

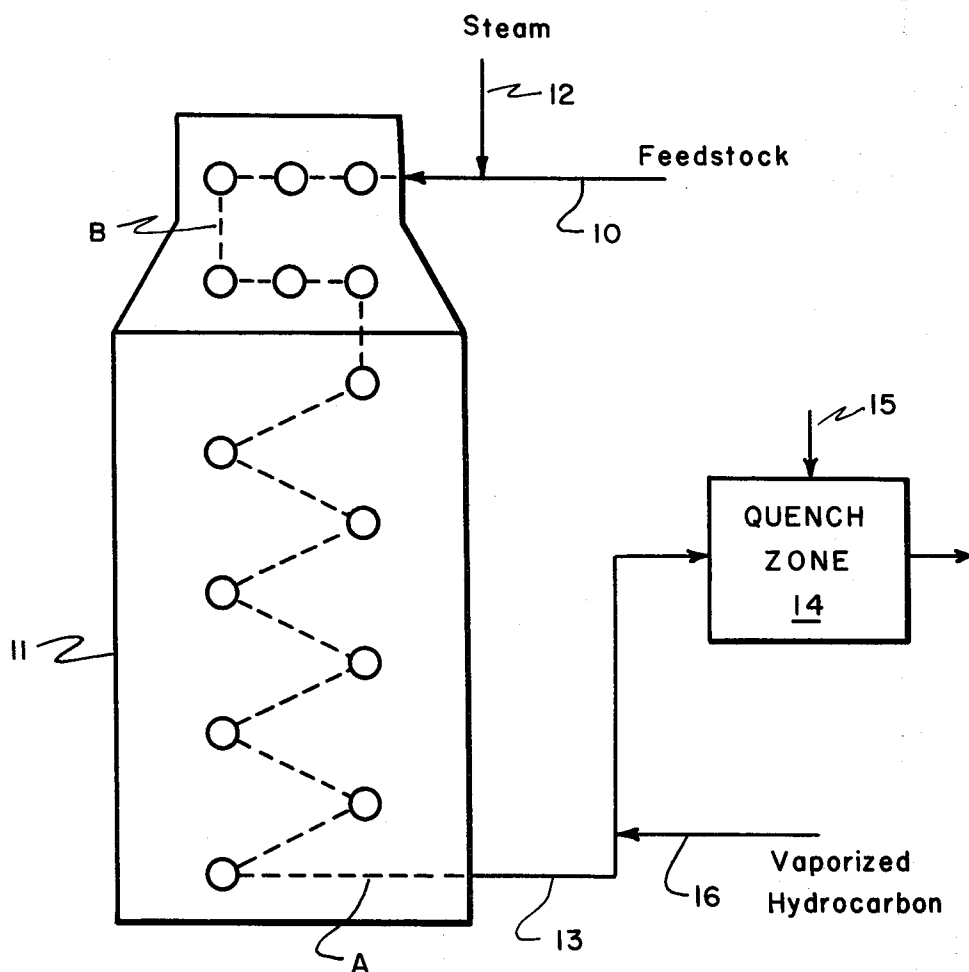
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3,579,438

THERMAL CRACKING

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3,579,438

THERMAL CRACKING

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Continuation-in-part of application Ser. No. 640,118,
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No. 30,252

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15 Claims

ABSTRACT OF THE DISCLOSURE

A process for thermally cracking a normally liquid hydrocarbon in a tubular reactor wherein C₄ and higher hydrocarbons are injected prior to the quench zone.

RELATED APPLICATION

This application is a continuation-in-part of applicant's copending application Ser. No. 640,118 filed May 22, 1967 and now abandoned.

BACKGROUND OF THE INVENTION

The present invention relates to the thermal cracking of normally liquid hydrocarbons in tubular reactors.

The thermal cracking of normally liquid hydrocarbons in tubular cracking furnaces is a well known process for the production of a wide variety of hydrocarbon products. Among such products may be mentioned the saturated aliphatic compounds of which the paraffins methane, propane, butanes, pentanes, hexanes and higher homologues are examples; the mono-olefins, of which ethylene, propylene, butylenes, amylenes, hexylenes and higher homologues are examples; the diolefins of which the conjugated diolefins, butadiene, isoprene, piperylene, hexadiene and others are examples; the acetylenes, of which acetylene, vinylacetylene, are examples. There may be also produced a variety of aromatic hydrocarbons containing only nuclear unsaturation such as benzene, toluene, xylenes, naphthalenes, anthracene, and others; as well as aromatic hydrocarbons containing other than nuclear unsaturation of which styrene, methyl styrenes, indene, methyl indenenes, phenyl acetylene, readily heat polymerizable unsaturated aromatic hydrocarbons boiling above 210° C. and others are examples. Various alicyclic hydrocarbons may also be produced of which cyclopentadiene, methyl cyclopentadiene, cyclohexene, cyclohexadiene, alkyl cyclohexadienes, and others are examples. Considerable quantities of hydrogen and carbon may also be produced depending upon the severity of the pyrolysis.

All of the above-mentioned compounds, as well as others may be produced under a given set of conditions. However the production of all of these compounds is not equally favored by any one set of conditions. It is due to this that studies are constantly being made in order to alter the cracking pattern so as to produce a more valuable cracked product. Of course it is obvious that the value of the various constituents of the cracked product vary from time to time and thus a product rich in aromatics might be more valuable at one time than one rich in olefins while a cracked product rich in olefins might be more valuable at other times.

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The tubular reactors used in the thermal cracking of normally liquid hydrocarbons are well known to those skilled in the art and are very well described in the literature, thus no detailed description of these furnaces need be given here. However, it might be generally pointed out that the tubular cracking furnaces utilized have length to diameter ratios which are generally above 100:1 and that these furnaces usually have both a convection section and a radiant section. Usually not too much cracking takes place in the convection section and such section is for the purpose of preheating and/or vaporizing the mixture of normally liquid hydrocarbon and diluent prior to its entry into the radiant section. The feed to furnaces having only a radiant section is usually preheated and/or vaporized in a separate apparatus. U.S. Patents 3,182,638, 2,618,688, 2,917,564 and 2,340,814 describe some of the tubular cracking furnaces used for thermally cracking of normally liquid hydrocarbons. Regardless of the configuration of the tubular cracking furnaces, one thing they have in common are burners or some other means to heat the reactants as they pass through the furnace tubes. These burners or heating means utilize some source of energy such as fuel gas or electricity and thus, in addition to the cracking pattern, another factor which effects the economics of a particular process is the amount of energy required to produce a given amount of cracked product.

The thermal cracking of normally liquid hydrocarbons is generally carried out in the presence of an inert diluent, preferably steam. The inert diluent is added in order to reduce the partial pressure of the feed in the conversion zone and thus allow 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 to a maximum for the desired conversion thereby reducing the possibility of excess carbon formation. The amount of inert diluent added will generally be from about 0.05 to 4.0 parts by weight per part by weight of normally liquid hydrocarbon charged to the cracking furnace. Preferably about 0.05 to about 1.5 pounds of diluent per pound of feed is added.

The thermal cracking of normally liquid hydrocarbons is carried out under various conditions of time, temperature, and pressure and the particular conditions used in any one situation will depend on such factors as furnace design and the desired distribution of products in the cracked effluent. Generally the temperature will be within the range of 1200° F. to about 1800° F. with pressures from about atmospheric to about 1,000 p.s.i.g. However, it is preferred to use temperatures of about 1300° F. to 1600° F. with pressures of from about 10 to 160 p.s.i.g. Residence time in the cracking zone is generally not greater than about 2.0 seconds if significant formation of undesirable by-products is to be avoided and may be as low as 0.01 second or lower. In order to avoid secondary reactions which would consume some of the valuable products produced in the cracking furnace, the effluent from the furnace is quenched in a quench zone as quickly as possible to temperatures below about 1200° F., generally below about 900° F. There are many quenching techniques known in prior art and these may involve the use of a single quench vessel or may involve the use of several vessels. Various materials may be used for quench-

ing such as oil, water, emulsions of oil and water, and the like. Quenching may also be accomplished by the use of indirect heat exchange. U.S. Patents 2,928,886, 2,608,527, and 2,899,475 are illustrative of quench techniques used in thermal cracking operations. Since the purpose of quenching is to cool the effluent of the cracking zone, the quench materials are naturally at much lower temperatures than the effluent, i.e., on the order of 250 to 700° F., and are almost always in liquid form, although steam is sometimes used. The amount of quench material utilized in quenching the effluent of a thermal cracking zone is usually at least 1.5 times as great as the weight of the normally liquid hydrocarbon feed to the cracking furnace, but is usually from 2.0 to 10.0 times as great.

SUMMARY

It is an object of the present invention to provide an improved thermal cracking process. It is a further object of the present invention to provide a process for the cracking of normally liquid hydrocarbons whereby the cracking pattern may be altered. It is also an object of the present invention to provide a process whereby the amount of material processed may be increased without any increase in the amount of energy required for cracking. Additional objects will become apparent from the following description of the present invention.

These and other objects are accomplished by the present invention which in one of its embodiments in an improvement in a process for the thermal cracking of a normally liquid hydrocarbon feedstock in a tubular reactor wherein the effluent from said tubular reactor is quenched in a quench zone, which improvement comprises injecting a vaporized hydrocarbon having at least 4 carbon atoms into the reactants at a point which lies beyond the first ninety percent of length of said tubular reactor and prior to said quench zone, said vaporized hydrocarbon being of different composition from said effluent, and under conditions at which the vaporized hydrocarbon reacts with the effluent to alter the cracking pattern thereof. The drawing is illustrative of one embodiment of the present invention wherein the vaporized hydrocarbon is injected between the outlet of a tubular reactor and the quench zone.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention is applicable to the thermal cracking of practically any normally liquid hydrocarbon feedstock. Generally the normally liquid feedstocks which are subjected to thermal cracking are comprised of mixtures of several hundred and sometimes thousands of different compounds, and therefore these feedstocks will have not a single boiling point but a boiling point ranging from an initial boiling point to a terminal boiling point. Those normally liquid hydrocarbons to which the present invention is most applicable are generally those having terminal normal boiling points above 200° F. Included in the normally liquid hydrocarbon feedstocks useful in the present invention are naphtha, natural crudes, fuel oils, gas oils, kerosene, gasoline, petroleum condensates, reduced crudes, residual oils, residuums, coal tar fractions, shale oil, and the like. Preferably the present invention is applied to petroleum-derived feedstocks having normal boiling ranges substantially within from about 100° F. to about 1200° F. Naphtha and petroleum condensates are preferred normally liquid hydrocarbon feedstocks with petroleum condensates being especially preferred. These petroleum condensates may be characterized by boiling point ranges substantially within 100° F. and 800° F. as determined by A.S.T.M. distillation. The present invention is not to be construed as being limited to the cracking of a feed consisting only of normally liquid hydrocarbons since coke inhibitors, compounds to modify cracking patterns, and the like may be present. Also a

great many processes have minor amounts of normally gaseous hydrocarbons such as butanes which may be recycled to the cracking furnaces with the normally liquid hydrocarbon feed and the present invention is to be construed as covering such processes.

Reference is now made to the drawing which represents one embodiment of the present invention in order to more fully describe the present invention. A normally liquid hydrocarbon feedstock is passed through line 10 to cracking furnace 11. Before entering cracking furnace 11, the feedstock is mixed with steam flowing through line 12. The effluent of cracking furnace 11 comprising cracked products exits through line 13 and is passed to quench zone 14 wherein quench material 15 is used to quench the hot cracked gas to the desired temperature. However, before the cracked gases are quenched, a vaporized hydrocarbon having at least 4 carbon atoms is injected through line 16 into the cracked gases under conditions at which further cracking will take place in accordance with the present invention. By the injection of this vaporized hydrocarbon having at least 4 carbon atoms, differing in composition from the effluent and capable of further cracking, it has been found that the cracking pattern can be materially altered and further, that more material may be processed for a given amount of fuel gas or other source of energy used in heating the cracking furnaces.

As was pointed out above, the drawing is merely illustrative of one embodiment of the present invention and the present process is not to be construed as limited thereto. For example, although the vaporized hydrocarbon is shown as being injected into the reactants at a point between cracking furnace 11 and quench zone 14 it is within the scope of the present invention to inject this vaporized hydrocarbon at a point within the cracking furnace 11 such as at point A. However when the injection of the vaporized hydrocarbon is made within a cracking furnace, it should be at a point within about the last ten percent of length of the tubes of the cracking furnace, i.e., beyond the first ninety percent of a length of the tubes. The injection of vaporized hydrocarbon in accordance with the present invention may be made by any convenient means such as by merely providing a T in the line having the reactants flowing therethrough. The vaporized hydrocarbon utilized in the present invention should have at least 4 carbon atoms, differ in composition from the reactant effluent and be capable of further cracking. It may be the same as the normally liquid hydrocarbon used as the feedstock for the cracking furnace. If the hydrocarbon to be injected in accordance with the present invention is not the same as the feedstock, then this hydrocarbon to be injected may be derived from various sources such as from the effluent of the quench zone of the present invention so long as such hydrocarbon stream is capable of further cracking. For example, suitable streams include a C₄ stream containing mainly monoolefins such as butene-1, isobutene, cis and trans butene-2, and butane, which has been separated from the effluent of a cracking process. Or hydrocarbons in the C₉ to 400° F. boiling range may be separated from the effluent of a cracking operation and utilized as the injected hydrocarbon in accordance with the present invention. Another example of a stream useful as the injected hydrocarbons is one containing mainly paraffins such as obtained in a hydrocarbon processing plant in the separation of aromatics and non-aromatics. Especially when it is desired to change the cracking pattern to yield more aromatics, it is preferred to use a normally liquid hydrocarbon as the injected hydrocarbon such as those having at least ninety percent by weight boiling in the range of 120° F. to 1,000° F.

The hydrocarbon having at least four carbon atoms may be injected in accordance with the present invention either alone or it may be admixed with an inert diluent such as steam prior to the injection. If a diluent is used, it generally should be present in amounts of from about 0.01 to 5.0 parts by weight per part of the vaporized, injected

hydrocarbon. It will frequently be desirable to inject the same normally liquid hydrocarbon-steam mixture as is used for the feed to the tubular cracking furnace and in such cases a convenient source of the material to be injected is the convection section of the cracking furnace itself. This is, of course, assuming that the cracking furnace utilized has a convection section, most of which do. For example, referring to the drawing, a mixture of steam and normally liquid hydrocarbon feedstock could be withdrawn from the convection section of cracking furnace 11 at point B and injected into the reactance prior to the entry to quench zone 14 in accordance with the present invention. The point at which such a mixture of steam and normally liquid hydrocarbons would be withdrawn from the convection section of a furnace will of course vary from furnace to furnace but it would be at a point where the temperature of the hydrocarbon-steam mixture is suitable for injection in accordance with the present invention, i.e. the temperature is sufficiently high to result in further cracking and alteration of the cracking pattern. Use of the convection section as the heater and/or vaporizer for the hydrocarbon to be injected is also possible where the vaporized hydrocarbon alone is to be injected, i.e., injected without being mixed with steam. For example, if the steam required for cracking should be mixed with the normally liquid hydrocarbon feedstock after point B in the drawing instead of being mixed prior to entry to the convection section, then a normally liquid hydrocarbon could be withdrawn from point B and injected in accordance with the present invention.

In order that the cracking pattern be altered the temperature of the vaporized hydrocarbon to be injected in accordance with the present invention should be between about 750° F. and 1300° F., preferably about 900 to 1100° F. Further, the weight ratio of the amount of normally liquid hydrocarbon being cracked to the amount of vaporized hydrocarbon being cracked to the amount of vaporized hydrocarbon being injected should be from about 2:1 to 30:1 but is preferably within the range from about 3:1 to 16:1. In the cases mentioned above wherein the hydrocarbon to be injected is withdrawn from the convection section of the cracking furnace, then in the determination of the above ratio the amount of hydrocarbon being cracked is of course only the amount which is left after the withdrawal of the portion to be injected and not the total amount of normally liquid hydrocarbon feedstock charged to the entry of the cracking furnace.

The following example is given to illustrate the present invention but is not to be taken in a limiting sense.

EXAMPLE

Several runs were made in order to thermally crack a normally liquid hydrocarbon in the presence of about 0.25 pound of steam per pound of hydrocarbon feed. The feed consisted of a petroleum condensate having an initial boiling point of about 100° F. and a terminal boiling point of about 750° F. as determined by A.S.T.M. Test No. D-86. The equipment used consisted of a tubular reactor having a length to diameter ratio of about 340:1. The mixture of petroleum condensate and steam was preheated to a temperature of about 932° F. before entering the tubular reactor, and the outlet temperature of the reactor was maintained at about 1475° F. in all of the runs. The outlet pressure was about 40 p.s.i.g. in all of the runs with the liquid hourly space velocity being maintained at about 260 lbs./hr.-ft.³ in all of the runs. In all of the runs except Run No. 1, the control run, vaporized petroleum condensate at a temperature of about 932° F. was injected in varying amounts to the effluent of the tubular reactor prior to its being quenched in accordance with the present invention. The injected petroleum condensate was injected by merely providing a T in the effluent line of the tubular reactor. The yield of various products in pound per 100 pounds of material processed (feedstock+injected material) is illustrated in Table I.

TABLE I.—YIELD OF PRODUCTS¹

Run Number	1	2	3	4
Pounds injected per pound feed	0	0.33	0.226	0.113
Weight ratio, hydrocarbon feed to injected material		3.03:1	4.42:1	8.85:1
Ethylene	20.7	13.9	14.8	17.6
Propylene	9.9	7.6	8.4	8.9
Butadiene	2.4	1.6	1.9	1.8
Butenes	2.6	2.0	2.2	2.2
Total C ₂ —C ₄	35.6	25.1	27.3	30.5
Benzene	7.7	12.2	11.1	13.7
Toluene	5.7	6.8	6.3	6.3
Styrene	1.8	2.0	1.9	1.7
C ₆ —C ₈ unsaturates	5.2	4.3	4.7	2.5
Ethylbenzene	0.2	0.5	0.5	0.3
Xylenes	1.4	3.2	2.8	2.1
Total C ₆ —C ₈	22.0	29.0	27.3	26.6

¹ Pounds of product per 100 pounds of hydrocarbon material processed.

As may be seen from Table I, from about 11.3% to 34% more material was processed in Runs 2, 3, and 4 than in Run 1 even though the energy requirements for heating the tubular reactor was the same in all the runs. Further, it is seen that the injection of the petroleum condensate caused a change in the cracking pattern so that substantially more aromatics were produced and less non-aromatics were produced than in Run 1. Irrespective of the change in cracking pattern induced by the injected hydrocarbon, more material can be processed per unit of energy expended in supplying heat to the cracking furnaces.

The composition of the hydrocarbon being injected does affect how the cracking pattern will change. In the above example the pattern changed so as to favor aromatic production but the injection of a stream comprising mainly C₄ mono-olefins will generally not favor an increase in the aromatics produced. Further, when the injected hydrocarbon is mixed with steam prior to its injection to the reactant, generally less aromatics are produced than when the steam is not used.

What is claimed is:

1. In a process for the thermal cracking of normally liquid hydrocarbon feedstock in a tubular reactor wherein the effluent from said tubular reactor is quenched in a quench zone, the improvement which comprises injecting a vaporized hydrocarbon having at least 4 carbon atoms at a point which lies beyond the first ninety percent of length of said tubular reactor and prior to said quench zone, said vaporized hydrocarbon being of different composition than said effluent and subject to cracking under conditions of said process.

2. The process of claim 1 wherein the said vaporized hydrocarbon is in mixture with an inert diluent.

3. The process of claim 1 wherein the weight ratio of said normally liquid hydrocarbon feedstock to said vaporized hydrocarbon is from about 2:1 to 30:1.

4. The process of claim 1 wherein the temperature of said vaporized hydrocarbon is between 750 and 1300° F.

5. The process of claim 1 wherein said vaporized hydrocarbon is a normally liquid hydrocarbon.

6. The process of claim 1 wherein said vaporized hydrocarbon is the same as said normally liquid hydrocarbon feedstock.

7. The process of claim 1 wherein said normally liquid hydrocarbon is a petroleum condensate.

8. The process of claim 1 wherein said normally liquid hydrocarbon is naphtha.

9. The process of claim 1 wherein said thermal cracking is carried out at temperatures of from about 1300° F. to 1600° F. in the presence of from about 0.05 to 4.0 part by weight of steam per part by weight of normally liquid hydrocarbon feedstock and wherein said vaporized hydrocarbon is a normally liquid hydrocarbon having at least ninety percent by weight boiling in the range of 120° F. to 1000° F.

10. The process of claim 9 wherein said vaporized hy-

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drocarbon is injected at a point between the outlet end of said tubular reactor and said quench zone.

11. The process of claim 9 wherein said vaporized hydrocarbon is at a temperature between about 900 and 1100° F. and wherein the weight ratio of said normally liquid hydrocarbon feedstock to said vaporized hydrocarbon is from about 3:1 to 16:1.

12. The process of claim 11 wherein said normally liquid hydrocarbon feedstock is a petroleum condensate having a boiling range substantially within 100° F. and 800° F.

13. The process of claim 11 wherein said vaporized hydrocarbon is the same as said normally liquid hydrocarbon feedstock.

14. The process of claim 13 wherein said vaporized hydrocarbon is in admixture with from about 0.01 to 5.0

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parts by weight of steam per part by weight of vaporized hydrocarbon.

15. The process of claim 14 wherein said tubular reactor has both a convection section and a cracking section and wherein the mixture of vaporized hydrocarbon and steam is withdrawn from said convection section.

References Cited

UNITED STATES PATENTS

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	3,365,387	1/1968	Cahn et al.	208—132

HERBERT LEVINE, Primary Examiner

U.S. Cl. X.R.

208—48Q, 95, 132

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,579,438 Dated May 18, 1971

Inventor(s) Carl M. Cruse

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 3, Line 28, after the word "embodiments" change "in" to --is--.

Column 5, Line 11, after the word "the" change "reactance" to --reactants--.

Column 5, Line 37 and 38 should be cancelled as follows:
"cracked to the amount of vaporized hydrocarbon being"

Column 5, Line 38, after the word "being" change "inected" to --injected--.

Column 6, Claim 6, Line 2, after the word "liquid" change "hydrocarbon" to --hydrocarbon--.

Signed and sealed this 28th day of December 1971.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Acting Commissioner of Patents