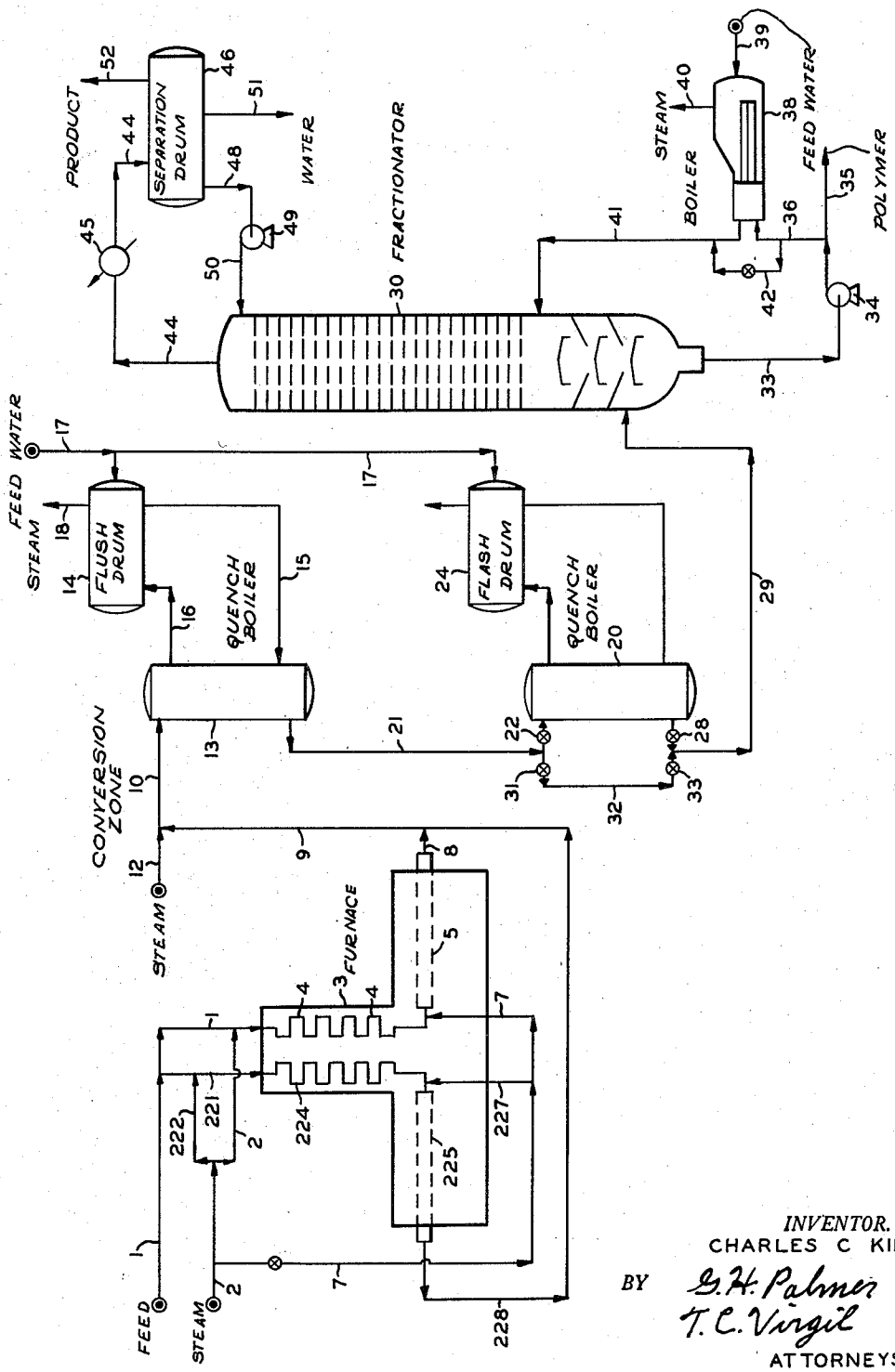
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PYROLITIC HYDROCARBON CONVERSION PROCESS FOR MAKING ETHYLENE

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PYROLITIC HYDROCARBON CONVERSION PROCESS FOR MAKING ETHYLENE

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This invention relates to the production of ethylene by the pyrolytic conversion of hydrocarbons. More particularly, it relates to an improved method for the production of ethylene by the pyrolytic conversion of saturated hydrocarbons containing two or more carbon atoms and unsaturated hydrocarbons containing three or more carbon atoms. My invention also relates to an improved method for quenching the product resulting from the production of ethylene by the pyrolytic conversion of hydrocarbons.

It is an object of my invention to provide an improved process for the production of ethylene by the pyrolysis of hydrocarbons.

It is another object of my invention to provide an improved method for quenching the reaction product resulting from the production of ethylene by the pyrolytic conversion of hydrocarbons.

According to my invention, hydrocarbon feed is partially converted to ethylene in a first conversion zone which is preferably an externally heated zone, such as a heated cracking coil. Additional conversion then takes place in a second conversion zone, preferably by contacting the effluent from the first conversion zone with superheated steam. In another aspect of this invention, quenching of the hot product resulting from the above conversion is accomplished by indirect contact with a heat exchange medium such that the reaction product is cooled to a temperature above the dew point and the quenched product is then passed to a separation zone where additional heat is removed.

By means of my invention, hydrocarbons are partially converted to ethylene in a first pyrolytic conversion zone and further conversion is effected in a second pyrolytic conversion zone. Preferably, the first conversion zone is externally heated, while the second is an adiabatic conversion zone, such as a transfer line conversion heated by injection of superheated steam.

The use of both types of pyrolytic conversion zones minimizes the difficulties inherent in the use of either type alone. An externally heated conversion zone, such as a furnace containing cracking coils, is more economical to operate from a heat supply standpoint than a transfer line conversion zone depending on injection of steam for a supply of heat. In the pyrolytic production of ethylene, however, it is desirable to operate at comparatively low pressures in order to promote maximum production of ethylene and minimum production of undesirable products and carbon deposits. If an externally heated conversion zone is used, practical design problems dictate tube sizes which cause an undesirable pressure drop if the hydrocarbon feed is allowed to remain in the conversion zone for a sufficient time to attain the desired degree of conversion. This results in an undesirable product distribution and excessive carbon deposits in the parts of the conversion zone where the pressure is greatest. For these reasons, the use of an externally heated conversion zone alone is not desirable.

Injection of heated material, such as superheated steam, has the advantage of being capable of supplying a large amount of heat to a given region. This enables the desired conversion to take place rapidly and in a comparatively small conversion zone, thus eliminating the necessity and disadvantages of excessive pressures. The disadvantage of this method of operation is that it is more expensive to supply heat in this manner than it is to supply heat to an externally heated conversion zone located in a furnace or heater. In addition, injection of heated material increases the size of the product stream which increases equipment capacity requirements.

The feed material for my process can be any saturated hydrocarbon containing two or more carbon atoms or any unsaturated hydrocarbon containing three or more carbon atoms. Thus, it is possible to use either normally gaseous or normally liquid hydrocarbons in my process. Hydrocarbon liquids, such as reduced crude, naphtha, and gas oil are readily obtainable and are well suited for use with my invention. Among the normally gaseous hydrocarbons, ethane or propane are, for example, suited for use in my invention as well as mixtures of normally gaseous hydrocarbons, e.g., propane and ethane or refinery gas containing 1 to 4 carbon atoms. The ultimate choice of feed material for any given situation depends primarily on availability and cost of the different types of feed. Feeds with lower molal boiling points generally produce a greater yield of ethylene than those with higher molal boiling points and feeds having higher Watson "K" factors generally produce a greater yield of ethylene than those having lower "K" factors.

It is desirable to add steam to the feed prior to passing the same to the externally heated conversion zone in order to reduce the partial pressure of the feed in the conversion zone. Reducing the partial pressure of the feed allows a greater degree of conversion to take place without excessive formation of undesirable products. Addition of steam also serves to keep the linear velocity of the feed through the conversion zone to a maximum for the desired conversion thereby reducing the possibility of excess carbon formation. The amount of steam added at this point will depend on the type of feed and the degree of conversion desired in the externally heated conversion zone. In general, about 0.05 to 1.0 pound of steam per pound of hydrocarbon feed is employed in the externally heated conversion zone. Preferably about 0.2 to about 1.0 pound of steam per pound of feed is added when a normally gaseous feed is being used and preferably about 0.05 to about 0.5 pound of steam per pound of feed is added when a normally liquid feed is being used. If too little steam is used, excessive production of undesirable products will result; whereas if excessive steam is used, operating costs are increased unnecessarily and there may be an undesired amount of carbon oxides produced.

The temperatures maintained in the externally heated conversion zone will also depend in part on the feed being used. In general, conversion is effected at an average temperature of about 900 to 1600° F. Preferably temperatures of about 1300 to about 1600° F. are used for normally gaseous feeds while temperatures of about 1000 to about 1400° F. are preferably used for normally liquid feeds. Residence time in the externally heated conversion zone is generally not greater than about 1.0 second if significant formation of carbon and undesirable side-products are to be avoided and is as low as 0.05 second. Conversion of about 3 to about 10% of the feed to ethylene is accomplished in the externally heated conversion zone. This value is considered important for the operation because it represents the best operation in the light of the foregoing considerations.

The effluent from the externally heated conversion zone is contacted with superheated steam in preference to other

inert materials because steam can be condensed and easily separated when the product is cooled and also because it does not contaminate the end products of the process. In general, about 0.5 to 3.0 pounds of steam per pound of feed are used in the second step. The amount of steam used will depend on its temperature since enough should be added to bring the resulting mixture to the desired conversion temperature. In general, the conversion temperature is about 1200 to 1700° F., and for a normally liquid feed the temperature is about 1200 to about 1500° F., whereas for normally gaseous feeds the temperature is about 1300 to about 1700° F. Steam temperatures of about 1500 to about 2000° F. will normally be sufficient. Residence time in this conversion zone is usually limited to about 0.5 to about 3.0 seconds in order to limit the amount of undesirable side products produced. It is desired that about 6 to about 55% of the hydrocarbon feed be converted to ethylene in this conversion zone due to the contact with superheated steam. A total of about 9 to about 65% of the hydrocarbon feed is usually converted to ethylene by my process.

The hot reaction product is quenched by indirect contact with a heat exchange medium to halt the formation of undesirable products, such as olefin polymers. Quenching to temperatures below about 1000° F. will normally accomplish this purpose when normally liquid feeds are used while quenching to temperatures below about 1200° F. will suffice when normally gaseous feeds are used. Normally, the product should not be quenched to a temperature lower than its dew point since lower temperatures result in condensation of olefin polymers which tend to create solids deposits in the quench boiler thereby reducing the efficiency of the quench boiler and possibly requiring a shutdown for cleaning.

Indirect quenching is used because it possesses definite advantages over direct quenching by injection of water or other matter into the hot conversion product. Direct quenching does not actually remove heat from the product stream but merely serves to reduce the temperature of the product stream by dilution. This means that not only the product but also the quenching medium must be cooled to comparatively low temperatures later in the process. In addition the dilution results in a larger product stream and consequently necessitates more expensive cooling and separating equipment. By the use of indirect quenching, the need for extra capacity equipment and the necessity of cooling the quenching medium to separate it from the product stream is eliminated. The quench system disclosed here utilizes the heat recovered from the product stream to produce high pressure steam which can be used elsewhere in the process.

As mentioned previously, it is preferred to cool the product stream to a temperature above its dew point to prevent the condensation of olefin polymers. If direct quenching is used, the product stream can be safely cooled to less than its dew point because the presence of the quenching medium dilutes the quenched polymer and tends to inhibit plugging of the quench boiler. Furthermore, by direct quenching, the product can be quenched to a low enough temperature so that it enters the separation zone at the proper temperature. Hence, some problems in indirect quenching are not present in direct quenching. If indirect quenching is used, the product, of necessity, enters the separation zone at a higher temperature than is desirable for proper operation of the separation zone. When using the indirect quenching of my process, it is desirable to provide additional cooling capacity in the separation zone to handle the additional cooling requirements at that point. By means of indirect cooling of the product to a temperature above the dew point, the removal of heat is partially shifted to the separation zone where about 12 to about 30% of the total heat removal is effected.

My invention can be utilized under any pressure conditions. As mentioned previously, however, excessive pressure in the conversion zone has an adverse effect on product distribution. For this reason, it is usually advisable to keep the pressure in the system as low as possible in order to avoid excessive pressure in parts of the conversion zones. From a practical standpoint it is not desirable to operate any part of the system under a vacuum because of the expense involved and the possibility of air leakage into the system. Normally, a pressure of about 1 to about 100 p.s.i.g., will give a good yield of ethylene while still maintaining a positive pressure in the system, but it should be clearly understood that my invention is also operable at higher or lower pressures.

For a better understanding of my invention, reference should be had to the accompanying drawing which illustrates a preferred embodiment of my invention.

In the drawing hydrocarbon feed enters through lines **1** and **221**. Steam is added to the feed by means of lines **2** and **222**. The addition of steam at this point serves to reduce the contact time of the hydrocarbon in the furnace and also to keep the linear velocity through the furnace to a maximum for the desired conversion. This reduces the possibility of excess carbon formation and tends to minimize undesirable reactions. About 0.1 pound of steam are added per pound of hydrocarbon feed. Following addition of steam, the feed enters furnace **3** which contains heating zones **4** and **224** and conversion zones **5** and **225**. In the heating zones the feed is vaporized and heated to near conversion temperature e.g., 1000° F. In the conversion zones the feed is further heated and partially converted to ethylene. Preferably about 5 percent conversion of feed to ethylene takes place in the conversion zones during which a temperature of about 1275° F. is attained. Residence time in the conversion zones is 0.5 second, consequently, formation of carbon and undesirable products is avoided substantially. If desired, additional steam may be injected into the feed through lines **7** and **227** before the feed enters the conversion zone. A split stream has been shown in furnace **3** merely for convenience, and it should be understood that such an arrangement is not necessary to the operation of my invention, but it represents a preferred operation.

The product from conversion zones **5** and **225** leaves furnace **3** through lines **8** and **228** and passes to transfer line conversion zone **10** by way of line **9**. Superheated steam is injected into conversion zone **10** through line **12** to effect the remainder of the desired conversion. Steam is injected into the transfer line conversion zone in preference to other inert materials because it can be condensed and easily separated when the product is cooled and does not contaminate the end products of the process. Steam entering through line **12** is preferably at a temperature of about 1700° F. and about 1.5 pounds of steam per pound of hydrocarbon feed are employed. This will raise the temperature of the resulting mixture to about 1500° F. in order to effect a sufficiently rapid conversion. Residence time in the transfer line conversion zone is about 1.5 seconds in order to limit the amount of undesirable products produced. About 18 percent conversion of hydrocarbon feed to ethylene occurs in the transfer line conversion zone.

The product from the transfer line conversion zone is quenched in quench boiler **13** to halt the formation of unwanted products, such as olefin polymers. Quenching to temperatures below about 1000° F., will normally accomplish this purpose although lower temperature may be employed.

According to my invention, quenching is accomplished by indirect contact with a heat exchange medium. A preferred method of accomplishing this is illustrated in the drawing wherein water is used to quench the product from conversion zone **10** in quench boiler **13**. Other heat exchange mediums may of course be used with suitable auxiliary equipment. Water is supplied to quench boiler **13** from flash drum **14** through line **15**. Steam generated in the quenching process returns to the flash drum through line **16**. The feed water is supplied to the flash drum

through line 17 and high pressure steam is removed through line 18. If two-stage quenching is desired, the product is only partially cooled in quench boiler 13 and is then passed to quench boiler 20 through line 21 and valve 22 for further cooling. Quench boiler 20 and flash drum 24 operate in exactly the same manner as quench boiler 13 and flash drum 14. From quench boiler 20 the product passes through valve 28 and line 29 to fractionator 30. If two-stage quenching is not desired, the cooling may be completely effected in quench boiler 13 and the product passed directly to fractionator 30 by way of line 21, valve 31, line 32, valve 33 and line 29.

In fractionator 30, the product stream is further cooled to condense a polymer fraction which is separated and removed from fractionator 30 as a bottom fraction through line 33 and pump 34. After leaving pump 34 through line 35, part of the bottoms fraction is sent to storage via line 35 and part is recycled to fractionator 30. The recycled fraction passes through line 36 to low pressure steam boiler 38 where it is cooled. Feed water for boiler 38 is supplied through line 39 and low pressure steam is removed through line 40. From boiler 38 the recycle stream is returned to fractionator 30 through line 41. By the use of by-pass line 42 it is possible to by-pass boiler 38 if cooling of all or part of the recycle stream is not necessary. Cooling the recycle stream is a convenient method of removing the excess heat which is introduced into fractionator 30 by the quenched product entering through line 29. In this way variations in the outlet temperature of the quench boiler can be compensated for, and a considerable variation in the temperature of the quenched product can be tolerated without affecting the proper operation of the fractionator.

The overhead fraction from fractionator 30 is removed through line 44 and passed through condenser 45 to separation drum 46. From the separation drum a hydrocarbon reflux stream is removed through line 48 and recycled to fractionator 30 by pump 49 and line 50. Steam is condensed in condenser 45 and removed from the separation drum through line 51. Hydrocarbon vapors are withdrawn from the separation drum through line 52 and passed to product recovery equipment.

The following specific example illustrates a practical application of my invention with a typical feed material as illustrated in the drawing.

EXAMPLE

A 52.2° A.P.I. naphtha feed having a molal boiling point of 300° F. and a Watson "K" factor of 11.8 is treated at the rate of 3,500 barrels per stream day in accordance with my invention under operating conditions and with results as shown in the table.

Table

	Pressure (p.s.i.g.)	Temperature, ° F.
Externally heated conversion zone:		
Inlet	91	900
Outlet	14	1275
Transfer line conversion zone:		
Inlet	13.1	1500
Outlet	13.0	1275
1st Stage quench boiler:		
Inlet	13.0	1275
Outlet	12.0	700
2nd Stage Quench Boiler:		
Inlet	11.0	700
Outlet	9.8	600
Fractionator:		
Entrance	9.3	400
Overhead Fraction	7.6	240

Steam added to feed	0.1 pound/pound of feed.
Percent conversion of feed to ethylene in externally heated conversion zone	5% of feed.
Steam injected into transfer line conversion zone	2.1 pounds/pound of feed.
Percent conversion of feed to ethylene in transfer line conversion zone	18.0% of feed.
Total conversion of feed to ethylene	23.5%.

I claim:

1. The process for the production of ethylene which comprises passing a hydrocarbon reactant through a tubular pyrolytic conversion zone under conditions suitable for the production of ethylene including a temperature between about 900 and about 1600° F. and a time sufficient to convert not more than 10% the hydrocarbons to ethylene and passing the product from said tubular conversion zone through an elongated pyrolytic conversion zone maintained at a temperature between about 1200 and about 1700° F. for a period of about 0.5 to about 3.0 seconds whereby a further portion of said hydrocarbons is converted to ethylene.

2. The process for the production of ethylene which comprises passing a mixture of steam and a hydrocarbon reactant selected from the group consisting of a saturated hydrocarbon containing at least 2 carbon atoms and an unsaturated hydrocarbon containing at least 3 carbon atoms through a tubular pyrolytic conversion zone under conditions including a temperature between about 900 and about 1600° F. and a time sufficient to convert not more than 10% of said hydrocarbons to ethylene and contacting the effluent from said tubular conversion zone in an elongated conversion zone with superheated steam for a period of about 0.5 to about 3.0 seconds under conditions such that the temperature of the resulting mixture is between about 1200 and about 1700° F. thereby converting an additional portion of said hydrocarbon reactant to ethylene.

3. The process for the production of ethylene which comprises passing a mixture of steam and a hydrocarbon reactant selected from the group consisting of a saturated hydrocarbon containing at least 2 carbon atoms and an unsaturated hydrocarbon containing at least 3 carbon atoms through a tubular pyrolytic conversion zone under conditions including a temperature between about 900 and about 1600° F. and a time sufficient to convert about 3 to about 10 percent of said hydrocarbon reactant to ethylene and contacting the effluent from said tubular conversion zone in an elongated conversion zone with superheated steam for a period of about 0.5 to about 3.0 seconds under conditions such that the temperature of the resulting mixture is between about 1200 and about 1700° F., thereby converting an additional 6 to 55 percent of said hydrocarbon reactant to ethylene.

4. The process for the production of ethylene which comprises passing a mixture of a hydrocarbon reactant selected from the group consisting of a saturated hydrocarbon containing at least 2 carbon atoms and an unsaturated hydrocarbon containing at least 3 carbon atoms and about 0.05 to about 1.0 pound of steam per pound of hydrocarbon through an externally heated pyrolytic conversion zone at a temperature of about 900 to about 1500° F., for about 0.05 to about 1.0 second, thereby converting about 3 to about 10 percent of said hydrocarbon reactant to ethylene, passing the product to a second conversion zone, injecting about 0.5 to about 3.0 pounds per pound of hydrocarbon of superheated steam at a temperature of about 1500 to about 2000° F., into said second conversion zone thereby raising the temperature of the resulting mixture to between about 1200 and about 1700° F., thereby converting about 6 to 55 percent of said hydrocarbons to ethylene and quenching the product of the second conversion zone about 0.5 to about 3.0 seconds after injecting said steam.

5. The process of claim 4 in which the pressure is maintained between about 1 and about 100 p.s.i.g.

6. The process for the production of ethylene which comprises passing a hydrocarbon reactant selected from the group consisting of a saturated hydrocarbon containing at least 2 carbon atoms and an unsaturated hydrocarbon containing at least 3 carbon atoms through a first tubular pyrolytic conversion zone under conditions suitable for the production of ethylene including a temperature between about 900 and about 1600° F. and a time

sufficient to convert not more than 10% the hydrocarbon reactant to ethylene, passing the product from said tubular conversion zone through an elongated pyrolytic conversion zone maintained at a temperature between about 1200 and about 1700° F. wherein a further portion of said hydrocarbon reactant is converted to ethylene, and quenching said product by indirect contact with a heat exchange medium to a temperature above the dew point of the reaction product.

7. The process for the production of ethylene which comprises passing a hydrocarbon reactant selected from the group consisting of a saturated hydrocarbon containing at least 2 carbon atoms and an unsaturated hydrocarbon containing at least 3 carbon atoms through a tubular pyrolytic conversion zone under conditions suitable for the production of ethylene including a temperature between about 900 and about 1600° F. and a time sufficient to convert not more than about 10% of the hydrocarbon reactant to ethylene, passing the product from said tubular conversion zone through an elongated pyrolytic conversion zone maintained at a temperature between about 1200 and about 1700° F. wherein a further portion of said hydrocarbon reactant is converted to ethylene, quenching said product by indirect contact with a heat exchange medium to remove part of the heat and passing said product to a fractionation zone wherein it is further cooled.

8. The process for the production of ethylene which comprises passing a mixture of steam and a hydrocarbon reactant selected from the group consisting of a saturated hydrocarbon containing at least 2 carbon atoms and an unsaturated hydrocarbon containing at least 3 carbon atoms through a tubular pyrolytic conversion zone under suitable conditions to convert not more than 10% said hydrocarbon reactant to ethylene including a temperature between about 900 and about 1600° F., contacting the effluent from said tubular conversion zone in an elongated conversion zone with superheated steam under conditions such that the temperature of the resulting mixture is between about 1200 and about 1700° F., thereby converting an additional portion of said hydrocarbon reactant to ethylene, indirectly cooling the product to above its dew point, and passing said cooled product to a separation zone wherein it is further cooled and a part of the liquid product is separated therefrom.

9. The process for the production of ethylene which comprises passing a mixture of a hydrocarbon reactant selected from the group consisting of a saturated hydrocarbon containing at least 2 carbon atoms and an unsaturated hydrocarbon containing at least 3 carbon atoms and about 0.05 to about 1.0 mol of steam per mol of hydrocarbon through an externally heated pyrolytic conversion zone at a temperature of about 900 to about 1500° F. for about 0.05 to about 1.0 second, thereby converting about 3 to about 10 percent of said hydrocarbon reactant to ethylene, passing the product thus formed to an elongated conversion zone, injecting about 0.5 to about 3.0 mols per mol of hydrocarbon of superheated steam at a temperature of about 1500 to about 2000° F. into said elongated conversion zone thereby raising the temperature of the resulting mixture to between about 1300 and about 1700° F. thereby effecting about 6 to 55 percent conversion of said hydrocarbon reactant to ethylene, quenching the product by indirect contact with water to a temperature of about 400 to about 800° F. and passing said product to a fractionation zone wherein it is further cooled to about 200 to about 500° F. and a part of the liquid product is separated therefrom.

10. The process according to claim 9 in which the pressure is maintained at about 1 to about 100 p.s.i.g.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 2,890,256

June 9, 1959

Charles C. King

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, line 49, after "conversion", second occurrence, insert -- zone --; column 6, line 6, for "than 10% the" read -- than about 10% of the --; line 21, after "than" insert --about --; line 72, strike out "first"; column 7, line 1, for "than 10% the" read -- than about 10% of the --; line 34, after "than" insert -- about --.

Signed and sealed this 20th day of October 1959.

(SEAL)

Attest:

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Attesting Officer

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Commissioner of Patents