July 16, 1940. J. M. DUNCAN 2,208,123

PROCESS FOR THE MANUFACTURE OF ETHYLENE

Filed Dec. 6, 1937 2 Sheets-Sheet 1

Fig. 1

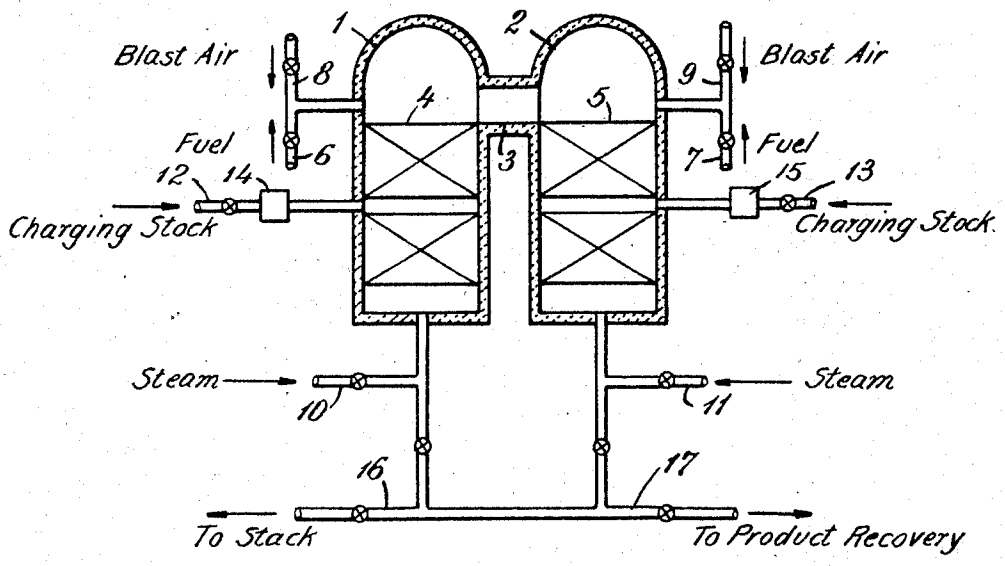


Fig. 1a

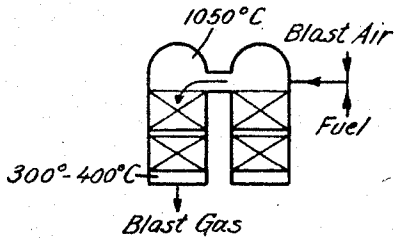


Fig. 1c

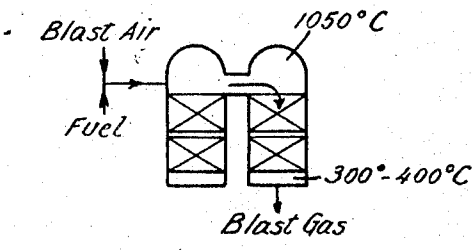


Fig. 1b

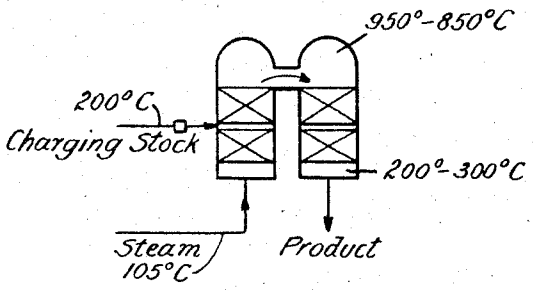
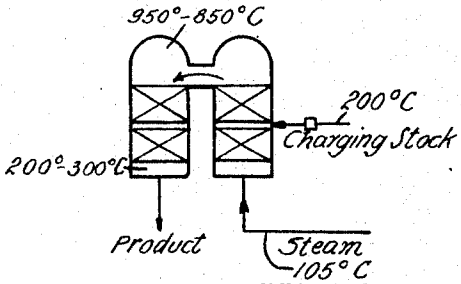


Fig. 1d



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Fig. 2.

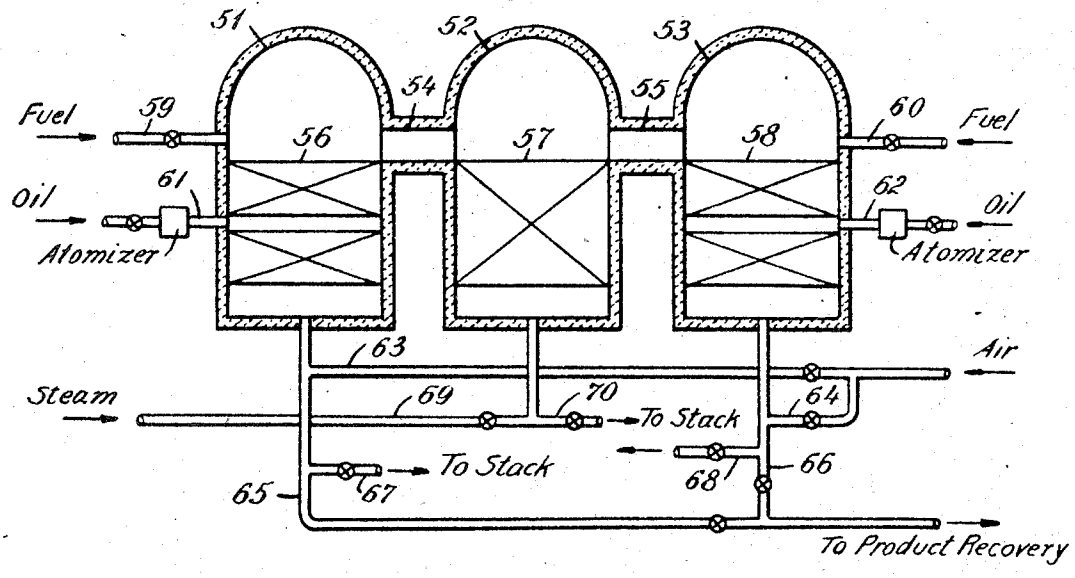


Fig. 2a

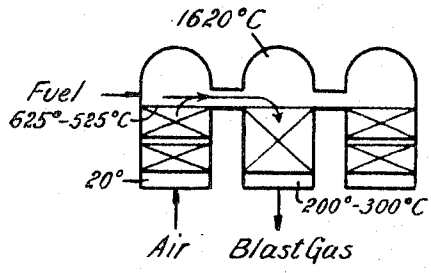


Fig. 2c

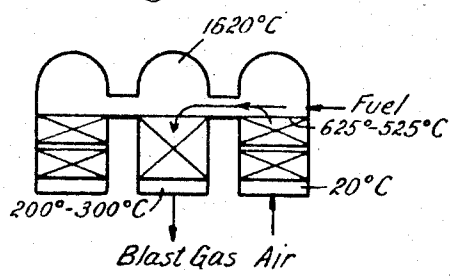


Fig. 2b

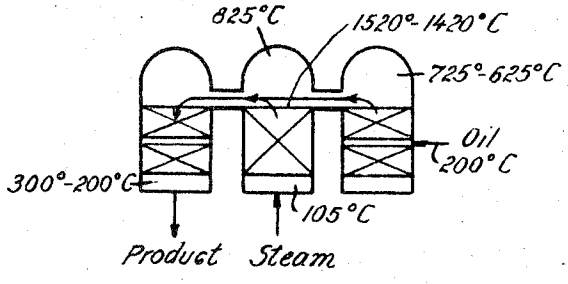
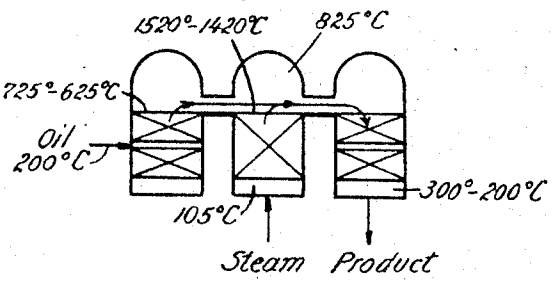


Fig. 2d



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UNITED STATES PATENT OFFICE

2,208,123

PROCESS FOR THE MANUFACTURE OF ETHYLENE

John Moyle Duncan, Petersburg, Va., assignor to The Solvay Process Company, New York, N. Y., a corporation of New York

Application December 6, 1937, Serial No. 178,303

3 Claims. (Cl. 260—683)

This invention relates to the manufacture of ethylene. It is particularly directed to the operation of regenerative cracking units in the vaporous or gaseous phase thermal cracking of hydrocarbons of higher molecular weight than ethylene.

The manufacture of ethylene by thermally 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 to be satisfactory and temperatures around 800° to 950° C. are preferable. Attempts to attain such cracking temperatures by heating the hydrocarbons or mixtures containing them through heat transfer walls of steel or other metals results in rapid destruction of the apparatus with consequent heavy replacement cost; iron surfaces furthermore have a deleterious effect upon the desired reaction. As a consequence the use of metal surfaces is not desirable. Refractory materials, on the other hand, do not possess the combination of tensile strength and heat conductivity essential for indirect heat transfer operations on an economical basis.

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.

The use of previously proposed regenerative cracking processes, which involve, in alternate periods, heating refractory material to cracking temperature with hot combustion gases and introducing hydrocarbon into the heated material for cracking, is open to the objection that an efficient utilization of the heat supplied is not obtained and consequently fuel costs are high.

The present invention has for an object the improvement in regenerative cracking of hydrocarbons at the high temperatures employed in the manufacture of ethylene whereby an efficient utilization of heat is made possible and operating costs may be substantially reduced.

In accordance with the present invention the vapor of hydrocarbon to be thermally cracked to form ethylene in a regenerative cracking unit is superheated by contact with refractory material which has been employed for cooling the products of a preceding cracking period. Thus the heat of the product gases and vapors is stored in the refractory material during one cracking period of a cycle and this heat is given up to vapors to be cracked in a succeeding period.

It has been found that by operating in this manner a remarkably high efficiency of heat transfer from outgoing hydrocarbon vapor to ingoing hydrocarbon vapor may be effected and substantial economies in fuel consumption thereby obtained.

The invention comprehends operations wherein all of the heat supplied to the refractory by cracked products, except for normal radiation and conduction losses, is supplied to ingoing hydrocarbon vapors and also to operations wherein only a part of the heat supplied to the refractory by cracked products is returned as preheat of vapors to be cracked. When only a part of the heat is recovered in accordance with the process of the present invention, the remainder thereof may be recovered in accordance with the process described and claimed in application Serial No. 178,320 of Donald A. Rogers of even date.

After refractory has been heated by contact with cracked products, it may be further heated by hot combustion gases.

In its preferred aspects the invention involves a cracking of hydrocarbon mixed with steam. An amount of steam from 1 to 3 times the weight of the total hydrocarbon present preferably is employed. The steam serves the purposes of maintaining refractory surfaces in a clean condition and of reducing the tendency of ethylene formed in the cracking step to polymerize or form benzene.

The invention is applicable to cracking processes in which the hydrocarbon, after the superheating step of the present invention, is heated to cracking temperature by direct contact with hot refractory and to processes in which all or part of the heat required for cracking is supplied to the hydrocarbon from such refractory through the interposition of steam as a heat transfer medium.

It is preferred to pass the hot combustion gases through a second zone of refractory material in the blast period to cool the gases to below 400° C., and to pass initially relatively cool (below 300° C.) steam or mixture of steam and hydrocarbon to be cracked through this refractory zone in a direction countercurrent to the blast gases. In this manner the blast gases serve not only to heat the cracking zone but to preheat the steam and in some cases the hydrocarbon to be cracked.

In order to secure the highest efficiency of

heat transfer from hydrocarbon vapors and gases from the cracking process to hydrocarbon to be cracked, it is preferred to pass the products of cracking through a refractory storage unit in one direction and to pass the vapors of the hydrocarbon to be cracked through this unit in the opposite direction. By this operation the products of cracking may be cooled from cracking temperature to between 150° C. and 400° C. in giving up their heat to the ingoing hydrocarbon vapor mixture, which in this way may be heated to 500° to 750° C.

The following description of two specific embodiments of the invention will serve as a further illustration thereof:

In the drawings, Fig. 1 designates one combination of refractory cracking and heat exchange units, which may be employed for carrying out the invention;

Figs. 1*a*, 1*b*, 1*c*, and 1*d* are flow diagrams showing a representative way of operating the apparatus of Fig. 1;

Fig. 2 shows an alternative apparatus embodying the invention; and

Figs. 2*a*, 2*b*, 2*c*, and 2*d* are flow diagrams for a representative cycle of operations in the apparatus of Fig. 2.

With special reference to Fig. 1, numerals 1 and 2 designate similar regenerative units connected by a conduit 3 and provided with packed sections 4 and 5. Packed sections 4 and 5 may consist of checker-work or crushed brick, for instance, 1 to 2 inch mesh broken fire-clay or any other suitable packing. Since in normal operation, as will be more fully explained hereinafter, the upper portions of the packing are maintained at relatively high temperatures compared with the lower portions, it may be advantageous to employ more than one type of packing. Thus in the lower half a fire-clay brick capable of withstanding moderately high temperatures and selected especially to withstand the pressure of the mass of material upon it, may be used; while in the upper half a crushed material especially selected to withstand high temperatures, for instance clay-bonded silicon carbide, may be employed. That packing nearest the bottom of the units may be somewhat larger than the rest.

Units 1 and 2 are provided with valve-controlled fuel inlets 6 and 7 and valve-controlled air inlets 8 and 9 disposed above the packed sections 4 and 5. Valve-controlled steam inlets 10 and 11 communicate with the units below the packed sections 4 and 5. Valve-controlled inlets 12 and 13, provided with atomizers 14 and 15, are arranged for the introduction of oil to be cracked. Units 1 and 2 are provided also with valved outlets 16 and 17 to the stack and to the product recovery system, which may be of any suitable type, such as that disclosed in the application of Frank Porter and John Moyle Duncan, Serial No. 153,496, filed July 14, 1937. The essential function of any such recovery system is merely to separate out the condensible constituents from the fixed gases produced by the cracking process. The fixed gases, after cooling and washing to remove condensible constituents, may be passed to suitable storage or may be subjected to further treatment for segregation of the individual constituents, of which ethylene may amount to between 25 and 40 mol percent.

The operation of the above apparatus for the cracking of gas-oil in a representative 4-period cycle may be as follows:

First blast period (Fig. 1a)

Air and liquid fuel, such as tar recovered from the products either with or without separation of the more valuable constituents and preheated or not, are introduced through inlets 7 and 9, to the combustion space above the packed section 5 of unit 2. The combustion gases at a temperature of about 1050° C. are passed through conduit 3 into unit 1 and down through packed section 4 thereof to heat the refractory material of which this section consists. The gases, cooled by the refractory to a temperature of about 300° C., are passed out at 16 to the stack. As the blast period continues the rising temperature of the refractory results in a rise of temperature in the gas leaving the regenerative unit 1 and at the end of this blast period the exhaust gases may have a temperature around 400° C.

Combustion products purge

When the refractory material at the top of packed section 4 has attained a temperature of about 1000° C., the blast is discontinued and steam is introduced at 11 for a brief period, the valves of the system being adjusted so that the steam passes up through the packed section of unit 2, through conduit 3, down through the packed section of unit 1, and out at 16 to the stack. By this brief purge the combustion gases are displaced from the units by steam without materially affecting their temperature. The valves on the steam inlet 11 and the outlet 16 to the stack are then closed and the system is ready to begin the first cracking period.

First cracking period (Fig. 1b)

Gas-oil previously heated to a temperature of about 200° C. under sufficient pressure to prevent vaporization, is admitted to atomizer 14 where a portion of the oil is flashed into vapor and the remainder in atomized state is carried along with the vapor thus formed. Steam at 105° C. is admitted through inlet 10 to provide a weight ratio of steam to hydrocarbon of about 1.7 to 1. The steam enters unit 1 at the bottom thereof, passes up through the highly heated refractory of section 4, which is at a temperature graduated from about 350° C. at the bottom to about 1000° C. at the top. The oil and vapor mixture enters the hot flow of steam at a point below cracking temperature but yet hot enough to convert all of the oil to vapor phase, and continues with the steam up through the hotter zones of refractory whereby it is heated to cracking temperature and cracked to form ethylene and other products of cracking in admixture with steam. This mixture at a temperature of about 950° C. is thereupon passed through conduit 3 into unit 2 and down through the progressively cooler refractory therein. By contact with the relatively cool refractory in the lower part of section 5, products of the reaction are cooled to a temperature of about 200° C. and at this temperature are exhausted through outlet 17 to the product recovery system for separation of condensible constituents. As the passage of the mixture through the regenerative units is continued, the maximum temperature of the mixture gradually falls. When this temperature reaches about 850° C., the introduction of gas-oil is discontinued. The products leaving the packed section 5 of unit 2 at this point may be at a temperature around 300° C., since

the absorption of heat from the cracked products has caused the refractory in section 5 to rise in temperature.

Cracked products purge

The flow of steam is continued for a further brief period to displace cracked products from units 1 and 2. The steam flow is then shut off by closing the valve on inlet 10 and the outlet 17 to product recovery also is shut.

Second blast period (Fig. 1c) and purge

Fuel and air are introduced through inlets 6 and 8, the valves being adjusted so that combustion gases pass through conduit 3, down through cracked section 5 of unit 2, and out at 16 to the stack. When the refractory temperature at the top of unit 2 has reached about 1000° C., the flow of fuel and air is discontinued.

Steam is introduced at 10 for a brief purge to expel combustion products. The steam and stack valves are then closed.

Second cracking period (Fig. 1d) and purge

Steam at about 105° C. and gas oil at 200° C. are introduced at 11 and 13 respectively at a suitable rate to provide a ratio by weight of 1.7 parts of steam to 1 part of hydrocarbon, and a maximum temperature of about 950° C. in the gas stream at the top of the regenerative units. The oil is thereby cracked to ethylene, etc. Reaction products pass down through packed section 4 of unit 1 and out at 17 to product recovery at an initial temperature around 200° C. The flow of steam and oil is continued until the maximum temperature attained has dropped to about 850° C., the product at this time having attained a temperature around 300° C., whereupon the cracking period is discontinued by stopping the flow of oil.

The flow of steam is continued briefly to purge the system of cracked products. After this purge the system is in condition for a second cycle commencing with the operation illustrated in Fig. 1*a*.

In the above operations packed section 4 is cooled by ingoing steam and oil during the cracking period illustrated in Fig. 1*b* so that the refractory material in this section has a final temperature around 900° C. at the top and around 150° C. at the bottom. This section remains idle during the blast period shown in Fig. 1*c* and, in the next cracking period, illustrated in Fig. 1*d*, serves to cool the product. Since the top of this section is at a temperature within the cracking temperature range, it will be appreciated that packed section 4 serves both as a cracking section near the top and as a cooling section near the bottom. The products of the cracking of Fig. 1*d* are cooled by the lower portion of section 4 down to a temperature of 200° to 300° C. Meanwhile section 5 is being cooled by charging stock and steam introduced at 13 and 11 and in this manner is being prepared to cool the products of the cracking period illustrated in Fig. 1*b* in a succeeding cycle. In both cracking periods, therefore, the product leaves the regenerators at a temperature only slightly higher than that at which it is introduced initially.

Since the reaction is endothermic and since 100% heat efficiency is not obtainable, it is necessary to introduce additional heat into the system and this is accomplished by passing hot combustion gases through the section of refractory which, in the previous period of the cycle, was heated by cracked products. For example, the refractory is heated by cracked products from an initial temperature of about 150° C. up to about 250° C. at the bottom; at the top the refractory temperature may have dropped to about 900° C. or 875° C.; but the temperature will have risen in the major portion of the refractory and the total heat content will have been increased; the hot combustion gases further heat this refractory to a temperature of about 1000° C. at the top and about 350° C. at the bottom.

In the above operating cycle it is advisable to avoid cooling the products of cracking to a temperature at which substantial amounts of condensible constituents separate. Since in normal operation the temperature of refractory with which the cracked products come into contact gradually rises as the cracking period progresses, small amounts of condensible constituents separated early in the cracking period may be evaporated later on by the hotter gases coming into contact therewith. However, the separation of such condensate on the surfaces of the refractory material promotes the deposition of solid material which adheres to the surfaces on evaporation of the liquid.

By the provision of somewhat larger or thermally less conductive fragments of packing at the exit or lower sides of the packed sections excessive cooling of products may be avoided. Even such fragments may be superficially cooled by entering steam to a temperature undesirably low. However, between each contact of the packing with relatively cold steam and use of the packing for cooling cracked products, the packing is permitted to remain idle for the duration of a blast period. Consequently time is afforded for the heat in the interior of each fragment to be conducted to the surfaces. This thermal soaking avoids the necessity for any further precautions to prevent excessive cooling of cracked products, such as preheating the steam to high temperatures prior to bringing it into contact with the refractory.

In Fig. 2 a three-unit system is shown. The central unit is subjected to blasting and only this unit is employed for heating the steam prior to cracking. The other two units are employed alternately for preheating the blast air, cooling cracked products, and superheating ingoing hydrocarbon vapors. Thus the heat given up to a refractory by the products of cracking is returned partly as preheat of blast air and partly as superheat of ingoing hydrocarbon.

Specifically the apparatus comprises three regenerative units, 51, 52, and 53, connected by conduits 54 and 55 and provided with heat storage sections 56, 57, and 58 containing refractory packing. Units 51 and 53 are provided with fuel inlets 59 and 60, oil inlets 61 and 62, air inlets 63 and 64, outlets 65 and 66 for the cracked products, and outlets 67 and 68 to the stack. Unit 52 is provided at its base with a steam inlet 69 and an outlet 70 to the stack.

The operation of this apparatus in a representative cycle is shown in Figs. 2*a*, 2*b*, 2*c*, and 2*d*.

The first blast period (Fig. 2a)

Air and fuel are introduced at 63 and 59, respectively, into unit 51. Combustion gases at about 1620° C. pass through conduit 54 into unit 52, down through section 57 where they give up most of their contained heat to the refractory packing of which this section consists and out

through 70 to the stack at about 200° C. at the beginning and about 300° C. at the end of the period. By this operation the packed section 57 is heated at its top to a temperature around 1570° and at its bottom to a temperature around 250° C. If the blast period is prolonged, the depth of the zone at approximately maximum temperature is increased. The most satisfactory depth will depend upon the amount of oil to be cracked in the succeeding cracking period, and this in turn will vary depending upon the operating characteristics of the particular apparatus involved. Packed section 56 serves no function in the initial heating up step but in subsequent blast periods will serve to preheat the air to from 625° C. at the beginning of the blast period to 525° C. at the end. In the initial heating up, section 58 may be blasted to heat it to about 800° C. at the top.

The combustion gas purge

After the blast period steam is introduced at 69 and passed through packed sections 57 and 56 to expel combustion products. Since the amount of such products is exceedingly small compared with the amount of cracked products produced, the purged gases may be sent to product recovery. It is preferred, however, to send such products through outlet 67 to the stack. During the purge steam also may be passed through packed section 58 in unit 53 and through outlet 68 to the stack to insure against the presence of combustion gases in unit 53.

The first cracking period (Fig. 2b)

Oil, preheated to 200° C. under pressure and partially vaporized as in the embodiments of Figs. 1, 1a, etc., is introduced at 62 and steam is introduced at 69. The vaporization of the oil is completed and the vapors are superheated to a temperature of about 725° C. in packed section 58. Steam introduced at 69 is heated in section 57 to about 1520° C. The preheated oil vapor mixes with the preheated steam in the vapor space above packed section 57 in unit 52 and the mixture at a temperature around 825° C. passes into unit 51, down through this unit where it is cooled by contact with refractory 56 to a temperature around 200° C. and thence by way of outlet 65 to the product recovery system. This period may be continued until the ingoing steam is heated to about 1420° C. and the ingoing oil is heated to only about 625° C. By this time the refractory section 56 will have been heated to about 775° C. at the top and about 250° C. at the bottom and the products leaving the system will be around 300° C.

Purge of products

The flow of steam may be continued after the cracking period is ended to expel cracked products from units 52 and 51. At the same time by opening outlet 66 a portion of the steam may be caused to flow through unit 53 to expel oil vapors from this unit. The steam flow is then stopped.

The second blast period (Fig. 2c) and purge

When the system has been purged of hydrocarbon vapors, air and fuel may be introduced at 64 and 60, respectively, and combustion products may be withdrawn at 70. Section 57 is thus again heated to about 1570° C. at the top by the combustion gases. When this temperature has been attained, the blast is discontinued.

Packed section 58, which has been cooled to about 675° C. in the previous cracking period by contact with ingoing oil, is further cooled by the air for combustion. The combustion air at the same time is heated to a temperature of about 625° C. at the commencement of the blast period. These temperatures may fall gradually about 100° C. during the blast period so that at the end the air is preheated to about 525° C. The system is now purged by passing steam in at 69, up through section 57, down through sections 56 and 58, and out to the stack.

The second cracking period (Fig. 2d) and purge

When the purge is completed the flows of oil and steam are started through inlets 61 and 69, respectively. The oil is heated in section 56 to a temperature of about 725° C. and the steam is heated in section 57 to a temperature around 1520° C. The steam and oil vapors are mixed in the vapor space above packed section 57 and pass thence into unit 53 at a temperature around 825° C. The mixture then passes down through section 58 where it is cooled by contact with the refractory material to about 200° C. before being sent to the product recovery system. As the cracking period continues the maximum temperatures of the steam and superheated oil vapor may fall about 100° each. The cracking period is then terminated. After the cracking period the system may be purged by means of steam as previously described.

The above described arrangement of regenerative unit may be operated on a schedule involving around 32% cracking period and 53% blast period; the remaining 15% being proportioned among the purges and valve operations.

The cracking temperature may be maintained substantially constant through the cracking period by varying the flow of oil only about 14% from the average rate, thus it may be 14% faster at the beginning of the cracking period and 14% slower at the end.

It is possible to revise the operation of the arrangement of Fig. 2 so that the periods follow in the order 2a, 2d, 2c, 2b. Such a regimen has the disadvantage that it reduces the heat efficiency slightly but has the advantage that it provides a thermal soak for the cooling unit after the refractory in this unit has been cooled by blast air and before it is used to cool reaction products. Hence, aside from possible provision of large refractory fragments in the lower parts of the sections 56 and 58, no further provision is required to prevent tar deposition as a result of overcooling.

If high ethylene yields are sought, it is desirable to adjust the cycle of operations so that the cracking time, i. e., time above 780° C., is not more than 0.3 second and not less than 0.006 second. The shorter time is more suitable for higher temperatures and vice versa. A time of about 0.05 second at the maximum temperatures given in the illustrative examples gives a product gas containing 30 to 40 mol percent of ethylene.

No claim is made herein to the feature of cooling refractory by contact with blast air and using the cooled refractory for cooling cracked products, since this is the subject matter of application Serial No. 178,320 of Donald A. Rogers, entitled "Process for the manufacture of ethylene," filed on the same date as this application.

I claim:

1. In the manufacture of ethylene from hydrocarbons of higher molecular weight by a cyclic

regenerative process of thermal cracking in the presence of steam involving four work periods A, B, C, and D, wherein heat of hot combustion gases is supplied to a cracking zone in periods B and D of the cycle and steam and hydrocarbon to be cracked in a weight ratio between 1:1 and 3:1 are supplied to said zone in periods A and C of the cycle and cracked therein to form a reaction mixture at a temperature between 780° and 1050° C., the improvement which comprises contacting vapors of the hydrocarbon with hot refractory of progressively higher temperature in one unit to superheat the vapor and cool said refractory and cracking said hydrocarbon in admixture with steam in a weight ratio between 1:1 and 1:3 at a temperature between 780° and 1050° C. in cracking period A of the cycle and contacting the mixture of steam and products of cracking formed in cracking period A of said cycle with progressively cooler refractory in another unit to cool the products to a temperature below about 400° C. and heat the refractory, and, in period C of the cycle, contacting vapors of the hydrocarbon with hot refractory at a progressively higher temperature in said other unit to superheat the vapor before cracking and to cool said refractory and cracking said hydrocarbon in admixture with steam in a weight ratio between 1:1 and 1:3 at a temperature between 780° and 1050° C. and then contacting the mixture of steam and products of cracking formed in cracking period C of said cycle with progressively cooler refractory in said one unit to cool the products to a temperature below about 400° C. and heat the refractory, and in each of periods B and D supplying heat to said cracking zone by a blast of hot combustion gas and during said blast maintaining one of said heat storage units idle.

2. In the manufacture of ethylene from hydrocarbons of higher molecular weight by a cyclic regenerative process of thermal cracking in the presence of steam wherein heat of hot combustion gases is supplied to a cracking zone in one period of a cycle and steam and hydrocarbon to be cracked in a weight ratio between 1:1 and 3:1 are supplied to said zone in another period of the cycle and cracked therein to form a reaction mixture at a temperature between 780° and 1050° C., the improvement which comprises passing hot combustion gases through one refractory heat storage unit to transfer the heat of combustion to refractory in said unit and cool the combustion gases to a temperature below about 400° C. in period A of a cycle, passing a mixture of steam and vapor of the hydrocarbon in a weight ratio between 1:1 and 3:1 through said refractory heat storage unit in a direction opposite to the flow of combustion gas therethrough to heat the mixture to a temperature between 780° and 1050° C. and thereby crack the hydrocarbon with the formation of ethylene, passing the mixture of cracked products through a second refractory heat storage unit comprising progressively cooler refractory in the direction of gas flow so as to transfer the heat from said cracked products to refractory in said second unit and cool the products to a temperature below about 400° C. in a period B of said cycle, passing hot combustion gases through said second refractory heat storage unit in the same direction as the flow of cracked products therethrough to transfer heat of combustion to refractory in said second heat storage unit and cool the hot combustion gases to a temperature below about 400° C. in a period C of said cycle, and passing a mixture of steam and vapor of hydrocarbon to be cracked through said second heat storage unit to heat the mixture to a temperature between 780° and 1050° C. and thereby crack the hydrocarbon with formation of ethylene, and passing the hot mixture of cracked products through said first heat storage unit in a direction opposite to the flow of steam-hydrocarbon vapor mixture therethrough in said period B so as to contact the products with progressively cooler refractory in said first unit and transfer the heat of said products to the refractory in said first unit and cool the products to a temperature below about 400° C. in a period D of said cycle.

3. In the manufacture of ethylene from hydrocarbons of higher molecular weight by a cyclic regenerative process of thermal cracking in the presence of steam wherein heat of hot combustion gases is supplied to a cracking zone in one period of a cycle and steam and hydrocarbon to be cracked in a weight ratio between 1:1 and 3:1 are supplied to said zone in another period of the cycle and cracked therein to form a reaction mixture at a temperature between 780° and 1050° C., the improvement which comprises passing air through hot refractory in refractory heat storage unit 1 to heat the air and cool refractory, burning fuel with said heated air to form hot combustion gases, passing the hot combustion gases through a refractory heat storage unit 2 to supply heat thereto and cool the combustion gases to a temperature below about 400° C. in a period A of a cycle, passing steam through the thus heated refractory in heat storage unit 2 in a direction opposite to the flow of combustion gas therethrough to heat the steam to a temperature above 1050° C., passing hydrocarbon vapor through a hot refractory heat storage unit 3 to superheat the vapor to a temperature between about 500° and about 750° C., mixing the hydrocarbon vapor and the steam to form a steam-hydrocarbon vapor mixture in a weight ratio between 1:1 and 3:1 at a temperature between 780° C. and 1050° C., and passing the mixture through said refractory heat storage unit 1 in a direction opposite to the flow of air therethrough to cool the mixture to a temperature below about 400° C. in a period B of said cycle, passing air through hot refractory in refractory heat storage unit 3 to heat the air and cool the refractory, burning fuel with said heated air to form hot combustion gases, passing the hot combustion gases through refractory heat storage unit 2 to supply heat thereto and cool the combustion gases to a temperature below about 400° C. in a period C of a cycle, passing steam through the thus heated refractory in heat storage unit 2 in a direction opposite to the flow of combustion gases therethrough to heat the steam to a temperature above 1050° C., passing hydrocarbon vapor through the hot refractory in heat storage unit 1 to superheat the vapor to a temperature between about 500° and about 750° C., mixing the hydrocarbon vapor and the steam to form a steam hydrocarbon vapor mixture in a weight ratio between 1:1 and 3:1 at a temperature between 780° C. and 1050° C., and passing the mixture through said refractory heat storage unit 3 in a direction opposite to the flow of air therethrough to cool the mixture to a temperature below about 400° C. in a period D of said cycle.

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