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PROCESS FOR STEAM CRACKING CRUDE OIL

FIELD OF THE INVENTION

This invention relates to an improved process for the steam cracking of crude oil and heavy unsaturated hydrocarbon feedstocks. More specifically, this invention relates to a two-stage process for steam cracking a crude oil feed wherein about 50 volume percent of the feed has a boiling point above 900° F. In the two-stage process of this invention, the feed is first passed to the convection section of a steam cracking furnace to flash off those volatile materials which vaporize below about 450° F. This vaporized portion of the feed, which corresponds approximately to a naphtha fraction, along with the remaining liquid portion of the crude feed is introduced into a separation zone, i.e. flash drum separator. The vaporized portion of the feed passes overhead from the separation zone and then being admixed with steam, is introduced back into convection and then the radiant section of the steam cracking furnace. The conditions under which the first cracking furnace are operated are those conditions, i.e. residence time and cracking temperature, which are optimum for the cracking of a naphtha fraction to form valuable chemical raw materials. The unvaporized, i.e. liquid portion of the feed is withdrawn from the first separation zone and passed through the convection section of a second steam cracking furnace and then introduced into a second separation zone. Stripping steam is introduced either into the liquid stream withdrawn from the first separation zone or into the bottom portion of the second separation zone, i.e. flash drum separator, to flash off i.e. overhead, materials boiling above about 450° F. and below about 1,100° F., i.e. a gas oil fraction. This vapor mixture, after leaving the second separation zone, is cooled about 50°-200° F. in order to liquefy a portion of said vapor mixture. Through this process, entrained droplets of liquid hydrocarbon are washed from the vapor mixture. Thereafter, the vapor fraction is introduced into the convection section and then the radiant section of the second steam cracking furnace. The cracking conditions employed in the second steam cracking furnace are those which are optimum for the cracking of a gas oil fraction. In this manner, both the naphtha fraction and the gas oil fraction are each cracked under their own specific optimum cracking conditions while eliminating the need for a crude still to separately form a naphtha fraction and a gas oil fraction. The cracking conditions (i.e. temperature, steam rate, pressure, etc.) and severities can be selected to optimize the product yields and minimize coking or operability problems for each feed stream. In addition, the use of stripping steam in the second flash drum separator serves not only to reduce the hydrocarbon partial pressure in the flash drum and thus allow more hydrocarbon to vaporize, but also provides the diluent steam, i.e. carrying and cracking medium, for the vaporized hydrocarbon fraction passing overhead from the second separation zone into the second steam cracking furnace. The products formed in the cracking process may then be separated using well-known separation techniques.

DESCRIPTION OF THE PRIOR ART

Conventional steam cracking processes are generally well known in the art and have been widely used in the preparation of valuable unsaturated hydrocarbon compounds and olefins by the thermal cracking of various hydrocarbons or hydrocarbon feedstocks. Nevertheless, crude oil has not been employed as a hydrocarbon feed in the steam cracking processes owing to the high degree of coking that results in the tubes in the furnace. Consequently, in conventional processes for the conversion of crude petroleum into more valuable hydrocarbon products, a combination of crude oil distillation and conversion processes have been employed.

Typically, the crude oil is fractionated in a crude still into a light fraction, i.e. naphtha, a middle fraction, i.e. gas oil and a heavy residuum fraction, i.e. topped crude. Either the naphtha or the gas oil fraction can be subsequently subjected to thermal-cracking, i.e. steam cracking or catalytic refining treat-

ment processes to obtain lower boiling products, i.e. ethylene, propylene, butadiene and the like. The topped crude is generally subjected to a further distillation at reduced pressure in a vacuum still to recover a light fraction, i.e. vacuum gas oil and a heavy fraction, i.e. vacuum residuum. The vacuum gas oil may then be steam cracked or catalytically treated, as above, and the vacuum residuum is burned as a fuel or upgraded by conversion processes such as coking.

For economical heat recovery, much heat exchange apparatus is required both within each unit and in combination between units. The vacuum distillation equipment normally employed for fractionating the reduced crude is expensive with respect to investment, operation and maintenance.

In addition, optimum conditions for steam cracking the above feedstocks, i.e. naphtha and gas oil, are different for each feed. For example, naphtha feeds require a higher temperature in the cracking zone than a gas oil. These temperatures are imposed largely by fouling or coking of the cracking coil as well as by the kinetics of the cracking reactions.

Furthermore, the type of crude oil which is employed as the hydrocarbon feed significantly affects the percentage of the naphtha and gas oil fractions obtained and thus the amount of the crude which can be ultimately subjected to thermal cracking processes. For example, in Netherlands Pat. application Ser. No. 6,814,184, a process is described wherein a crude oil feed, having a high gasoline content is heated with steam in the convection section of a cracking oven; passed into a separation zone where nonvolatilized components are separated off, and thereafter the volatilized components are thermally cracked. A major deficiency associated with such a process is that lower temperatures must be used in the cracking zone to prevent fouling. This results in significant losses in yields to valuable low molecular weight hydrocarbons than could be realized when the naphtha and gas oil fractions are cracked separately. Another deficiency associated with this process is that with only one separation zone, crudes, particularly heavy crudes, i.e. crudes with high average boiling points, are not vaporized as completely as can be accomplished in a crude still. Thus, some of the valuable gas oil is not vaporized and is burned as fuel. From a practical standpoint it is essential to avoid entrainment of residual liquid in the flash zone since it would excessively foul the convection or radiant section of the furnace. Therefore, special precautions must be taken, as described above. Thus, the art is in need of an economic process for the thermal cracking of crude oils, particularly heavy crude oils wherein about 50 volume percent of the crude oil has a boiling point above 900° F. under such conditions that maximum yields are obtained from the more valuable naphtha and gas oil fractions.

SUMMARY OF THE INVENTION

It has now been discovered that the heretofore mentioned attendant difficulties in the cracking of crude oil may be overcome by employing the two-stage flash process of the instant invention. In accordance with the instant invention, the crude oil feed is passed into the convection section of a steam cracking furnace wherein the temperatures are in the range of from about 450° to 700° F. in order to vaporize the materials in the feed boiling below about 450° F. the vaporized portion of the crude feed, which is in the range of from about 20 to 50 wt. percent based on feed, is then introduced along with the liquid portion of the feed, i.e. that portion of the feed which was not flashed in the convection section of the furnace, into a separation zone, i.e. a flash drum separator. The separation zone is operated at a pressure of from about 30 to about 100 p.s.i.g. or greater such that the vaporized portion of the feed passes overhead and is then admixed with about 0.1 to 2.0, and more preferably 0.4 to 0.7 pounds of steam per pound of hydrocarbon before being introduced into the cracking zone in the steam cracking furnace. Thus, the feed to the first cracking zone comprises about 10 to 67 wt. percent steam in order to lower the hydrocarbon partial pressure and thus in-

crease yields to low molecular weight hydrocarbons. This vaporized portion of the feed, which approximates a naphtha fraction, along with the above-described amount of steam, is cracked in the radiant section of a steam cracking furnace under those conditions which are optimum for the cracking of a naphtha fraction. Thus, the vaporized feed in the cracking zone is cracked at a temperate at the outlet of the furnace coil between about 1,500° to about 1,700° F., with a residence time in the radiant section, i.e. cracking section of the steam cracking furnace of about 0.1 to 0.5 seconds with a steam dilution of about 0.4 to about 0.7 pounds of steam per pound of hydrocarbon feed.

The liquid portion of the crude feed which forms a liquid phase in the bottom portion of the first flash drum separator is withdrawn therefrom and passed through the convection section of a second cracking furnace wherein the feed is heated to a temperature of from about 600° to about 900° F. Since low boiling materials have been removed in the first flash zone, it is now possible to operate this second convection zone at a higher liquid/vapor ratio, which improves heat transfer and reduces the fouling tendency. The materials which are vaporized by being passed through the convection section of the second cracking furnace are those materials in the crude feed which vaporize below about 850° to 1,100° F., more preferably about 950° F. These vaporized materials comprise about 35 to 90 wt. percent of the unvaporized material withdrawn from the first flash drum and about 15 to 25 wt. percent based on total crude feed. This vaporized portion of the feed along with those materials which have not been vaporized by passage through the convection section of the second cracking furnace, are passed together into a second separation zone. Steam is introduced into the hydrocarbon stream before entering the convection section of the second cracking furnace or into the second flash drum or into both in order to strip the gas oil fractions from the heavy residua and to provide diluent steam for the subsequent steam cracking process step. This steam can be preheated above the oil temperature to provide additional heat. The amount of stripping steam which is employed is in the range of from about 0.1 to 2.0, and more preferably from about 0.2 to about 0.7 pounds/steam per pound of hydrocarbon feed such that the feed to the second cracking zone comprises about 17 to 38 wt. percent steam. The gas oil fraction along with steam, thus passes overhead from the second separation zone and is passed into the second cracking zone in the radiant section of the second steam cracking furnace. The conditions in the second cracking zone are those optimum conditions for steam cracking a gas oil fraction. Accordingly, the contact time of vaporized portion in the second cracking zone, i.e. radiant section of second steam cracking furnace is in the range of from about 0.1 to 1.0 seconds, preferably 0.3 to 0.6 seconds. The temperature at the coil outlet of the cracking zone i.e. the radiant section of the furnace, is within the range of 1,350-1,700° F. Pressures within the tubes may range from to 200 p.s.i.g. at the coil outlet. The liquid portion remaining in the bottom of the second flash drum, i.e. heavy residua of the crude feed oil, may be stripped with steam and withdrawn and employed as a fuel. Thus, it can be seen that the two-stage flashing process of the instant invention provides both an economical and technical advance over the prior art.

Economically, the present invention eliminates much of the heat exchange apparatus which was heretofore required, while utilizing the convection sections of the cracking furnace to vaporize those fractions, i.e. naphtha and gas oil fractions which may be conventionally steam cracked to produce high yields of valuable chemical raw materials. In addition, a significant advantage of the instant process is the steam cracking of crude oils and hydrocarbon feeds wherein about 50 volume percent or higher of the materials in said feed have a boiling point above 900° F. Furthermore, the use of the two-stage process of this invention allows the naphtha fraction and the gas oil fraction each be cracked under their optimum cracking conditions in order to increase overall yields of unsaturated

cracked hydrocarbon products, especially C₄-C₆ diolefins such as butadiene, isoprene and cyclopentadiene and the like without significant loss of ethylene, etc. Moreover, special equipment such as a heat exchanger on the furnace effluent (to make steam) can then be used on the naphtha cracker, whereas it is not considered operable with gas oil feeds.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Having set forth its general nature and advantages, the invention will be best understood from the more detailed description hereinafter which refers to the accompanying drawing, wherein a schematic flow diagram of the steps used in the present invention is shown.

Referring to the drawing, a crude oil feed is fed by way of line 1 through the convection section of a cracking furnace 2 in order to flash off i.e. vaporize that portion of the feed which boils below about 450° F. It is to be understood that other feeds in addition to crude oils may also be employed in the practice of the instant invention. Other feeds include, but are not limited to, hydrocarbon feedstocks wherein about 5 to about 50 volume percent of the materials in such a feedstock have a boiling point above 900° F. As mentioned above, a significant advantage of the instant invention is that feedstocks wherein as high as about 50 volume percent of the materials in such feedstock have a boiling point above 900° F., may be successfully employed in the process of this invention.

The vaporized portion of the crude feed along with the non-vaporized portion are passed by way of line 3 into the upper portion of a flash drum separator 4. The flash drum separator 4 is operated under a pressure in the range of from about 30 to about 100 p.s.i.g. in order to effect a phase separation between the gas phase containing approximately the naphtha fraction and the liquid phase containing that portion of the feed which comprises above about 30 wt. percent based on total feed. The vaporized portion of the feed thus passes overhead by way of line 5, is admixed with steam via line 6 and reintroduced back into the convection section of the cracking furnace via line 7. The conditions under which the cracking furnace is operated are those which are optimum for the cracking of a naphtha fraction, as described above. These cracking conditions increase the cracking selectivity to C₄-C₆ diolefins such as butadiene and isoprene over that which would be obtained by cracking the naphtha and gas oil fractions together at other than optimum conditions for the naphtha fraction.

The unvaporized, liquid portion of the feed which settles to the bottom of the first flash drum separator 8 is withdrawn therefrom and passed by way of line 9 through the convection section of a second cracking furnace 10. The temperature of the liquid which is withdrawn from the flash drum separator is in the range of about 450° to about 700° F. After passing through the convection section of the second cracking furnace, the temperature of the feed has been raised to about 600° to about 900° F. The portion of the feed which has been vaporized by passing through the second convection zone 10 along with the remaining liquid portion of the feed is passed by way of line 11 into a second flash drum separator 12. The second flash drum separator is operated at a pressure in the range from about 30 to about 100 p.s.i.g. Steam is introduced into the second flash drum separator 12 by way of line 13 or into line 9 in order to reduce the partial pressure of the hydrocarbon in the flash drum in order to increase the vaporization of the hydrocarbon and to provide diluent steam for the subsequent steam cracking of the vaporized products recovered from the second flash drum separator. The vaporized products, which are produced by passing the feed through the convection section of the second cracking zone and by steam stripping, are passed overhead from the flash drum by way of line 14 into the convection section of the second cracking furnace and thence through the radiant section from which the cracked products are recovered. The vapor leaving the separator is cooled about 20°-200° F. to

condense a small part of the vapor stream in a partial condenser 15. The condensed portion is used to scrub or wash the vapor stream to remove droplets or mist particles that are carried by the vapor stream. Removal of the droplets are necessary to prevent fouling of the steam cracker coil by heavy fractions contained in said droplets. The residue from the second flash drum separator, which is in liquid phase, is withdrawn from the flash drum separator 12 by way of line 14.

What is claimed is:

1. A process for cracking a hydrocarbon feedstock which comprises:
 - a. passing feedstock containing materials having boiling points above and below 450° F. into the convection section of a steam cracking furnace to vaporize the materials in the feedstock boiling below about 450° F.;
 - b. introducing the vaporized and unvaporized fractions of the feedstock into a first separation zone;
 - c. recovering the vaporized fraction of the feed from the first separation zone and passing said vaporized fraction, with steam, into the cracking zone of a first steam cracking furnace;
 - d. withdrawing the unvaporized fraction of the feedstock from the first separation zone and passing said unvaporized fraction into the convection section of a second steam cracking furnace, to vaporize those materials boiling below about 1,100° F.;
 - e. passing the vaporized and unvaporized fractions formed in step (d) into a second separation zone;
 - f. introducing from about 0.1 to about 2.0 pounds of steam per pound of hydrocarbon into said second separation zone; and thereafter
 - g. recovering the vaporized fraction and steam from the second separation zone and introducing said fraction containing steam into the cracking zone of the second steam cracking furnace.
2. The process of claim 1 wherein from about 5 to about 50 vol. percent of the materials in the feedstock have a boiling point above 900° F.
3. The process of claim 1 wherein the first cracking zone is operated under cracking conditions which are optimum for cracking a naphtha fraction.
4. The process of claim 1 wherein the second cracking zone is operated under cracking conditions which are optimum for cracking a gas oil fraction.
5. A process for cracking a hydrocarbon feedstock which comprises:
 - a. passing a feedstock containing materials having boiling points above and below 450° F. into the convection section of a steam cracking furnace to vaporize the materials in the feedstock boiling below about 450° F.;
 - b. introducing the vaporized and unvaporized fractions of the feedstock into a first separation zone;
 - c. recovering the vaporized fraction of the feedstock from the first separation zone and passing said vaporized fraction, with steam, into the cracking zone of the first steam cracking furnace;
 - d. withdrawing the unvaporized fraction of the feedstock from the first separation zone and passing said unvaporized fraction, with steam, into the convection section of a second steam cracking furnace, to vaporize those materials boiling below 1,100° F.;
 - e. passing the vaporized and unvaporized fractions formed in step (d) into a second separation zone;
 - f. recovering the vaporized fraction and steam passing overhead from the second separation zone and introducing said fraction containing steam into the cracking zone of the second steam cracking furnace.
6. The process of claim 5 wherein from about 5 to about 50 vol. percent of the materials in the feedstock of a boiling point above 900° F.

7. The process of claim 5 wherein the first cracking zone is operated under cracking conditions which are optimum for cracking the naphtha fraction.

8. The process of claim 5 wherein the second steam cracking zone is operated under cracking conditions which are optimum for cracking a gas oil fraction.

9. The process of claim 5 wherein about 0.1 to about 2.0 pounds of steam per pound of hydrocarbon is introduced into the second separation zone.

10. A process for cracking a crude hydrocarbon feedstock which comprises:

- a. passing a feedstock wherein about 5 to about 50 percent of the materials in said feedstock have a boiling point above 900° F. into the convection section of a first steam cracking furnace to vaporize materials in the feedstock boiling below about 450° F.;
- b. introducing the vaporized and unvaporized fractions of the feed into a first separation zone;
- c. recovering the vaporized fraction of the feed from the first separation zone and passing said vaporized fraction, with from about 0.4 to about 0.7 pounds of steam per pound of hydrocarbon, into the cracking zone of the first steam cracking furnace;
- d. withdrawing the unvaporized fraction of the feed from the first separation zone and passing said unvaporized fraction into the convection section of a second steam cracking furnace to vaporize those materials boiling below about 1,100° F.;
- e. passing the vaporized and unvaporized fractions formed in step (d) into a second separation zone;
- f. introducing from about 0.2 to about 0.7 pounds of steam per pound of hydrocarbon into said second separation zone;
- g. recovering the vaporized fraction and steam passing overhead from the second separation zone and introducing said fraction containing steam into the cracking zone of the second steam cracking furnace.

11. The process of claim 10 when the first separation zone is operated at a pressure in the range of from about 30 to 100 p.s.i.g.

12. The process of claim 11 wherein the temperature in the convection section of the first steam cracking furnace is in the range of from about 450°-750° F.

13. The process of claim 12 wherein the vaporized feed is cracked in the cracking zone of the first steam cracking furnace at a temperature at the outlet of the furnace coil between about 1,500° to about 1,700° F. with a residence time in the range of from about 0.1 to about 0.5 seconds and a steam dilution of about 0.4 to about 0.7 pounds of steam per pound of hydrocarbon feed.

14. The process of claim 13 wherein the convection section of the second steam cracking furnace is at a temperature in the range of from about 600° to about 900° F. fraction introduced into the cracking zone of the second steam cracking furnace comprises about 17 to about 38 wt. percent steam.

15. The process of claim 14 wherein the vaporized fraction introduced into the cracking zone of the second steam cracking furnace comprises about 17 to about 38 wt. percent steam.

16. The process of claim 15 wherein the vaporized fraction containing steam which is introduced into the cracking zone of the second steam cracking furnace is cracked at a temperature at the outlet of the furnace coil at a temperature between about 1,350° to 1,700° F., said vaporized fraction having a residence time in the cracking zone of from about 0.3 to about 0.6 second.

17. The process of claim 16 wherein about 50 vol. percent of the materials in the feedstock have a boiling point above 900° F.

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