is especially advantageous, since it lowers very materially the ignition temperature of the carbon deposited on the pebbles, thus permitting more effective operation of the regenerator on unheated inlet air.

The following example will further illustrate the invention:

Example

A stream of gas oil and water, in the ratio of 1:1.7 parts by weight, was passed through a cracking zone maintained at a temperature of 1450° to 1500° F. to effect cracking. About 80 percent by weight of the oil was converted to cracked gas having the analysis shown in the following table, in which all percentages are by volume (dry basis).

This cracked gas, at a temperature of 1470° F. was then passed into a quenching zone into countercurrent contact with a moving mass of high-alumina aluminum silicate pebbles impregnated with cupric oxide as previously described. The temperature of the entering pebbles and of the gas leaving the quench zone was 500° F. The pebble flow rate was controlled at 8.7 times the weight rate of flow of the cracked gas stream, thus producing a pebble outlet temperature of 825° F. Total contact time in the quench was 0.66 second. The analysis of the quenched gas is given in the following table. About 0.24 percent carbon was deposited on the pebbles and burned off in a regeneration zone.

Table

Component	Cracked Gas	Quenched Gas
	Percent	*Percent*
C_2H_2	0.82	0.00
C_3H_4	0.09	0.02
C_2H_4	33.7	32.8
C_3H_6	4.3	3.8
CH_4	27.9	29.2
C_2H_6	2.4	2.6
C_3H_8	0.16	0.22
Higher Saturates	4.14	4.17
H_2	20.6	20.0
H_2S	0.15	0.00
O_2	0.2	0.0
Inerts	5.8	7.2

From these analyses it will be seen that the quench procedure removed all the acetylene, virtually all the methyl acetylene, all of the hydrogen sulfide, and a small part of the hydrogen in the cracked gas without significant loss of ethylene or propylene.

What is claimed is:

1. In a continuous process of making lower olefins by cracking a hydrocarbon stream at a temperature above 1300° F., a procedure for quenching the hot cracked gas and removing acetylene therefrom which comprises: passing the hot cracked gas through a quench zone into contact with a mass of relatively cool moving refractory pebbles supplied to the zone at an initial temperature below 600° F. and having deposited thereon at least one substance of the class consisting of the oxides of copper and iron to quench the stream, during which operation acetylene is decomposed and the pebbles become heated and coated with carbon, transferring the heated coated pebbles to a regeneration zone and moving them therethrough, passing a non-combustible oxygen-containing gas countercurrent to the mass in the said zone to catalytically burn off carbon from the pebbles, cooling the regenerated pebbles to a quenching

temperature, and returning them to the quench zone.

2. In a continuous process of making lower olefins by cracking a hydrocarbon stream at a temperature above 1300° F., a procedure for quenching the hot cracked gas and removing acetylene therefrom which comprises: passing the hot cracked gas stream through a quench zone into countercurrent contact with a mass of relatively cool moving refractory pebbles supplied to the zone at an initial temperature below 600° F. and having copper oxide deposited thereon to quench the stream during which operation acetylene in the gas is decomposed and the particles become heated and coated with carbon, transferring the heated coated pebbles to a regeneration zone and moving them therethrough, passing relatively cool air countercurrent to the mass in the said zone in a proportion sufficient to burn off carbon from the pebbles and to cool them to a quenching temperature, and returning the cool particles to the quench zone.

3. In a continuous process of making lower olefins by cracking a hydrocarbon stream at a temperature above 1300° F., a procedure for quenching the hot cracked gas and removing acetylene therefrom which comprises passing the hot cracked gas stream through a quench zone into countercurrent contact with a mass of relatively cool moving refractory pebbles supplied to the zone at an initial temperature below 600° F. and having copper oxide deposited thereon to quench the stream, during which operation acetylene in the gas is decomposed and the pebbles become heated and coated with carbon, transferring the heated coated pebbles to a regeneration zone and moving them therethrough, passing air countercurrent to the mass in the said zone in a proportion sufficient to burn off the carbon but insufficient to cool the pebbles materially, transferring the regenerated pebbles to a cooling zone and moving them therethrough while abstracting heat therefrom by indirect heat transfer to cool the pebbles to a quenching temperature, and returning the cooled pebbles to the quench zone.

4. A method according to claim 3 wherein the pebbles are made of mullite.

5. A method according to claim 3 wherein the concentration of copper oxide in the pebbles is from 0.5 to 2 percent by weight.

6. In a continuous process of making ethylene by cracking a normally liquid aliphatic hydrocarbon stream at a temperature above 1500° F., a procedure for quenching the hot cracked gas and removing acetylene therefrom which comprises passing the hot cracked gas stream through a quench zone into countercurrent contact with a compact mass of refractory pebbles having from 0.5 to 2.0 percent by weight of copper oxide thereon and entering the zone at a temperature of 500° to 600° F. and moving downwardly therein while regulating the relative rates of flow of pebbles and gas to cool the latter to a temperature below 600° F. and to heat the pebbles to a temperature well above 600° F., during which operation acetylene in the gas is decomposed, copper oxide in the pebbles is at least in part reduced to copper, and the carbon is deposited in the pebbles, transferring the heated pebbles to a regeneration zone and moving them downwardly therethrough, passing air countercurrent to the pebbles in the said zone in a proportion sufficient to convert the copper in the pebbles to copper oxide and to burn off the carbon but insufficient to cool the pebbles materially, transferring the regenerated pebbles to a cooling zone and moving them therethrough while cooling them by indirect heat transfer to a temperature of 500° to 600° F., and returning the cooled pebbles to the quench zone.

7. A process according to claim 6 wherein the relative rates of flow of pebbles and gas in the quench zone are regulated so that the pebbles are heated to a temperature of at least 900° F.

LUDO K. FREVEL.
WILSON W. HUNT.
JOHN J. GREBE.

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