Jan. 2, 1940. F. PORTER ET AL 2,185,566

PROCESS FOR THE MANUFACTURE OF ETHYLENE

Filed July 14, 1937

Fig. 1,

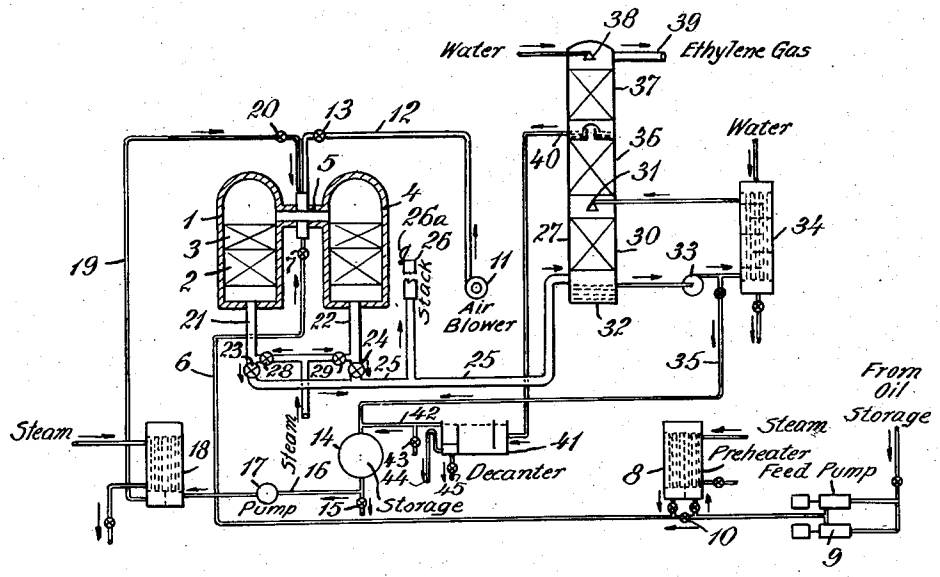


Fig. 2,

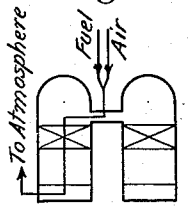


Fig. 3,

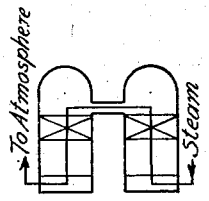


Fig. 4,

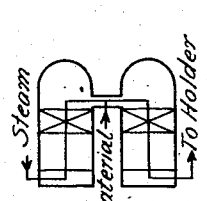


Fig. 5

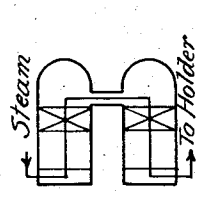


Fig. 6,

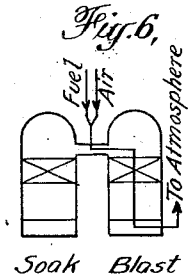


Fig. 7,

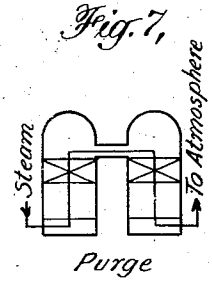


Fig. 8,

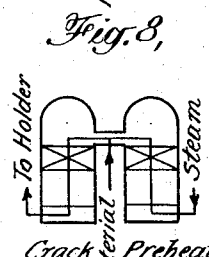
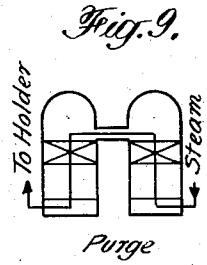


Fig. 9.



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UNITED STATES PATENT OFFICE

2,185,566

PROCESS FOR THE MANUFACTURE OF ETHYLENE

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Application July 14, 1937, Serial No. 153,496

10 Claims. (Cl. 260—683)

This invention relates to the manufacture of ethylene. It is particularly directed to the operation of paired regenerative cracking units in the cracking of mineral hydrocarbons in vapor or gaseous phase.

The manufacture of ethylene by cracking hydrocarbons, such as ethane, propane, butane, and higher hydrocarbons or mixtures thereof, such as gas oil, kerosene, crude petroleum or topped petroleum, requires for efficient operation the maintenance of relatively high temperatures in the cracking zone. Temperatures in the range 780° to 1050° C. have been found most satisfactory. Attempts to attain such cracking temperatures by heating the hydrocarbons or mixtures containing them through heat transfer walls of steel or other metals result in rapid destruction of the apparatus with consequent heavy replacement costs. Iron surfaces furthermore have a deleterious effect upon the desired reaction. As a consequence it becomes desirable to use refractory materials, but such materials do not possess the combination of tensile strength and heat conductivity essential for indirect heat transfer operations.

The use of regenerative types of equipment possesses the advantage that highly refractory materials may be employed and a relatively long equipment life may be obtained. This type of equipment is subject to the disadvantage, however, that it is more difficult to control within narrow ranges of temperature and consequently optimum conversion efficiencies usually are not obtainable.

It is an object of the present invention to improve the control of the operating cycle of regenerative equipment for the manufacture of ethylene whereby high yields of ethylene may be obtained.

It is a further object of the invention to so utilize the heat storage capacity of the refractory material that a maximum of heat may be usefully employed for the cracking operation.

In accordance with the present invention a pair of refractory heat storage chambers of any suitable type is employed. These heat storage units are arranged for alternate operation in a cycle involving a blast period wherein one of the units is heated by combustion gases and a cracking period wherein a mixture of the hydrocarbon to be cracked and steam is passed through the unit thus heated to effect cracking and formation of ethylene from the hydrocarbon.

While the customary procedure in cracking by regenerative equipment involves a blast period followed by a cracking period in the same unit, the present process involves blasting one unit while the other unit is still at a temperature sufficiently high for cracking and then passing steam through the first unit prior to admixing it with hydrocarbon to be cracked and passing the mixture through the second unit. After this cracking period is terminated, the flow is reversed, the first (or steam-treated) unit now being employed for the cracking and the second unit for the preheating of steam.

By employing the first unit to preheat the steam to be mixed with hydrocarbon, the portion of refractory material nearest the inlet for steam is cooled to approximately the inlet temperature for the steam and on reversal of the cycle this refractory material absorbs heat from the cracked hydrocarbon steam mixture. By this procedure the sensible heat of the steam-hydrocarbon mixture is returned to the refractory material so that the cracked hydrocarbon steam mixture leaves the apparatus at substantially lower than usual temperatures with a consequent saving in fuel cost. At the same time, since the newly blasted refractory is in a highly unstable thermal condition, the use of this refractory for preheating steam serves to stabilize the refractory and render it more suitable for the cracking operation subsequently to be conducted therein. Thus, if a bed of refractory material is heated by means of combustion gases, the temperature of the refractory nearest the combustion attains a very high temperature whereas refractory more remote from the combustion is at a sharply lower temperature. Similarly in a short blast period the refractory surfaces are heated to a high temperature but the heat does not penetrate uniformly into each piece of refractory. With the passage of time the high temperature of the surface is reduced by conduction to the interior of each piece of refractory, so that while not materially less heat is present, it is now present at a lower temperature more uniformly distributed and hence more satisfactory for the cracking step.

In the preferred embodiment of our invention, we employ, following the heating or blast period, a short purge with steam (although other inert gaseous media may be employed). This purging steam passes through the two units serially, the unit just blasted being the second in the series. Since the first unit is still at a high temperature, the purging steam is heated to around 1000° C. in this unit; it then passes into the second unit in a direction concurrent

with the direction of flow during the blast. As just noted, the temperature of the refractory nearest combustion will be at a much higher temperature than the refractory more remote therefrom; the steam at around 1000° C. absorbs heat from the hotter section with which it first contacts and then gives up this heat to the cooler section. Thus the most extreme temperatures in the hot section are tempered without however losing any substantial amount of heat.

During the blasting of the second unit, the first unit is permited to remain idle and the purge with steam following this idle period assists in maintaining the low temperature at the outlet for the subsequent cracking.

In order that the present invention may be more fully understood, there follows a description of one embodiment of the invention which is illustrated in the accompanying drawing, wherein

Fig. 1 shows diagrammatically a pair of twin cracking units with the necessary gas and oil lines and recovery apparatus, adapted for the production of ethylene from crude petroleum or other mineral hydrocarbons, and

Figs. 2 to 9 respectively show the operation of the twin regenerative units in successive periods of the operating cycle.

With particular reference to Fig. 1, numeral 1 represents a tower lined with refractory material and provided with refractory packing 2 and 3. Packing 2 may consist of fire-clay brick crushed to between 1 and 2 inch mesh; packing 3 preferably is composed of a crushed material of similar size and especially resistant to high temperatures, for instance clay-bonded silicon carbide. Numeral 4 is a second unit identical with unit 1. The units and packing are shown approximately to scale.

A single conduit 5 connects opposite sides of units 1 and 4 near the top. A crude oil line 6, having a valve 7, leads to conduit 5 from a preheater 8 fed by feed pump 9. The preheater is shown with a by-pass 10 for temperature control. An air blower 11 supplies air by way of conduit 12, provided with valve 13, to conduit 5. Tar for use as fuel or for other purposes can be stored in tank 14 having a valved draw-off 15 and connected by line 16 with pump 17 and preheater 18. A line 19 having a valve 20 leads from the preheater to conduit 5. Conduits 21 and 22 provided with valves 23 and 24 join a draw-off conduit 25 connected with a stack 26 (having a valve 26a) and a cooling tower 27. Conduits 21 and 22 are also joined to steam inlets 28 and 29 respectively.

Tower 27 is composed of three sections packed with any suitable material. The lowermost section 30 has at its top tar inlet spray 31 and at its bottom a basin 32. A pump 33 is arranged to circulate tar from basin 32 through a cooler 34 to the spray inlet 31. A draw-off line 35 leads to storage tank 14. The middle section 36 of the tower is employed for the purpose of removing entrained mist or spray. It is provided with packing but is wet only with the mist which is collected. The top section 37 has at the top a spray inlet 38 for water and a gas outlet 39. At its bottom, it is provided with a draw-off 40 leading to decanter 41 which in turn has an oil outlet 42 leading to storage tank 14. This draw-off may be provided with a bleed 43 for separate withdrawal of the oil so that it may be treated apart from the tar recovered in section 30 if desired. The tar decanter also is equipped with water outlet 44 and drain 45.

The above apparatus may be operated for the production of ethylene in the following manner—

Tar or any suitable fuel is pumped from storage tank 14 by means of pump 17 through preheater 18 and pipe 19 into conduit 5 in which it is atomized into air simultaneously forced by blower 11 through conduit 12 into conduit 5. The mixture is ignited by any convenient means (not shown). For initial heating to bring the apparatus to operating temperature both units may be blasted at the same time or the units may be blasted individually and successively.

The operation of a representative cycle is as follows:

The flow during the blast period for unit 1 is shown in Fig. 2. With valves 7, 24, 28, and 29 closed and valves 13, 20, 23, and 26a open, preheated tar is burned with air in the combustion space above packing 3 in unit 1. The combustion gases pass down through unit 1 and through conduits 21 and 25 to stack 26 and out the stack. This blast is continued until the refractory near the top of the packing in unit 1 has attained a temperature around 1500° C. The packing may be around 600° C. at the bottom.

When the above temperature conditions have been attained, a short purge shown in Fig. 3 is conducted. Valves 13 and 20 are closed and the valve on line 29 is opened for a brief period to pass steam up through unit 4, down through unit 1, and out through the stack. This brief purge removes any air that may be in the units and thereby avoids the possibility of explosions in the subsequent cracking step. This purge also may cool the packing at the bottom of unit 4 somewhat so that the temperatures in unit 4 at the end of the purge are around 100° C. at the bottom and 1050° C. at the top. In unit 1 the purge serves to reduce the temperature slightly at the top and to increase the temperature at the bottom so that after the purge the packing in this unit may be around 1400° C. at the top and 700° C. at the bottom.

The subsequent cracking step is illustrated in Fig. 4. Valves 23 and 26a are now closed. Steam flow is shut off in line 29 and turned on in line 28. Valves 7 and 24 are opened. Feed pump 9 is thus caused to force oil through preheater 8 and through inlet line 6 into conduit 5. This oil may be at a temperature of around 200° C. and a pressure of 200 to 300 pounds per square inch. Pump 9 may be operated either intermittently or continuously. In the former case it will be started at the same time that valve 7 is opened. In the latter case it will be provided with sufficient excess storage capacity so that it will not be overloaded during the period valve 7 is closed. Steam enters by way of line 21, passes up through the packing of unit 1 and is thereby heated to a temperature around 1000° C. to 1200° C. The flows of oil and steam are preferably controlled to provide a weight ratio of 1.7 part of steam for each part of oil. The oil is atomized into the steam as it passes through conduit 5 and the resultant mixture then passes down through the packing of unit 4, out through conduit 22 to conduit 25 and thence into tower 27. The gas mixture in its passage through unit 4 passes first through the upper hot zone where cracking takes place. This cracking zone may be defined as that zone in which a temperature above about 780° C. prevails. The mixture passes then through a lower

cooling zone where the heat of the mixture is given up to the cooler refractory. The temperature of the gases leaving unit 4 during this period may be around 150° C. to 300° C. at the start of the period and around 250° to 400° C. at the end of the period.

The partially cooled, cracked gases pass through section 30 of tower 27 countercurrent to a flow of washing tar which further cools the gases and washes tarry constituents therefrom. This washing is preferably controlled (by regulation of the flow of water through heat exchanger 34) so as to maintain a temperature between 100° and 150° C. in the stream of gases entering section 37. Any entrained matter caught in section 36 will, of course, be returned to section 30 where it is blended with the tar used for washing. In section 37 the gases are further cooled by contact with water to recover remaining oil constituents and the major part of the steam used in the cracking process. The oil and steam pass through outlet 40 to decanter 41, while gases freed from most of their condensible constituents pass through outlet 39 to suitable treatment apparatus or to a gas holder. By proper regulation of the temperature, steam to hydrocarbon ratio, and time of contact, a gas containing on the order of 25 to 40 mol percent ethylene may be obtained. The flow through the cracking unit may be substantially constant to provide a time in the cracking zone around .03 to .07 second or the flow may be graduated providing a cracking time on the order of 0.006 second when the zone is hottest up to around 0.3 second when it has cooled off to 850° C. This cracking period is terminated when the temperature at the top of the packing in unit 4 has been cooled to such an extent that efficient cracking cannot be obtained without undesirably reducing the speed of the gases; for instance, when the maximum temperature has dropped to around 780° to 850° C. The temperature at the bottom of the packing may be as high as 300° to 400° C. by this time.

At this point valve 7 is closed and the flow of steam is permitted to continue for a short period to purge the system of oil vapors. The flow is shown in Fig. 5. Since the direction of steam flow is not altered in this step, the general temperature conditions will not be materially affected.

After the brief purge is completed, the apparatus is ready for the blast or heating of unit 4, flow for which is shown in Fig. 6. Steam flow through line 28 is cut off and valves 13, 20, 24, and 26a are opened so that the blast passes down through unit 4 and out through the stack. During this period, unit 1 is permitted to lie idle or "soak". The passage of steam through this unit during the previous cracking step has removed a considerable proportion of the stored heat. The unit may now have a temperature at the top of the packing around 1100° C. and at the bottom around 100° C. During the idle period the top temperature may drop slightly and the bottom temperature rise.

When unit 4 has attained the desired operating temperature, say around 1500° C. at the top, valves 13 and 20 are closed, and steam is admitted through line 28 to purge the system as shown in Fig. 7.

After this brief purge the stack valve 26a is closed, the flow of steam through line 28 is cut off and through line 29 turned on. Valve 7 is opened to inject the hydrocarbon to be cracked into the steam passing through conduit 5 and the mixture then passes down through unit 1 out through conduits 21 and 25 and into the cooling tower 27 as previously described in connection with unit 4, and as shown in Fig. 8.

When the cracking period has been continued as long as considered desirable, depending upon the thermal condition of the cracking zone, valve 7 is closed, and the passage of steam is continued to again purge the system of cracked vapors as shown in Fig. 9. The system is now ready to begin a second cycle.

The length of each cycle will depend upon the size, mass, thermal conductivity, and specific heat of refractory materials, the maximum temperature drop permissible, etc. It may be, for instance, a short cycle such as 2 to 4 minutes or a relatively long cycle. With the conditions and materials employed above, a short cycle has been found to be most efficient.

We claim:

1. The method of operating a pair of refractory regenerative units, A and B, for cracking hydrocarbons to produce ethylene, which comprises heating refractory material in unit A by passing a hot gas in contact therewith while unit B is maintained idle and at least a portion of the refractory material in unit B is maintained at a temperature above 780° C., subsequently and before substantial heat is abstracted from unit A passing steam through unit A to heat said steam, forming a mixture of said steam with the hydrocarbon to be cracked and passing the mixture through unit B while refractory material in unit B is at a temperature between 780° C. and 1050° C., subsequently heating refractory material in unit B by passing a hot gas in contact therewith while unit A is maintained idle and at least a portion of the refractory material in unit A is maintained at a temperature above 780° C., subsequently and before substantial heat is abstracted from unit B passing steam through unit B to heat said steam, forming a mixture of said steam with additional hydrocarbon to be cracked, and passing said mixture through unit A, while refractory material in unit A is at a temperature between 780° C. and 1050° C.

2. The method of operating a pair of refractory regenerative units, A and B, for cracking hydrocarbons to produce ethylene, which comprises heating refractory material in unit A by passing a hot gas in contact therewith while unit B is maintained idle and at least a portion of the refractory material in unit B is maintained at a temperature above 780° C., before substantial heat is abstracted from unit A passing steam through unit A to cool refractory material in unit A and to heat said steam, forming a mixture of said steam with the hydrocarbon to be cracked and passing the mixture through unit B, while refractory material in unit B is at a temperature between 780° C. and 1050° C., subsequently heating the refractory material in unit B by passing a hot gas in contact therewith while unit A is maintained idle and at least a portion of the refractory material in unit A is maintained at a temperature above 780° C., before substantial heat is abstracted from unit B passing steam through unit B in a direction countercurrent to the previous flow of steam and hydrocarbon therethrough to cool refractory in unit B and to heat said steam, forming a mixture of said steam with additional hydrocarbon to be cracked and passing

said mixture through unit A while refractory material in unit A is at a temperature between 780° C. and 1050° C. in a direction countercurrent to the aforementioned passage of steam through unit A.

3. The method of operating a pair of refractory regenerative units, A and B, for cracking hydrocarbons to produce ethylene, which comprises heating refractory material in unit A to a temperature above 1050° C. by passing a hot gas in contact therewith while at least a portion of the refractory material in unit B is maintained at a temperature between 780° C. and 1050° C., subsequently passing steam through unit A to heat said steam, forming a mixture of said steam with the hydrocarbon to be cracked and passing the mixture through unit B, subsequently heating refractory material in unit B to a temperature above 1050° C. by passing a hot gas in contact therewith while at least a portion of the refractory material in unit A is maintained at a temperature between 780° C. and 1050° C., subsequently passing steam through unit B to heat said steam, forming a mixture of said steam with additional hydrocarbon to be cracked, and passing said mixture through unit A.

4. The method of operating a pair of refractory regenerative units, A and B, for cracking hydrocarbons to produce ethylene, which comprises blowing unit A with fresh hot combustion gas to heat refractory material therein while at least a portion of the refractory material in unit B is maintained at a temperature above 780° C., subsequently passing steam through unit A to heat said steam, forming a mixture of said steam with the hydrocarbon to be cracked and passing the mixture through unit B while refractory material in unit B is at a temperature between 780° C. and 1050° C., subsequently blowing unit B with fresh hot combustion gas to heat the refractory material therein while at least a portion of the refractory material in unit A is maintained at a temperature above 780° C., subsequently passing steam through unit B to heat said steam, forming a mixture of said steam with additional hydrocarbon to be cracked, and passing said mixture through unit A while refractory material in unit A is at a temperature between 780° C. and 1050° C.

5. The method of operating a pair of refractory regenerative units, A and B, for cracking hydrocarbons to produce ethylene, which comprises blowing unit A with fresh hot combustion gas to heat refractory material therein while at least a portion of the refractory material in unit B is maintained at a temperature above 780° C., subsequently passing steam through unit A in a direction countercurrent to the direction of flow of said combustion gas through said unit to heat said steam, forming a mixture of the resulting heated steam with the hydrocarbon to be cracked and passing the mixture through unit B while refractory material in unit B is at a temperature between 780° C. and 1050° C., subsequently blowing unit B with fresh hot combustion gas to heat refractory material therein while at least a portion of refractory material in unit A is maintained at a temperature above 780° C., subsequently passing steam through unit B in a direction countercurrent to the flow of combustion gas therethrough to heat said steam, forming a mixture of the resulting heated steam with additional hydrocarbon to be cracked, and passing said mixture through unit A while refractory material in unit A is at a temperature between 780° C. and 1050° C.

6. The method of operating a pair of refractory regenerative units, A and B, for cracking hydrocarbons to produce ethylene, which comprises blowing unit A with fresh hot combustion gas to heat the refractory material therein to a temperature above 1050° C. while at least a portion of the refractory material in unit B is maintained at a temperature above 780° C., subsequently passing steam through unit A in a direction countercurrent to the flow of combustion gas therethrough to heat said steam, forming a mixture of the resulting heated steam with the hydrocarbon to be cracked and passing the mixture through unit B, subsequently blowing unit B with fresh hot combustion gas to heat refractory material therein to a temperature above 1050° C. while at least a portion of the refractory material in unit A is yet at a temperature above 780° C., subsequently passing steam through unit B in a direction countercurrent to the flow of combustion gas therethrough to heat said steam, forming a mixture of the resulting heated steam with additional hydrocarbon to be cracked, and passing said mixture through unit A in a direction countercurrent to the aforesaid flow of steam therethrough.

7. The method of operating a pair of refractory regenerative units, A and B, for cracking hydrocarbons to produce ethylene, which comprises blowing unit A with fresh hot combustion gas to heat the refractory material therein to about 1500° C. while a portion of the refractory material in unit B is maintained at a temperature above 780° C. and another portion thereof is maintained at a temperature below about 400° C., then passing steam serially through units B and A to expel combustion products, subsequently passing initially cool steam through unit A in a direction countercurrent to the flow of combustion gas therethrough to heat said steam and cool a portion of refractory material therein to a temperature below about 400° C., forming a mixture of the resulting heated steam with the hydrocarbon to be cracked and passing the mixture through unit B first in contact with refractory material therein at a temperature between 780° C. and 1050° C. and then in contact with refractory material therein at a temperature below 400° C., subsequently blowing unit B with fresh hot combustion gas to heat refractory material therein to about 1500° C. while a portion of the refractory material in unit A is yet at a temperature above 780° C. and another portion thereof is maintained at a temperature below about 400° C., then passing steam serially through units A and B to expel combustion products, subsequently passing initially cool steam through unit B in a direction countercurrent to the flow of combustion gas therethrough to heat said steam and cool a portion of refractory material therein to a temperature below about 400° C., forming a mixture of the resulting heated steam with additional hydrocarbon to be cracked, and passing said mixture through unit A first in contact with refractory material therein at a temperature between 780° C. and 1050° C. and then in contact with refractory material therein at a temperature below 400° C. and in a direction countercurrent to the aforesaid flow of steam therethrough.

8. The method of cracking hydrocarbons to produce ethylene in a pair of refractory regenerative units A and B connected at one end by a gas conduit so as to provide a continuous passage serially through the two units, which comprises blowing unit A with fresh hot combustion gas with a direction of gas flow away from the connected unit A aforesaid so as to heat the refractory material in unit A while at least a part of the refractory material in unit B is at a temperature above 780° C., subsequently passing steam through unit A in a direction countercurrent to the direction of flow of said combustion gas through unit A to heat said steam and to cool the refractory material in unit A, forming a mixture of the resultant heated steam with hydrocarbon to be cracked and passing the mixture through unit B while refractory material in unit B is at a temperature between 780° C. and 1050° C. in a direction of flow away from its connected end aforesaid, subsequently blowing unit B with fresh hot combustion gas with a direction of gas flow away from its connected end aforesaid so as to heat the refractory material in unit B while at least a part of the refractory material in unit A is at a temperature above 780° C., subsequently passing steam through unit B in a direction countercurrent to the direction of flow of said combustion gas through unit B to heat said steam and to cool the refractory material in unit B, forming a mixture of the resultant heated steam with hydrocarbon to be cracked and passing the mixture through unit A while refractory material in unit A is at a temperature between 780° C. and 1050° C. in a direction of flow away from its connected end aforesaid.

9. In the operation of a pair of refractory regenerative units A and B in a four-period cycle with intermediate steam purges for the production of ethylene, the method which comprises in period 1 blowing unit A with hot combustion gas to heat the refractory material therein to a temperature above 780° C. while causing unit B to remain idle at a temperature above 780° C., in period 2 passing the steam through the refractory material of unit A to heat the steam, mixing the resultant heated steam with hydrocarbon to be cracked and passing the mixture through unit B while refractory therein is at a temperature between 780° C. and 1050° C., in period 3 blowing unit B with hot combustion gas to heat the refractory material therein to a temperature above 780° C. while causing unit A to remain idle at a temperature about 780° C., and in period 4 passing steam through unit B to heat the steam, mixing the resultant steam with hydrocarbon to be cracked and passing the mixture through unit A while refractory therein is at a temperature between 780° C. and 1050° C.

10. The method of the preceding claim wherein the flow through unit A in periods 1 and 2 is countercurrent, the flow through unit B in periods 2 and 3 is concurrent, the flow through unit B in periods 3 and 4 is countercurrent, and the flow through unit A in periods 4 and 1 is concurrent.

FRANK PORTER.
JOHN MOYLE DUNCAN.

CERTIFICATE OF CORRECTION.

Patent No. 2,185,566. January 2, 1940.

FRANK PORTER, ET AL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 5, second column, line 21, claim 9, for the word "about" read above; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 13th day of February, A. D. 1940.

Henry Van Arsdale,
Acting Commissioner of Patents.

(Seal)