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PYROLYSIS OF HYDROCARBONS

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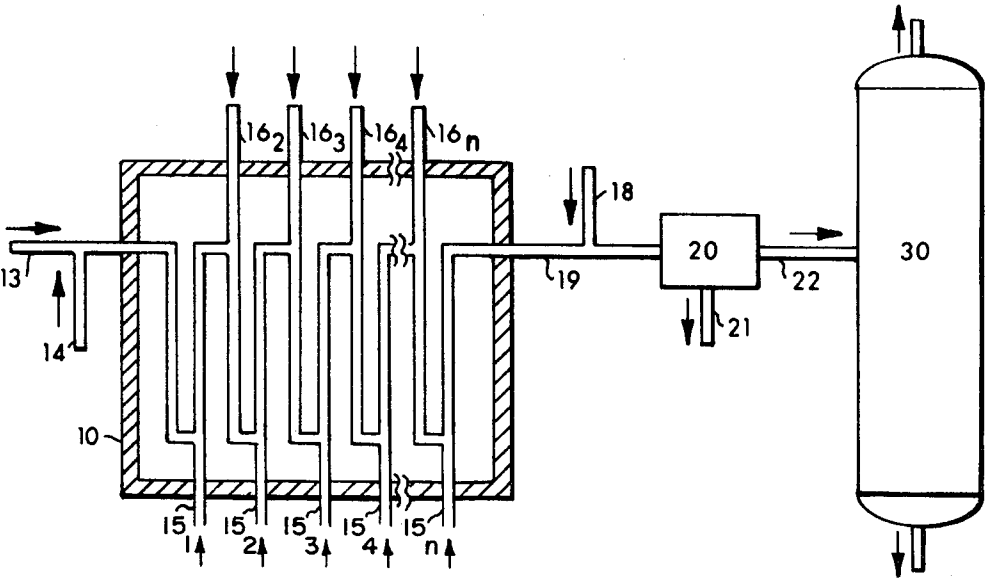


FIGURE-1

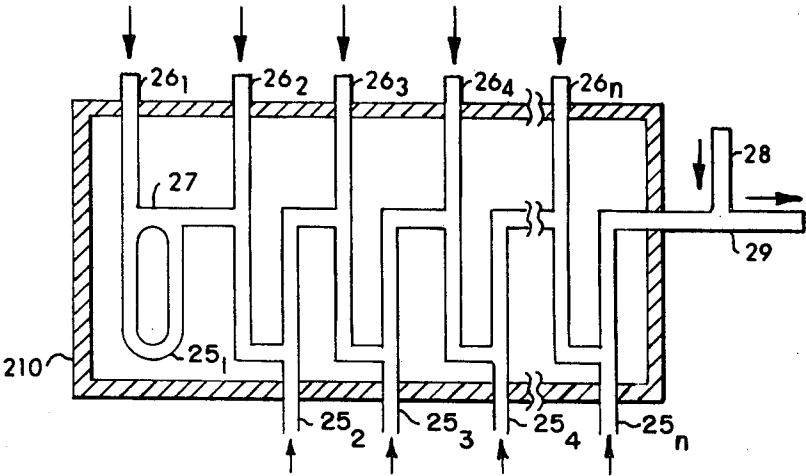


FIGURE - 2

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PYROLYSIS OF HYDROCARBONS

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ABSTRACT OF THE DISCLOSURE

This invention relates to process and apparatus for the pyrolysis, or thermal cracking, of hydrocarbons or hydrocarbon feedstocks to produce products useful as chemical raw materials or fuels. In particular, mobile hydrocarbons, i.e., normally gaseous or liquid paraffinic hydrocarbons, or other suitable feedstocks, are cracked to obtain unsaturated hydrocarbon compounds, particularly olefins. Faster reaction rates, increased product yields, and better selectivities are obtained by thermally cracking (with or without steam) a raw, or fresh hydrocarbon feed in admixture with a stream of hot reacting, thermally cracked (with or without steam) product. The process is thus characterized by steps wherein a feed is thermally cracked to form at least partially converted products, and fresh feed, which preferably is preheated to supply some of the needed sensible and reaction heat, is thermally cracked in admixture with the said at least partially converted products. In one embodiment, fresh hydrocarbon feed, and steam if desired, is preheated and fed at spaced locations through a tubular reactor, or reaction zone, resulting in fresh feed being contacted with at least partially converted products from a preceding portion of the tubular reactor, or reaction zone (except for the portion introduced at the entrance to the reactor).

It is well known to prepare fuels, and more particularly chemical raw materials such as unsaturated hydrocarbon compounds and olefins, by the pyrolysis, or thermal cracking of various hydrocarbon feeds, or hydrocarbon feedstocks, in both liquid and vapor phase reactions. The hydrocarbon is typically preheated, or vaporized and fed with or without steam, into the reaction zone, and cracked at a generally higher reaction temperature.

Ethylene, for example, a particularly valuable chemical raw material, is produced by steam cracking alkanes such as ethane or propane, naphthas, kerosene, gas oils or other distillates in a tubular reactor, or reaction zone. In such reaction, e.g., ethane is fed with steam at considerable velocities through a high temperature reaction zone. Thus, e.g., the ethane is generally preheated by circulation through the convection zone of a furnace to conserve heat. The ethane is then fed with steam (generally about 20:60 mole percent) through the heated metal tubes or coils of a furnace, and elevated to temperatures ranging up to about 1800° F., or more generally from about 1400° F. to about 1700° F. so that the ethane is cracked desirably into substantially ethylene and hydrogen. Sometimes the cracked by-product is reheated and recycled as make-up feed after separation of the ethylene.

In such reactions, unfortunately, all of the feed is not converted into hydrogen, olefins, diolefins or other desirable chemical raw materials. Important side reactions occur, and these invariably give rise to various problems not the least of which is degeneration of the desirable product into carbonaceous products, including carbon and coke.

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Yields are lower and selectivities poorer than desirable. Among suggested improvements have been tangential feeding of liquid hydrocarbon feedstock onto the side wall and into contact with a hot gas injected into the reaction chamber. Thus, the liquid hydrocarbon is spread out over the sides of the reaction chamber and cracked by contact with the hot gas to improve the yield of olefins.

Another suggested improvement is introducing hydrocarbon feedstocks into loop reactors, characterized by the presence of a reaction tube which curves back upon itself to provide an adjacent feed inlet and gasified product outlet, adjoined one to the other so that a portion of the gasified product is recirculated with the entering feed.

It is the primary objective of the present invention to substantially improve yields and selectivities in thermal cracking and thus to advance the state of the art. In particular, it is an object to provide a new and improved process and apparatus for pyrolysis of hydrocarbons, or hydrocarbon feedstocks, e.g., alkanes, to obtain high yields of olefins and other unsaturated compounds. More particularly, it is an object to provide a process which is highly selective in the formation of olefins and other unsaturated hydrocarbon products. A specific object is to provide a simple and convenient process for reducing the formation of undesirable by-products, e.g., undesirable alkanes and carbonaceous deposits such as carbon and coke.

These and other objects are achieved in accordance with the process of the present invention which comprises thermally cracking a hydrocarbon, or hydrocarbon feedstock, in a reaction zone, and then contacting the reacting product before quenching with a fresh, preferably preheated hydrocarbon feed, similar to or different from the feed used to form the gasified product, to form a reaction product mixture rich in unsaturated hydrocarbons. In other words, the process is characterized by incremental feed additions including steps wherein a hydrocarbon feed is used to form thermal cracking products, and fresh feed with or without preheating is cracked in admixture with the cracking products of a previous thermal cracking reaction. A fresh feed, or preheated feed, can thus be fed via a suitable inlet into a reaction zone, preferably a heated tubular reaction zone, straight or curved, and thermally cracked. The cracking product is moved along the flow path of the heated tubular reaction zone and, downstream of the initial point of entry, is contacted with fresh preheated feed, which can be the same as or different from the initially thermally cracked, and the mixture thermally cracked. The cracking product formed from this second reaction can be further moved along the flow path of the heated reaction zone, and again contacted with fresh preheated feed to produce a fresh cracking reaction and these steps thereafter repeated ad infinitum.

Surprisingly, it is found that faster reaction rates, increased yields of unsaturated hydrocarbons and better selectivities can be obtained by the present process of contacting increments of feed with the cracking product, or products, of previous reactions vis-a-vis a process wherein the total feed, with or without recycle of by-products, is fed into the initial portion and exited from the terminal portion of the reaction zone.

In a preferred embodiment, temperatures are held relatively constant through the reaction zones with the amounts of fresh feed added at each reaction zone being progressively larger (based on total feed) because of the larger proportion of reaction products present at each successive zone. Preferred temperatures range from about 1100° F. to about 2000° F., and more preferably from

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about 1300° F. to about 1500° F. Where the same feed is supplied in each zone, reaction times in each zone are preferably equal (requiring either progressively larger tubes or greater tube length because of the increased volume of reactants). Conversions of combined reaction products from a preceding zone and fresh feed preferably range from about 40 to about 95 percent, and more preferably from about 40 to about 70 percent for naphthas and gas oil feeds. Conversions range from about 60 to about 95 percent for C₂ through C₄ feeds. Amounts of steam added at each zone are in one embodiment proportional to the feed added and in another embodiment all of the steam added to the initial zone.

Where different feeds are employed in one embodiment, a light gas, e.g., ethane is supplied to the first reaction zone and reacted to obtain from about 60 to about 70 percent conversion and then a heavier oil, e.g., a gas oil, is added in subsequent zones to obtain a conversion of the gas oil of from about 40 to about 60 percent and an increase in conversion of the light gas to from about 70 to about 90 percent. All other conditions are the same as indicated above where the same feed is employed.

In a preferred embodiment the number of reaction zones in which additional fresh feed is added ranges from about 1 to about 20, and more preferably from about 3 to about 10. Additional feed is injected via inlets into the tubular reactor, or reaction zone, at spaced locations to provide contact of fresh feed with the cracking product from prior reactions. Parameters such as distance between injection points, tube length and cross-section, injection velocities, pressures and temperatures are suitably selected to provide a residence time, from a previous gasification to a succeeding fresh feed addition, ranging up to about 5 seconds. Preferably, however, the residence time should range from about 0.3 to about 2 seconds, residence times of less than 1 second being more preferred.

The reaction tubes, as suggested, can be straight or curved, but in a preferred embodiment a loop-type coil is used to process the fresh feed, this coil being followed by straight or curved tubes into which fresh feed is injected for contact with the cracking products from preceding gasification reactions. By use of this arrangement, somewhat better selectivities to unsaturated hydrocarbons can be obtained.

The reactions taking place in the tube will depend upon the nature of the feed and the reaction conditions. Normally, the reactions will be endothermic and the heat input may be achieved both by preheating the steam or the hydrocarbon feedstock, or both, before and after mixing. The tube is preferably located in a furnace to provide an additional supply of heat. The actual reaction temperature will normally depend upon the feedstock employed and the desired distribution of products.

Preferred feeds are alkanes such as ethane, propane, butane, and the like; unsaturates such as propylene and the like; commercial mixtures such as light naphthas boiling up to about 180° F., intermediate naphthas boiling from about 180° F. to about 300° F., heavy naphthas boiling from about 300° F. to about 430° F., light and heavy gas oils boiling from about 430° F. to about 1000° F., and higher, and combinations thereof.

Feeds are normally injected at high velocities ranging from about 200 to about 1500 feet per second, and preferably from about 600 to about 1200 feet per second.

Referring to FIG. 1, a feed is injected via line 13 into the furnace 10. The feedstock is heated by contact with hot steam injected into line 13 via line 14. Suitable apparatus for carrying out the present invention contemplates a mixing nozzle, defined schematically by lines 13, 14, wherein the hydrocarbon feedstock is heated by contact with superheated steam to provide the desired preheat temperatures, ranging typically on the order of from about 800° F. to about 1500° F., and preferably on the order of from about 800° F. to about 1300° F.

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Often, the feedstock per se is maintained at ambient temperature while the steam is superheated to provide the desired preheat temperature. Typically, a 500° F. feed is vaporized with 1500° F. steam to provide a 1000° F. to 1200° F. preheat temperature.

The furnace 10 contains a plurality of sections, i.e., a plurality of furnace sections or coils having *n* top injection ports (or nozzles) 16₂, 16₃, 16₄ . . . 16_{*n*}, and, if desired, *n* lower injection ports—15₁, 15₂, 15₃, 15₄ . . . 15_{*n*}. As suggested, the sum total number of injection ports 15, 16 can preferably range as high as twenty. The first of the sections can constitute an initial reaction coil wherein the preheated feed is quickly heated to the desired reaction temperature and reacted. The remaining sections are cracking coils maintained at substantially reaction temperature. Fresh hydrocarbon feed is preheated in the conversion portion of furnace 10 as it is introduced into the cracking coils via injection ports 15₂ through 15_{*n*}, and ports 16₂ through 16_{*n*}. A single reaction span is defined by the distance between a feed injection point or port and a succeeding feed injection point, or port, e.g., 15₂ to 16₃ or 15₃ to 16₄. A reaction span can also be defined by the distance between gasification injection points. Such latter points thus also define the locations of a previous gasification and a succeeding fresh preheated feed addition, and hence it is this distance which is important with regard to residence times.

The reaction product mixture, in the form of an effluent, is removed from the furnace 10 via line 19 and quenched with water or oil by injection through line 18. A condenser 20 can be provided, if desired, and water can be withdrawn from the condenser via line 21. Product is passed via line 22 into a distillation column 30 for separation of the desired products. Alternately, the product can be cooled by passing it through a heat exchanger before passing it into distillation column 30.

Referring to FIG. 2, the furnace 210 depicted is generally similar to that shown by reference to the preceding figure except that loop-coil precedes other coils such as described with reference to the preceding figure. Within this furnace, fresh preheated feed is cracked in the loop coil by introduction of feed into inlet port 26₁. The cracking product passes through the curved portion of the tube 25₁, a portion of the cracking product is recycled through portion 27 of the tube and another portion is passed to line 26₂ to contact fresh feed. Thereafter, fresh preheated feed is added as described previously. Each of the reaction tubes are thus provided with inlet ports 25₂, 25₃, 25₄ . . . 25_{*n*} and 26₁, 26₂, 26₃, 26₄ . . . 26_{*n*}.

Effluent removed from the reactor 210 via line 29 can be quenched as described by reference to FIG. 1.

The invention will be better understood by reference to the following illustrative examples which show the production of reaction product mixtures rich in unsaturated hydrocarbon compounds.

EXAMPLE 1

In a typical operation, as described by reference to FIG. 1, a gas oil feed boiling between 500 and 700° F. is preheated to 400° F., contacted with 1500° F. steam, and reacted at 1300° F. providing a contact time of .7 second in the initial reaction zone. Additional gas oil feed, also boiling between 500 and 700° F., amounting to 50 weight percent of the gas oil feed introduced initially, is mixed with 1500° F. steam and introduced to the furnace coil through a second inlet, downstream of the first. The combined material is then held at about 1300° F. and reacted for an additional .7 second. Similarly, gas oil feed and steam are introduced at three additional points, i.e., through a third, fourth and fifth inlet. In each case, at a rate amounting to about 50 weight percent of the hydrocarbon exiting from the previous zone and held in each zone for residence time of about .7 second at about 1300° F. The entire material is then removed from the furnace and rapidly quenched. The following yields are typical of

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those which can be obtained from the above-described cracking process:

	Yield, wt. percent on fresh feed
H ₂ -----	0.75
CH ₄ -----	11.2
C ₂ H ₆ -----	2.35
C ₂ H ₄ -----	29.5
C ₂ H ₂ -----	0.2
C ₃ H ₈ -----	0.4
C ₃ H ₆ -----	14.3
C ₃ H ₄ -----	0.4
Total C ₃ - -----	59.10

In sharp contrast, when the foregoing is repeated except that the total feed is injected through the first coil, ethylene yield decreases to 17 weight percent. Under conditions which optimize the yield of ethylene at between about 21 and 22 weight percent, the yield of propylene is reduced from 13 percent to 8 percent.

EXAMPLE 2

By way of further example, a loop coil can be utilized for the initial reaction zone as shown in FIG. 2. Under general identical conditions as given in the preceding example, the following results tabulated below are obtained:

	Yield, wt. percent on fresh feed
H ₂ -----	0.7
CH ₄ -----	10.5
C ₂ H ₆ -----	2.3
C ₂ H ₄ -----	30.5
C ₂ H ₂ -----	.1
C ₃ H ₈ -----	.3
C ₃ H ₆ -----	14.8
C ₃ H ₄ -----	.3
Total C ₃ - -----	59.5

It is thus observed that ethylene yield is increased, while the yield of methane is decreased.

It is apparent that various changes and modifications can be made without departing the spirit and scope of the invention.

Having described the invention, what is claimed is:

1. A process for the production of a reaction product mixture rich in unsaturated hydrocarbon compounds comprising thermally cracking a hydrocarbon feed in a first reaction zone at temperatures ranging from about 1100° F. to about 2000° F. at residence times ranging up to about 5 seconds, sufficient to effect at least partial chemical conversion of the feed to produce a product having a composition different from the feed, passing and thermally cracking it in 1-20 additional reaction zones, the product from each reaction zone being contacted, without appreciable cooling, with additional fresh hydrocarbon feed and thermally cracked at temperatures ranging from 1100° F. to about 2000° F. at residence times ranging up to about 5 seconds sufficient to effect at least partial chemical conversion of the combined feed to a product having a composition different from the combined feed.

2. The process of claim 1 in which the number of reaction zones ranges from about 3 to about 10.

3. The process of claim 1 in which fresh steam is added to at least one of the reaction zones,

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4. The process of claim 1 wherein the residence time ranges from about 0.3 second to about 2 seconds.

5. The process of claim 1 wherein the residence time ranges up to about 1 second.

6. A tubular reactor for thermally cracking hydrocarbon feeds to produce reaction product mixtures rich in unsaturated hydrocarbon compounds comprising a tube having an initial fresh feed inlet and outlet for exit of cracked products, and from about 1 to about 20 additional fresh feed inlets along the length of the tube wherein the portion of the tube between the initial fresh feed inlet and the next adjacent added fresh feed inlet is bent back on itself, and connected together to provide a looped portion through which a portion of the cracking product can be recirculated with the entering feed.

7. A process for the production of a reaction product mixture rich in unsaturated hydrocarbon compounds which comprises contacting a hydrocarbon feedstock with steam in order to preheat said hydrocarbon feedstock to a temperature in the range from about 800° to about 1500° F. and thereafter thermally cracking said preheated feed in a first reaction zone at a temperature in the range of from about 1100° F. to about 2000° F., at residence times in the range of about 0.3 to about 2 seconds, to form thermal cracking products, passing said products into from 1 to about 20 additional reaction zones, the product from each reaction zone being contacted, without appreciable cooling, with additional fresh hydrocarbon feed and thermally cracked at temperatures ranging from about 1100° to about 2000° F. at residence times in the range from 0.3 to about 2 seconds in order to produce a reaction mixture rich in unsaturated hydrocarbon compounds.

8. The process of claim 7 wherein the residence time is less than about 1.0 second.

9. The process of claim 8 wherein the temperature in the reaction zones is in the range from about 1300° to about 1500° F.

10. The process of claim 9 wherein the number of reaction zones ranges from 3 to about 10.

11. The process of claim 10 wherein said additional fresh hydrocarbon feed introduced into the reaction zone is admixed with steam.

12. The process of claim 11 wherein said hydrocarbon feedstock is a gas oil having a boiling point in the range of from about 430° to about 1000° F.

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