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1

ABSTRACT OF THE DISCLOSURE

A process for cracking naphtha to increase the production of ethylene wherein a feed, containing in addition to the naphtha, steam and propylene recycled from the cracking process is cracked under the following conditions: a residence time of less than one second, a heat input of 20–40M B.t.u./hr. per sq. ft.; and an outlet gas temperature of at least 1500° F. The propylene comprises up to 25% of the feed, exclusive of steam.

This invention relates generally to the conversion of hydrocarbons and, more particularly, to an improved process for producing ethylene from such hydrocarbons. The process of the invention is characterized by higher conversion rates, lower coking, greater ethylene formation and more economic operation, including less downtime.

In the cracking of a hydrocarbon feed, such as a crude naphtha for the production of ethylene, significant quantities of propylene are unavoidably produced. Where there is no independent market need for propylene, it has been customary to either burn this fraction of the cracked naphtha as fuel gas, or pass it to a hydrogenation unit. A propane product is withdrawn from the latter and this is generally cracked in a separate furnace under conditions controlled to produce a maximum amount of ethylene. The recycling of propylene to the naphtha cracking furnace has been limited to very small quantities or, in most cases, avoided altogether, due to the increased coking in the furnace tubes caused thereby, with the resultant shortening of the furnace run.

The rate of conversion of a naphtha feed in a pyrolytic cracking operation increases with increasing temperature. On the other hand, at the temperatures where at least a satisfactory conversion rate takes place, about 1400° F., the reaction products are subject to polymerization and condensation reaction, which reactions are highly exothermic. A short residence time at reaction temperature is thus preferred. Dilution of the feedstock with steam reduces the hydrocarbon partial pressure and reduces coke formation, and dilution of about 30–50% is common practice. Additionally, steam serves to maintain the linear velocity of the hydrocarbon feed at the maximum for the desired conversion, thereby reducing the formation of carbon and other secondary reactions. Rapid quenching to below about 1000° F., outside the furnace to prevent polymerization reactions, is thus common practice.

The rate of conversion of naphtha indicates how much of the raw material is reacting, but the reaction products contain a variety of compounds ranging from light ends to tars and aromatics and, as noted above, includes substantial quantities of propylene. Selectivity of the reaction to producing the desired product is very important. Thus, any method of cracking which produces more ethylene and less propylene, and which avoids the coking problems noted above, will effect substantial economies.

It is therefore a general object of the present invention to provide a process for conversion of hydrocarbon feeds

2

which is generally more efficient and economical than prior art practices.

Another object of the present invention is to provide a process for producing ethylene, in which total ethylene produced for a given conversion rate is greater than has been heretofore possible.

Yet another object of the invention is to provide a process for increasing the yield of ethylene and decreasing the net propylene without increasing formation of coke.

Still another object of the present invention is to provide a process for producing ethylene by pyrolysis in a cracking furnace wherein substantially all of the propylene produced may be recycled directly to the cracking furnace without rapid coking of the process tubes.

Various other objects and advantages of the invention will become clear in the course of the following description of an embodiment thereof, and the novel features will be particularly pointed out in connection with the appended claims.

As noted hereinabove, the efficiency of a given cracking operation is dependent on a number of factors, principal among which are residence time, outlet gas temperature, heat flux and steam to hydrocarbon ratio. The efficiency of the operation is judged by the ethylene output for a given energy input.

While one skilled in the art might logically expect that a higher energy input (i.e., heat flux), shorter residence time and higher outlet gas temperature would increase the conversion rate, he would also expect thermal efficiency and selectivity to decrease.

The present invention is based, at least in part, on the discovery that with a very substantially increased heat flux and an even more substantial reduction in residence time, the conversion rate increases somewhat, as would be expected, but contrary to expectations, the selectivity to ethylene is also increased. Moreover, it has been discovered that an improved ethylene yield without any increase in coking, and recovery of substantial quantities of benzene, can be achieved by recycling up to 100% of the recovered propylene fraction to the feed. Thus, recycle propylene, in an amount of up to 25% of the combined feed but preferably about 10–20%, will be converted in part to ethylene and in part to benzene. In this manner, ethylene yields may be increased up to 10%, and a substantial quantity of benzene recovered. At the same time, the necessity of a separate hydrogenation unit and cracking furnace for disposal of the propylene fraction is eliminated.

In brief, the process of the invention may be carried out, for example, with a crude naphtha-propylene mixture introduced into a pyrolysis heater, with a residence time of about 0.4 to 0.6 second, as opposed to 2.4 or 2.5 seconds in conventional units. Heat flux to the tubes is about 20–40M B.t.u./hr. per square foot of tube surface, as opposed to 5–15M B.t.u./hr. per square foot conventionally employed. Outlet gas temperature is about 100° F. higher than normal, i.e., 1500° to 1600° F. Thus, according to the invention, residence time is about one-fifth that employed in conventional operations and heat flux is two to six times greater. These changes in operating parameters, however, result in both a more efficient and more economic operation. Selectivity to ethylene at a given conversion rate rises. While more fuel is expended according to the invention, the energy is recoverable to a large extent in heat exchangers following pyrolysis.

Operation in accordance with the invention also yields economics in construction and maintenance of the pyrolysis heater. Thus, whereas a conventional heater may require a 675 foot process coil, a heater for use with the present invention may require only a 200 foot coil, as a result of higher heat flux and shorter residence times involved.

It has been found that, along with increased selectivity to ethylene production, the production of coke precursors is correspondingly decreased. This feature allows a given furnace to run for longer periods. While not wishing to be bound to a particular theory of operation, it is believed that the higher process gas temperature favors primary over secondary reactions, which of course reduces coke-forming reactions. Also, the high temperature favors reaction between coke which is formed and the dilution steam. It is a significant feature of the invention that the recycled propylene stream, which increases ethylene yield and produces benzene, does not appear to encourage coke formation.

Operation at a higher temperature, albeit for longer runs, might be expected to materially shorten tube life due to the adverse effects of thermal cycling from the higher temperature on the microstructure of the tube material. While this might be true if conventional tube cleaning procedures were followed, operation in the 1500° to 1600° F. range according to the invention makes possible the use of a novel tube cleaning method, which in fact lengthens tube life rather than shortening it. This procedure forms another aspect of the present invention, and comprises the following steps: without extinguishing or turning down the burners in the heater, the feed gas and recycle streams are turned off, allowing only steam to pass through the heater. The steam temperature can be allowed to rise somewhat above 1800° F., and the temperature at the skin of the metal tube will be within about 100° F. of this temperature. At 1800° F.+, the steam-coke reactions will take place rapidly and, after a short period, the tubes will be clean. Of course, during this period, the outlet stream is diverted and the water gas produced is either vented or recovered, depending on the economies of the particular installation. When the process tubes are clean, the feed gas and recycle streams are opened and normal operations resumed. The advantage of this type of operation is that the tubes are kept hot on a continuous basis, and the deleterious effects of thermal cycling on tubes and furnace refractories are avoided. With a plurality of heaters operating in parallel, continuous heater operation is possible. Decoking is thus reduced to periodic shut-off of the feed and diversion of the product stream, and thus becomes a routine operation which may be subjected to automatic (i.e., programmed) control.

It is believed that a better understanding of the invention will be gained by referring to the following specific examples thereof, which are intended to be illustrative only and are not to be interpreted in a limiting sense. For purposes of better illustrating the advantages to be gained by the process steps of the present invention, Example I hereinbelow represents operation without recycling of any fraction, Example II illustrates operation wtih recycling of an ethane fraction, and Example III illustrates operation wherein the process of the invention is followed.

Example I

Five thousand pounds per hour of a light naphtha feed containing 90% paraffins and having a 250° F. end point are admixed with 2,500 pounds per hour of steam. The resulting mixture is introduced into a pyrolysis heater having a 250 foot coil (4″ I.D.). The feed is passed through the coil at a residence time of 0.5 second and is heated to a temperature of 1550° F. to effect pyrolysis of the feed. The effluent from the heater was cooled and had the yields as set forth in Table I below.

Example II

The conditions described in Example I were repeated except that the ethane fraction (Example I) was recycled to a separate heater. The effluent from the heater had the yields as set forth in Table I below.

Example III

The conditions described in Example I were repeated except that the fractions (Example II) containing propylene and propane were recycled and admixed with naphtha feed. The effluent from the heater had the yields as set forth in Table I below.

TABLE I.—PYROLYSIS YIELDS (WT. PERCENT)

Examples	I	II	III
Components			
Fuel gas	18.0	18.6	21.2
C_2H_4	32.0	35.6	40.8
C_2H_6	4.5		
C_3H_6	18.0	18.1	
C_3H_8	0.5	0.5	
C_4+	10.0	10.1	11.0
Gasoline	14.5	14.6	22.5
Fuel oil	2.5	2.5	4.5
	100.0	100.0	100.0

As can be seen from the results summarized in Table I, the effluent gas of Example III contained substantially more ethylene than Examples I and II.

As will be obvious to those skilled in the art, various feeds will produce varying amounts of propylene, and the optimum percentage which should be recycled is a matter of individual determination. As a general rule, the recycled propylene should not constitute more than 25% of the combined feed, and 10–20% is the preferred range.

The term "hydrocarbon feed" as used in the appended claims is to be interpreted as including those hydrocarbons which, when subjected to pyrolysis under conditions to produce primarily ethylene, will also contain propylene in the effluent from the pyrolysis heater. Thus, in the pyrolysis of propane to produce ethylene, propylene will also be formed during pyrolysis, whereas substantially little is formed during the pyrolysis of ethane to produce ethylene. Additionally, the term is also to be interpreted as including a mixture of hydrocarbons, such as ethane and propane wherein propylene is included in the reactor effluent where such mixture is pyrolyzed under conditions to produce ethylene.

It is to be understood that various changes in the details, steps, materials and arrangements of parts, which have herein been described to illustrate the invention, may be made by those skilled in the art within the scope of the invention as defined in the appended claims.

What is claimed is:

1. in the production of ethylene from a hydrocarbon feed which upon pyrolysis primarily produces ethylene and some propylene; a process for increasing ethylene selectivity comprising:
   mixing said feed with recycled propylene and dilution steam;
   introducing the resulting mixture into a pyrolysis tube;
   maintaining a heat input to said mixture within the range of about 20,000 to 40,000 b.t.u./hr. per square foot of tube surface, based on outside tube diameters of 3 to 6 inches;
   maintaining said mixture within said tube for no more than one second;
   withdrawing a gaseous effluent from said tube at a temperature of at least about 1500° F.;
   cooling said effluent, including desired ethylene, to a temperature of less than about 1000° F.;
   separating ethylene as product from said effluent; and
   separating propylene from said effluent and recycling at least a portion thereof to said mixing step.

2. The process as defined in claim 1, wherein said mixture is maintained within said pyrolysis tube for from 0.4 to 0.5 second.

3. The process as defined in claim 1, wherein said recycled propylene comprises up to 25% of the feed gas, exclusive of dilution steam.

4. The process as defined in claim 1, and additionally comprising the separation and recovery of benzene from said effluent.

5

5. The process as defined in claim **1**, wherein the temperature of said effluent is from about 1,500° F. to 1,650° F. when withdrawn from said tube.

6. The process as defined in claim **1**, wherein naphtha is the hydrocarbon feed.

7. In the production of ethylene from a hydrocarbon feed which upon pyrolysis primarily produces ethylene and some propylene a continuous process for increasing ethylene selectivity comprising:

mixing said feed with dilution steam and recycled propylene;

introducing the resulting mixture into a pyrolysis tube in a pyrolysis heater;

maintaining a sufficient heat flux around said tube to provide about 20,000 to 40,000 b.t.u./hr. per square foot based on outside tube diameters of 3 to 6 inches;

maintaining said mixture within said tube for about 0.4 to 0.5 second;

withdrawing from said tube a gaseous effluent, including desired products, at a temperature of about 1,500° F. to 1,650° F.;

cooling said effluent to a temperature of less than about 1,000° F.;

separating and recovering in separate fraction, ethylene, propylene and benzene from said effluent; and

recycling at least a portion of said propylene to said mixing step.

8. The continuous process as defined in claim **7**, and additionally comprising:

periodically discontinuing the flow of said feed and said recycle gas to said tube while maintaining the flow of said steam;

maintaining within said tube a temperature of at least 1,800° F.;

diverting the effluent steam from further process steps;

continuing the passage of steam through said tube until the same is cleaned of coke and any other accretions; and

resuming the flow of said feed and said recycle gas to said tube.

6

9. In the production of ethylene from a hydrocarbon feed which upon pyrolysis primarily produces ethylene and some propylene; a continuous process for increasing ethylene selectivity comprising:

mixing said feed with up to 25% by weight of propylene;

maintaining a sufficient heat flux around said tube to provide from 20,000 to 40,000 b.t.u./hr. per square foot based on outside tube diameters of 3 to 6 inches;

passing the mixture through said tube in a maximum time of one second; and

withdrawing a gaseous effluent from said tube at a temperature of at least 1500° F.

10. The process as defined in claim **9**, wherein said propylene is recycled gas, and comprises from 10–20% by weight of the hydrocarbon feed-propylene mixture.

11. The process as defined in claim **9**, and additionally comprising the separation and recovery of ethylene, propylene and benzene as separate fractions, and recycling at least a potrion of the propylene fraction.

References Cited

UNITED STATES PATENTS

2,123,799	7/1938	Podbielniak	260—683
2,498,806	2/1950	Hachmuth	260—683
2,537,079	1/1951	Nicolai et al.	134—39
2,620,286	12/1952	Shaw	134—2
2,904,502	9/1959	Shapleigh	260—683
2,917,564	12/1959	Pollock	260—683

FOREIGN PATENTS

457,560   6/1949   Canada.

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