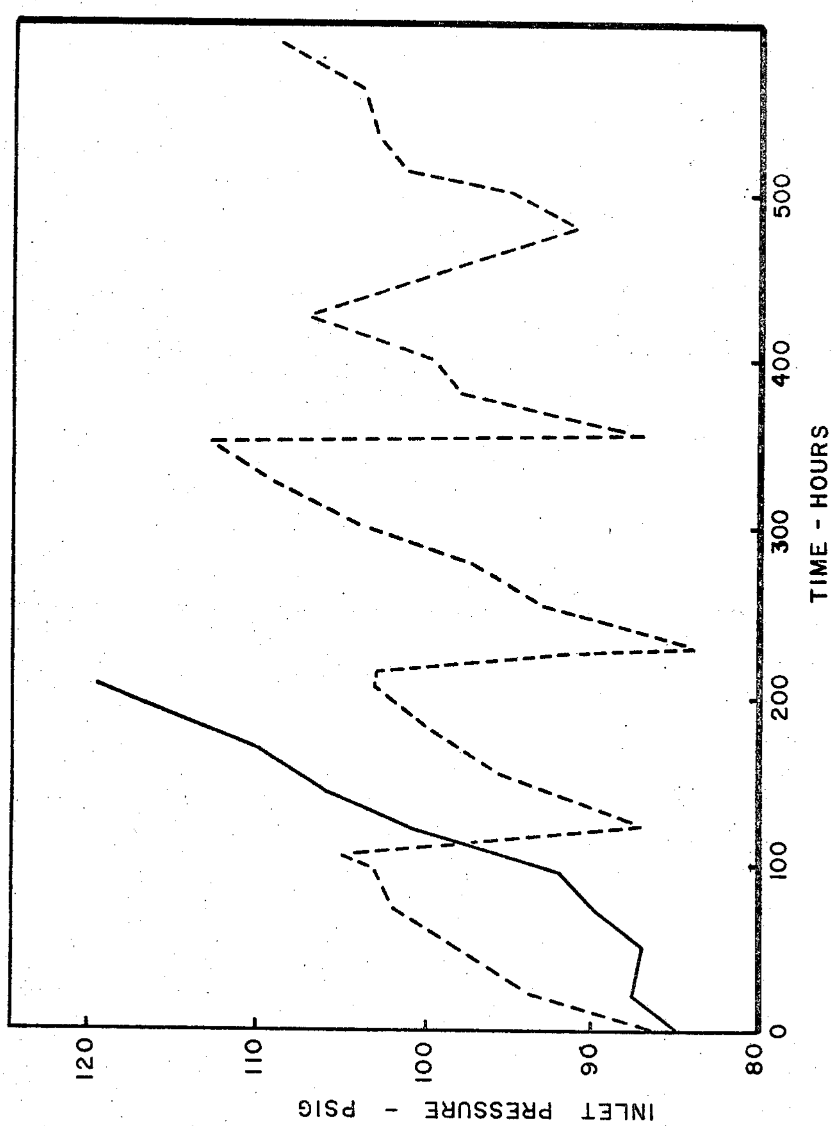
March 18, 1969 G. D. OLIVER 3,433,731

COIL DECOKING IN STEAM CRACKING BY INTERMITTENT SWITCH TO ETHANE FEED

Filed March 1, 1967



INVENTOR.
George D. Oliver
BY Stewart N. Rice
ATTORNEY

3,433,731

COIL DECOKING IN STEAM CRACKING BY INTERMITTENT SWITCH TO ETHANE FEED

George D. Oliver, Texas City, Tex., assignor to Monsanto Company, St. Louis, Mo., a corporation of Delaware

Filed Mar. 1, 1967, Ser. No. 619,669
U.S. Cl. 208—48 12 Claims
Int. Cl. C10g *9/16*

ABSTRACT OF THE DISCLOSURE

An improved method for cracking normally liquid hydrocarbons whereby on-stream decoking is accomplished comprising alternately cracking a normally liquid hydrocarbon and a normally gaseous hydrocarbon such as ethane.

Background of the invention

The present invention relates to a process for the thermal cracking of hydrocarbons. More particularly the present invention relates to an improvement in a process for the thermal cracking of normally liquid hydrocarbons whereby on-stream decoking of cracking furnaces is accomplished.

One of the growing sources of olefins, diolefins, and aromatics is the thermal cracking of hydrocarbons. The cracking of these hydrocarbons to olefins, diolefins, and other products is well known and at the present time is generally carried out in the presence of steam in tubular furnaces such as the type described in U.S. Patents 2,608,527, 2,340,814, 2,917,564, and 3,182,638. The length to diameter ratio of these tubular furnaces is generally greater than 100:1. In all of these processes, one of the most serious problems is the formation of coke in the furnace tubes which necessitates expensive shutdowns of the cracking furnaces in order to decoke. While this coking occurs with light hydrocarbon feedstocks such as ethane, the problem is especially severe when cracking heavier liquid feedstocks such as naphtha and crudes wherein shutdowns of the furnaces for decoking are often necessary after on-stream times as short as 100 hours.

Summary

It is thus an object of the present invention to provide a method for the cracking of normally liquid hydrocarbons wherein on-stream cracking times are lengthened. It is a further object of the present invention to provide an improved method for the cracking of normally liquid hydrocarbons wherein decoking of the cracking furnace occurs while the furnace is on stream. Additional objects will become apparent from the following description of the present invention.

In one of its embodiments the present invention comprises an improvement in a process for the thermal cracking of normally liquid hydrocarbons in a tubular cracking furnace wherein substantial coking on the furnace occurs, which improvement comprises cyclically cracking a normally liquid hydrocarbon feed and a normally gaseous hydrocarbon feed, each cycle comprising a first time period during which said normally liquid hydrocarbon feed is cracked and a second time period during which said normally gaseous hydrocarbon feed is cracked, the time ratio of said first time period to said second time period being at least 10:1.

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 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 1500° F. Petroleum condensates are an especially preferred normally liquid hydrocarbon feedstock. These preferred petroleum condensates may be characterized by boiling point ranges substantially within 100° F. to 800° F. as determined by ASTM Test No. D-86. 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 not to be construed as not covering such processes.

The normally gaseous hydrocarbons useful in the present invention may be saturated or unsaturated. Ethane, propane, butane, propylene, and isobutylene are examples of such normally gaseous hydrocarbons as well as mixtures of normally gaseous hydrocarbons, e.g., propane and ethane of refinery gas containing one to four carbon atoms. The preferred normally gaseous hydrocarbons are saturated hydrocarbons, especially ethane. In a preferred embodiment of the present invention, the normally gaseous hydrocarbons are those separated from the effluent of the cracking of the normally liquid hydrocarbon feeds and recycled to the furnaces.

In carrying out the present invention, the thermal cracking of both the normally liquid hydrocarbons as well as the normally gaseous hydrocarbons will generally be 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 hydrocarbon charge to the cracking furnace. Preferably about 0.2 to about 2.0 pounds of inert diluent per pound of feed is added when a normally gaseous hydrocarbon feed is being used and preferably about 0.05 to about 1.5 pounds of diluent per pound of feed is added when a normally liquid hydrocarbon feed is being used.

The thermal cracking of both the normally liquid hydrocarbon or the normally gaseous hydrocarbon may be carried out under various conditions of time, temperature, and pressure and will depend on such factors as furnace design and the desired products in the effluent. Generally the temperature will be within the range of 850° F. to about 1800° F. with pressures from about atmospheric to about 1,000 p.s.i.g., preferably 10 to 160 p.s.i.g. Temperatures of about 1350° F. to 1650° F. are preferably used for normally gaseous hydrocarbon feeds while temperatures from about 1100° F. to 1550° F. are preferably used for normally liquid feeds. 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 and lower.

Example

Two runs were made during which a petroleum condensate having an initial boiling point of about 116° F. and an end point of about 625° F. as determined by ASTM Test D-86 was cracked in a tubular furnace at temperatures of about 1500° F. A stream to hydrocarbon weight ratio of about 0.25 was maintained during the cracking of the petroleum condensate. One run was made in accordance with the present invention with an ethane feed being periodically cracked and one run was made without the benefit of the present invention. During the periods of ethane cracking, temperatures of about 1550° F. and a steam to ethane weight ratio of about 0.4 were used. The results of both runs are illustrated in the drawing which represents a plot of the inlet pressure of the cracking furnace (sometimes referred to as the back pressure) vs. time. The run made in accordance with the present invention is shown as a dashed line and the run made without the benefit of the present invention is shown as a solid line. The furnace inlet pressure is a good indication of the amount of coking in the furnace tubes and increases as coking of the furnace tubes increases In the particular furnace used in this example, shutdown for decoking has been found to be necessary after reaching a back pressure of about 120 p.s.i.g. when operating under the conditions of the present example.

As may be seen from the drawing, the run made without the benefit of the present invention, as represented by the solid line, remained on stream for only 200 hours before becoming so badly coked as to require shutdown of the furnace for decoking. However, the run made in accordance with the present invention wherein ethane and petroleum condensate were alternately cracked, was able to remain on stream some 590 hours or about 25 days. This latter run consisted of about 4½ cycles according to the present invention wherein the first cracking cycle consisted of about 100 hours of cracking petroleum condensate and 4 hours cracking ethane, the second cycle consisted of about 104 hours petroleum condensate cracking and 3½ hours ethane cracking, the third cycle consisted of about 139 hours petroleum condensate cracking and 4 hours ethane cracking, and the fourth cycle consisted of about 111 hours petroleum condensate cracking and 3 hours ethane cracking. Following the fourth cycle, petroleum condensate was cracked for about 120 hours at which time the run was discontinued for routine maintenance even though, as indicated by the back pressure, the furnace did not require shutdown for decoking. Thus it can be seen from this example that the present invention provides significantly longer onstream times than can be obtained without periodic ethane cracking.

In a cracking cycle of the present invention, the ratio of time of a period during which a normally liquid hydrocarbon feed is cracked to a period during which a normally gaseous hydrocarbon feed is cracked will generally be greater than 10:1 and may be as large as 400:1 and larger. Usually, however, this ratio will be from about 20:1 to 300:1 and is preferably from about 50:1 to 250:1. The actual number of hours spent during the periods of cracking each type feed will depend mainly on the particular normally liquid hydrocarbon feed being cracked since some feedstocks form coke more readily than others. For example, in the cracking of a petroleum condensate such as that of the above example, it is advantageous to have cycles comprised of 80 to 160 hour periods of petrolueum condensate feed followed by one-half to five hour periods of normally gaseous hydrocarbon feed. The periods for cracking the normally liquid hydrocarbons and/or the normally gaseous hydrocarbons may also vary from cycle to cycle. Usually the normally liquid hydrocarbon will be cracked until a particular inlet pressure is reached at which time the feed will be changed to a normally gaseous hydrocarbon. The lengths of the periods in which the normally liquid hydrocarbon is cracked can be readily ascertained by one skilled in

the art and will vary according to the particular furnace, feed, feed rate, reaction conditions, and the like. However, if it has been found that operation of a particular furnace without alternate cracking of a normally gaseous hydrocarbon results in sufficient coke formation after seven or eight days to require shutdown for decoking, then certainly the periods during which the normally liquid hydrocarbon is cracked in accordance with the present invention should be less than seven or eight days.

In operations conducted in accordance with the present invention, reduction of back pressure or inlet pressure due to decoking sometimes occurs during the periods of cracking the normally gaseous hydrocarbon and sometimes occurs after the feed has been switched back to a normally liquid hydrocarbon. Also the rate at which the inlet pressure decreases to indicate decoking is taking place may vary from cycle to cycle. The applicant does not understand what causes the on-stream decoking to take place when operating according to the present invention and does not wish to be bound to any particular theory. The only thing certain is that longer on-stream times are possible since decoking is taking place without having to take the furnace off stream for a day or so in order to carry out the usual decoking procedures. These on-stream times are advantageous not only in that increased production may be accomplished but in that mechanical failure due to the fact that metal fatigue often occurs when shutting down a furnace for decoking because of the extreme temperature changes which the furnace tubes undergo.

What is claimed is:

1. In a process for thermal cracking of a feed comprising normally liquid hydrocarbons in a tubular furnace wherein substantial coking of the furnace occurs, the improvement which comprises cyclically cracking said feed comprising normally liquid hydrocarbons and a normally gaseous hydrocarbon feed, each cycle comprising a first time period during which said feed comprising normally liquid hydrocarbons is cracked and a second time period during which said normally gaseous hydrocarbon feed is cracked, the time ratio of said first time period to said second time period being at least 10:1.

2. The process of claim **1** wherein the ratio of the time spent cracking said normally liquid hydrocarbon to the time spent cracking said normally gaseous hydrocarbon is from about 20:1 to 300:1.

3. The process of claim **1** wherein said normally gaseous hydrocarbon consists essentially of ethane.

4. The process of claim **2** wherein the cracking of said feed comprising normally liquid hydrocarbons and said normally gaseous hydrocarbon feed takes place at a temperature of from about 850° F. to about 1800 F. and at a pressure of from about atmospheric to about 1000 p.s.i.g.

5. The process of claim **4** wherein the cracking of said feed comprising normally liquid hydrocarbons is conducted in the presence of an inert diluent in an amount of 0.05 to 4.0 pounds of inert diluent per pound of hydrocarbon charge to the furnaces.

6. The process of claim **5** wherein said inert diluent is steam.

7. The process of claim **6** wherein said feed comprising normally liquid hydrocarbons is naphtha.

8. The process of claim **6** wherein said normally gaseous hydrocarbon is ethane and said ethane is cracked in the presence of from 0.05 to 4.0 pounds steam per pound of ethane.

9. The process of claim **8** wherein said ethane is separated from the effluent of the cracking of said normally liquid hydrocarbon.

10. The process of claim **8** wherein said normally liquid hydrocarbon is a petroleum condensate substantially boiling within the range of 100° F. to 800° F. as determinated by ASTM Test No. D-86.

11. The process of claim **9** wherein the periods of cracking of said normally liquid hydrocarbons are from about 80 to 160 hours in length and the periods during which said normally gaseous hydrocarbons are cracked are about 0.5 to 5.0 hours in length.

12. In a process for thermal cracking of a feed comprising a petroleum condensate in a tubular furnace wherein substantial coking of the furnace occurs, the improvement which comprises cyclically cracking said feed comprising a petroleum condensate and ethane, each cycle comprising a first time period of from about 80 to 160 hours during which said feed comprising a petroleum condensate is cracked and a second time period of from about 0.5 to 5.0 hours during which said ethane is cracked, said feed comprising a petroleum condensate being cracked in the presence of from 0.05 to 1.5 pounds of steam per

pound of feed comprising a petroleum condensate and at temperatures within the range of from about 1100 to 1550° F., said ethane being cracked in the presence of from about 0.2 to 2.0 pounds of steam per pound of ethane and at temperatures of from about 1350° F. to 1650° F.

References Cited

UNITED STATES PATENTS

3,365,387 1/1968 Cahn et al. ---------- 208—48

DELBERT E. GANTZ, *Primary Examiner.*

G. E. SCHMITKONS, *Assistant Examiner.*

U.S. Cl. X.R.

260—683