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HYDROCARBON PYROLYSIS

Mou Neng M. Lo, Philadelphia, Pa., assignor to Mobil Oil Corporation, a corporation of New York
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16 Claims

ABSTRACT OF THE DISCLOSURE

High temperature hydrocarbon conversion reactions displaying a strong tendency toward carbon formation, as exemplified by the thermal cracking of hydrocarbons, are carried out in a reaction chamber constructed of or lined with a metal-ceramic material containing particles of a catalytically inert, refractory solid material (e.g., aluminum oxide) dispersed in chromium to minimize the deposition of carbon on equipment surfaces and to substantially eliminate the carburization of such surfaces.

BACKGROUND OF THE INVENTION

Field of the invention

The present invention relates to the conversion of hydrocarbons at elevated temperatures and more particularly to the vapor phase cracking of hydrocarbons into products having fewer carbon atoms per molecule than the material charged and/or a higher content of unsaturated hydrocarbons than the charge. In one specific embodiment, it is concerned with an improved procedure for the production of ethylene in high yields by the non-catalytic cracking of hydrocarbons at relatively high temperatures and extremely short reaction times.

Description of the prior art

The thermal cracking of hydrocarbons derived from petroleum sources has long been practiced for a variety of purposes including the conversion of heavy feedstocks into more volatile liquid hydrocarbons suitable for use as motor fuel components and more recently for the production of olefins and aromatic hydrocarbons as raw materials for the chemical industry. In thermal cracking, coke formation has always been a problem as carbon deposits inside the cracking tubes or coils reduce the heat transfer through the tube walls and also restrict the flow of the reaction mixture through the tubes with a consequently increasing pressure drop until the equipment is plugged. There is usually a concomitant carburizing action or destructive attack on the internal surfaces of the cracking tubes which weakens the metal. In addition, the conversion of part of the charge stock into carbon reduces the yield of the desired products.

The various expedients adopted for handling this coking problem have usually involved compromises which include some undesirable features. Frequent decoking of the equipment reduces the amount of productive or on-stream time; and frequent shutdowns for the replacement of badly carburized tubes have the same effect. Lowering the reaction severity, e.g., by lowering the reaction temperature, results in lower product yields along with lower coke formation. Increasing the diameter of the cracking tubes or chamber to reduce the resistance to gas flow created by coke deposits therein is generally undesirable for reactions involving a high heat flux and short residence time in that it reduces the surface area available for indirect heat transfer at any given charging rate and it does not cure the sharp decrease in the heat transfer coefficient as carbon deposits accumulate on the heating surfaces.

The present invention is directed at minimizing coke formation in hydrocarbon conversion reactions by an im-

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proved procedure which does not involve accepting undesirable compromises in product yield, on-stream time and corrosion of equipment.

SUMMARY OF THE INVENTION

The present invention is a process for the conversion of hydrocarbons characterized by the vapor phase reaction of a hydrocarbon charge under high temperature conversion conditions while confined within a reaction zone boundary surface of metal-ceramic material comprising particles of a catalytically inert, refractory solid material dispersed in chromium. Thus, the reaction vessel is constructed of said metal-ceramic material or the surfaces of the vessel exposed to the hot reaction mixture are lined or clad with that material which contains a refractory solid substance having no substantial tendency toward catalyzing the formation of carbon in the reaction.

Certain embodiments of the invention are concerned with the thermal cracking of hydrocarbon feedstocks, and it has particular application to the production of ethylene by the noncatalytic cracking or normally gaseous hydrocarbons containing at least 2 carbon atoms per molecule. Other aspects of the invention relate to indirectly heating endothermic conversion reactions by transferring the heat through the metal-ceramic material to the reaction mixture; the preferred constituents and proportions thereof in said metal-ceramic material as well as preferred reaction temperatures. Other features, benefits and advantages of the invention will be apparent to those skilled in the art upon consideration of the following disclosure.

Although the procedure of the present invention is particularly useful in the thermal cracking of hydrocarbons, it is also applicable to a wide variety of hydrocarbon conversion reactions at elevated temperatures, especially where problems are encountered with carburization or coke deposition. For example, it is contemplated that this technique can be used to advantage in thermal hydrodealkylation reaction, such as the treatment of toluene or methylnaphthalenes with hydrogen at elevated pressures and temperatures of the order of 1200–1400° F. to form benzene or naphthalene, wherein the rapid and destructive corrosion of reactor surfaces is often a source of trouble. In the case of noncatalytic or thermal cracking, a wide variety of feedstocks may be processed according to the new method, as exemplified by ethane, propane, propylene, butane, isobutane, butylene and its isomers, the butadienes, pentane, cyclopentane, other C₅ saturated and olefinic hydrocarbons, naphthas, kerosines, gasolines, gas oils and heavier hydrocarbon stocks which can be vaporized for thermal cracking, as well as naphthenic and aromatic hydrocarbons.

Varying reaction severities may be utilized in the practice of the present invention. For example, relatively low cracking temperatures in the range of about 1300 to 1500° F. may be employed with residence times of about 0.1 to 5 seconds. However, it is usually preferable to utilize considerably higher temperatures in the range of about 1600 to 7850° F. with residence times of about 5 to 200 milliseconds (0.005 to 0.200 second) to obtain maximum yields when thermally cracking hydrocarbons at atmospheric or slightly elevated reaction pressures to form olefins. In producing acetylenes, higher temperatures ranging up to about 2600° F. are recommended. The tube or reactor temperatures are usually about 50 to 300° higher than the aforesaid temperatures of the reaction mixture.

Certain metal-ceramic materials are employed as the confining or boundary surfaces of the reaction zone in the present process. The reaction vessel or tubes may be constructed from these materials or made of conventional construction materials (e.g., metals and alloys) which are clad, lined or coated with one of the metal-ceramic materials on the equipment surfaces which are

exposed to the hot reaction mixture. By reason of their low coking tendencies, the metal-ceramic materials described herein are particularly well adapted for operations employing a high heat flux and low residence time in reactors wherein the reaction zone may desirably have a relatively narrow cross section as in the case of small diameter tubes or narrow slots of annular configuration.

Suitable metal-ceramic compositions contains an inert refractory substance dispersed as solid particles in chromium metal. The chromium apparently provides a continuous metal matrix for the dispersed particles which are of a refractory nature and thus not subject to decomposition at the elevated temperatures involved in the present invention, as the dispersed phase component of the metal-ceramic material, excellent results are obtainable with finely divided aluminum oxide, and silicon dioxide or silicon carbide may be used as well as other refractory substances or mixtures thereof suitable for sintering with metallic chromium and which are also substantially devoid of deleterious catalytic activity relative to the particular type of hydrocarbon conversion taking place as well as any associated side reactions, especially those involving carbon formation. Thus, in the case of a thermal cracking process, the dispersed component should be free of any significant catalytic effect that promotes either carbon formation or the polymerization of olefins. The refractory material may constitute about 5 to 30% or even more of the total weight of the metal-ceramic composition so long as the chromium content is still sufficient to provide a continuous chromium phase or matrix; and in the case of aluminum oxide, a content of between about 15 and 30% is usually preferable.

The entire metal-ceramic composition should be substantially free of any impurities or minor constituents which are capable of inducing the aforesaid undesired catalytic effects to any significant extent. For example, it is considered detrimental in many thermal cracking processes, especially those involving extremely high reactor wall temperatures, for the metal-ceramic material to contain any significant amounts of metals of Group VIII of the Periodic Table (e.g., iron, nickel and cobalt) and their compounds in view of the indications herein that these substances exert a pronounced catalytic effect upon the reaction mixture.

One example of a suitable metal-ceramic material is Haynes® metal-ceramic LT-1 and excellent results were obtained in the specific reactions described hereinafter using LT-1 reaction tubes. This material contains 23 parts by weight of aluminum oxide in the form of minute particles of colloidal size uniformly dispersed in 77 parts of chromium metal. It has a coefficient of thermal expansion close to that of Type 446 stainless steel; hence, the latter may serve as a substrate for some purposes. In addition to its desirable lack of catalytic activity, this chromium-alumina composition has very good chemical and physical properties, particularly at extremely high temperatures. Its weight to strength ratio is relatively high and the resistance to thermal shock is better than that of ceramic structures. It displays high mechanical strength at elevated temperatures, as exemplified by its ultimate tensile strength of 11,700 p.s.i. at 2000° F.; and it retains sufficient strength for some purposes in continuous operations at 2800° F. where most metals fail rapidly. This material has a melting point of approximately 3270° F. and it possesses high resistance to abrasion and erosion as well as corrosion by many severely corrosive compounds. Also, it has a relatively high thermal conductivity approximating that of cast iron—a highly desirable factor in high heat flux operations.

The metal-ceramic materials and structural elements utilized in this invention may be compounded and formed by various known techniques, such as slip casting or casting and sintering, and any necessary or desirable further shaping may be accomplished by machining with tungsten carbide-tipped tools, drilling with "high speed" alloy

steel drills and finish grinding using the customary precautions for working hard and brittle metal alloys.

DESCRIPTION OF SPECIFIC EMBODIMENTS

The advantages of the present procedure are apparent upon reference to the data set forth in the table hereinafter which lists some of the operating conditions and results obtained in extended cracking runs employing several tubes of different chemical composition for the cracking of a mixture of propane and propylene in an approximate 80:20 weight ratio under generally comparable conditions to produce ethylene. These operations were conducted at atmospheric pressure with the charge gas admitted at ambient temperature into 14-inch long cracking tubes of small diameter. The midsection of the reactor tube was enclosed within a 40-kilowatt induction heater and a 6-inch length of the cracking tube was heated to provide tube wall temperatures in the 1800–1850° F. range by radiation from the metal sleeve in the induction heater which was adjusted to maintain a constant internal temperature of approximately 2050° F. The reaction products left the cracking zone at temperatures in the 1550–1700° F. range and were substantially instantaneously quenched to a temperature below the cracking level while flowing through unjacketed tubes cooled by normal air circulation.

THERMAL CRACKING OF PROPANE-PROPYLENE MIXTURE

Cracking tube	Alloy X ¹	Stainless steel type 304	Metal-ceramic 77% Cr, 23% Al ₂ O ₃
Internal diam., in.	0.18	0.18	0.28
External diam., in.	0.25	0.25	0.50
Charge rate, s.c.f./hr.	1.5	1.5	2.85
Residence time, milliseconds	53	53	68
Cracked products:			
C ₂ H ₄ , initial wt. percent	43.2	48.9	43.4
C ₂ H ₄ , final wt. percent	45.4	44.9	39.6
Pressure drop in tube:			
Initial, in. water	0.4	0.3	0.2
Final, in. water	8.0	7.0	1.3
Run duration, hrs.	14	17	139

¹ A heat-resistant metal alloy commonly used in naphtha cracking tubes and containing essentially 20% chromium, 32% nickel and 47% by weight of iron.

From the tabulated data, it is clearly evident that strikingly superior results were obtained in employing a metal-ceramic reaction tube according to the present invention. While good yields of ethylene were obtained in the runs in the two ferrous alloy tubes designated as alloy X and Type 304, it was necessary to terminate these runs after relatively short periods due to the rapid fouling of the tubes with heavy coke deposits as indicated by the twenty-fold increases in the pressure drop through the tubes and further confirmed by observation upon disassembling the apparatus at the end of the runs. The rapid carbon accumulation is attributed to the catalytic effect of the nickel and iron contents of these tubes. In sharp contrast with this, the duration of the cracking run in the metal-ceramic tube was about ten times as long while also providing good yields, and total coke depth position over this prolonged run was still only a small fraction of that occurring in the metal alloy tubes as evidenced by the relatively small final pressure drop in the metal-ceramic reaction tube. The performance of the metal-ceramic tube was a distinct surprise in view of the possibility of a rapid formation of chromium carbide leading to early tube failure.

Following the aforesaid run, heavy carbon deposition was deliberately induced in the interior of the same metal-ceramic reactor tube by cracking undiluted propylene which has a greater proclivity toward coking than propane at a drastically reduced feed rate. After this metal-ceramic tube was decoked in conventional manner by burning out the carbon deposits, it was then subjected to a second cracking cycle under substantially the same conditions, and the pressure drop increased to only 1.5 inches of water during an operating period of 130 hours. For com-

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parative purposes, the alloy X reaction tube was decoked after the 14-hour first cycle, and another cracking run started under similar conditions but this second cycle was terminated after only 2 hours due to an excessive pressure drop. Both the alloy X and metal-ceramic tubes were cut or broken in the midsection; and a microscopic examination of the cross sections of the tube walls disclosed heavy carburization of the alloy X tube but no evidence whatsoever of such attack in the metal-ceramic tube wall.

Extensive operations involving repeated cracking-decoking cycles of various lengths and two different charge stocks were carried out according to the present procedure in a 36-inch long metal-ceramic tube (77% chromium=23% alumina) of 0.28" internal and 0.5" external diameter with a 12-inch midsection of the tube length enclosed within a furnace operating at 2100° F. The wall temperatures of the cracking section of the tube were in the 1850–2000° F. temperature range and residence times in the cracking section ranged from 60 to 80 milliseconds. When propane-propylene mixtures containing about 20% by weight of propylene were cracked at these higher temperatures, the initial ethylene yield was typically 42 to 44% by weight of the total reaction products and the runs were usually terminated when the ethylene yield dropped to the level of about 35% as the result of the decreased heat transfer and consequent decreased reaction severity produced by the accumulation of a thin layer of coke inside the reaction tube. Even in runs lasting more than 100 hours, the increase in pressure drop was an acceptable doubling or tripling of the initial value. A more heavily coking charge in the form of 100% propylene was employed in five of these cracking runs with a typical duration of 25 hours, and the initial conversion of propylene was usually about 72% in producing an ethylene yield of the order of 32% with a gradual decrease to a conversion of 55% and ethylene yield of 22% by the end of the run. No run in this series was terminated by reason of the development of an excessive pressure drop in the reaction tube. After 17 cracking-decoking cycles totaling 831.4 hours of exposure to hydrocarbons, there were no indications that the rate of coke buildup in the 17th cycle was higher than that in the first cycle in the metal-ceramic tube. Nor was there evidence of attack on the tube wall material.

In marked contrast with the above results, it was necessary to discontinue a series of cracking-decoking cycles in a 36-inch alloy X reactor tube under comparable conditions as the on-stream or cracking cycle time decreased from 17 hours initially to a few minutes in the fifth cycle as a result of a progressively increasing rate of carbon deposition. It was also evident that the alloy X tube was progressively more carburized and otherwise attacked from cycle to cycle.

While the present invention has been described in considerable detail in regard to a few specific embodiments, it is apparent that the practice of this invention is not restricted to such embodiments and details for it is adaptable to many modifications and variations in its wide application to other hydrocarbon reaction mixtures and conversion conditions. Accordingly, the present invention should not be construed as limited in any particulars except as may be recited in the appended claims or required by the prior art.

I claim:

1. In a process for the conversion of a hydrocarbon charge in a vapor phase reaction under high temperature conversion conditions in a confined reaction zone, the improvement which comprises confining said charge substantially entirely within reaction zone boundary surfaces of metal-ceramic material comprising particles of a catalytically inert, refractory solid ceramic substance dispersed in chromium.

2. A process according to claim 1 in which at least a substantial proportion of the heat required for said reac-

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tion is substantially continuously transferred through said metal-ceramic material to the reaction mixture.

3. A process according to claim 1 in which said metal-ceramic material contains at least about 5% by weight of a finely divided refractory solid ceramic substance and sufficient chromium to provide a continuous chromium matrix.

4. A process according to claim 1 in which said metal-ceramic material contains a substantial proportion by weight of aluminum oxide.

5. A process according to claim 1 in which said metal-ceramic material contains between about 15 and 30% by weight of finely divided aluminum oxide.

6. A process according to claim 1 in which a substantial yield of ethylene is produced by thermally cracking a charge containing a major molar proportion of hydrocarbon material having at least 2 carbon atoms per molecule at a reaction temperature between about 1600 and 1850° F. without excessive carbon deposition on said metal-ceramic material during prolonged operations.

7. A process according to claim 1 in which a hydrocarbon charge is cracked under thermal cracking conditions.

8. A process according to claim 7 in which said metal-ceramic material is externally heated to a temperature between about 1650 and 2200° F. for the indirect transfer of heat to the cracking reaction mixture.

9. A process according to claim 7 in which said metal-ceramic material contains a substantial proportion by weight of aluminum oxide.

10. A process according to claim 7 in which said metal-ceramic material contains at least about 5% by weight of aluminum oxide and sufficient chromium to provide a continuous chromium matrix.

11. A process according to claim 7 in which said metal-ceramic material comprises a dispersion of substantially 23% of finely divided aluminum oxide in 77% by weight of chromium.

12. A process according to claim 7 in which said metal-ceramic material contains between about 15 and 30% by weight of finely divided aluminum oxide.

13. A process according to claim 12 in which a substantial yield of ethylene is produced by cracking a charge containing a major molar proportion of hydrocarbon material having at least 2 carbon atoms per molecule at a reaction temperature between about 1600 and 1850° F. without excessive carbon deposition on said metal-ceramic material during prolonged operations.

14. A process according to claim 1 in which said refractory ceramic substance is a compound of the group consisting of aluminum oxide, silicon dioxide and silicon carbide.

15. A process according to claim 1 in which said metal-ceramic material contains a substantial proportion by weight of silicon carbide.

16. A process according to claim 1 in which said metal-ceramic material contains a substantial proportion by weight of silicon dioxide.

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DELBERT E. GANTZ, Primary Examiner

J. M. NELSON, Assistant Examiner

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

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Inventor(s) Mou ^Neng M. Lo

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

Column 2, line 21: for "or" read -- of --.
Column 2, line 45: for "a" read -- as --.
Column 2, line 49: for "olis" read -- oils --.
Column 2, line 58: for "7850°F." read -- 1850°F. --.
Column 3, line 8: for "contains" read -- contain --.
Column 4, line 62: for "reaction" read -- reactor --.
Column 5, line 15: for "=" read -- - --, i.e., a hyphen.
Column 5, line 51: for "progresively" read -- progressively --.

SIGNED AND
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(SEAL)

Attest:

Edward M. Fletcher, Jr.

Attesting Officer

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Commissioner of Patents