

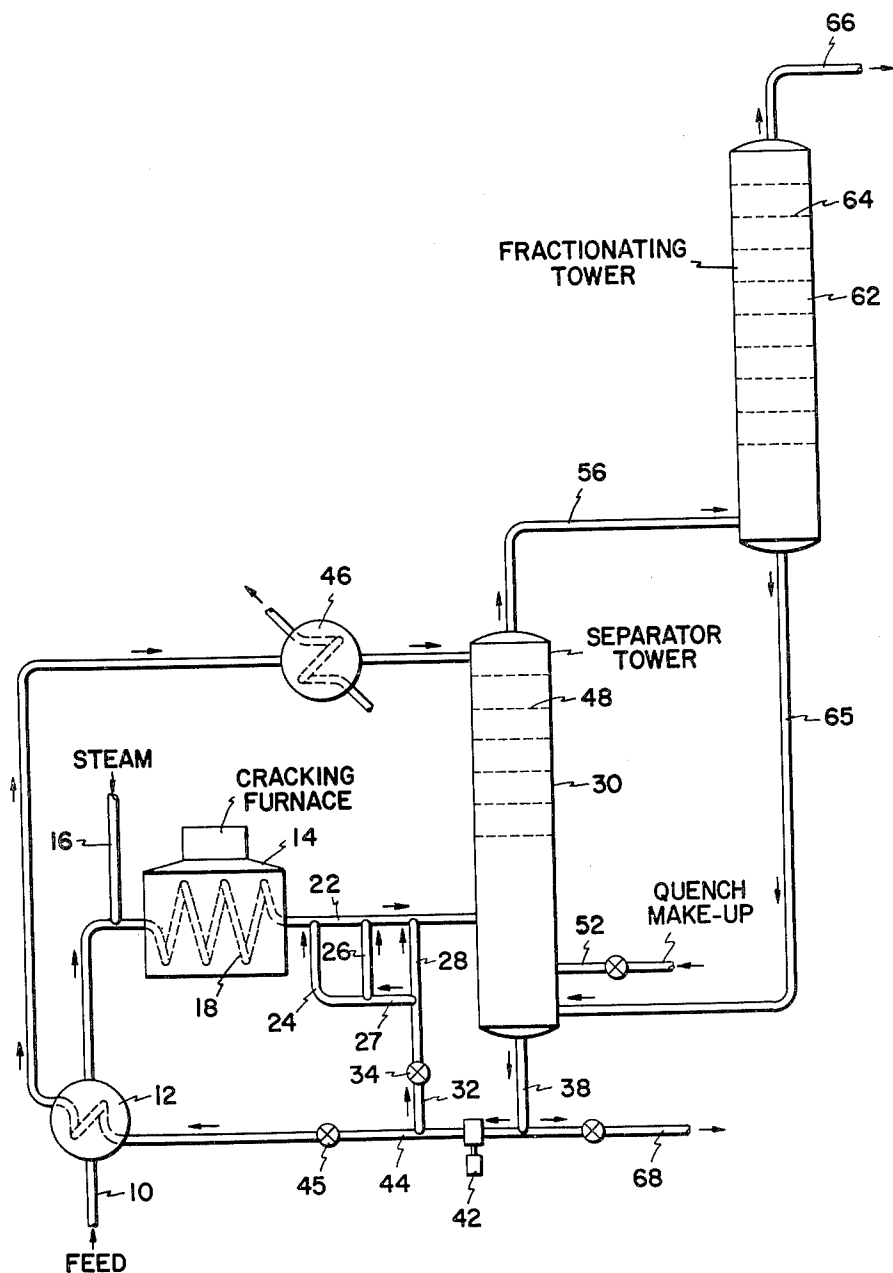
Nov. 20, 1962

M. B. AMIS ET AL

3,065,165

THERMAL CRACKING OF HYDROCARBONS

Filed Nov. 24, 1959



Maurice Brewer Amis
Samuel Winfield Wilson

Inventors

By *George J. J. J.*

Attorney

1

3,065,165

THERMAL CRACKING OF HYDROCARBONS

Maurice Brewer Amis and Samuel Winfield Wilson, Baton Rouge, La., assignors to Esso Research and Engineering Company, a corporation of Delaware

Filed Nov. 24, 1959, Ser. No. 855,098

5 Claims. (Cl. 208—48)

This invention relates to high temperature thermal non-catalytic cracking of hydrocarbons to produce olefins, diolefins and aromatic hydrocarbons, and more particularly relates to steam cracking in which an improved quench make-up and quench medium are used to quench the cracked products.

Various processes have been described in the prior art on high temperature thermal cracking or steam cracking of hydrocarbons including high boiling liquid hydrocarbons, such as residual oils and gas oils, and lower boiling hydrocarbons such as naphtha, and hydrocarbon gases such as ethane, propane, etc. to produce olefins such as ethylene, propylene, diolefins such as butadiene and aromatic hydrocarbons such as benzene, toluene etc. In these high temperature cracking processes it is necessary to quench the products from the cracking zone, that is, chill or cool them suddenly and rapidly to a lower temperature to prevent or minimize side reactions which reduce yields of desired products and increase yields of undesired products.

In the prior art there are numerous disclosures of different quenching agents or mediums and among these are high boiling hydrocarbons, lower boiling hydrocarbons, water, steam etc. In many cases fouling occurs at or beyond the quench point or region and the process must be terminated to clean the equipment. In one process of cracking kerosene or heavy naphtha a cycle oil from catalytic cracking (boiling between about 406° F. and 634° F.) was considered a satisfactory quench make-up and the process operated for extended periods with no difficulty in the quenching step but with some fouling. Then, at a later date it became expedient to feed a mixed light and heavy naphtha to the unit and shortly after this change, fouling of the equipment occurred by deposition of tars and solids and resulted in inability to maintain satisfactory tower top temperature due to fouling of the cooler for the reflux liquid and, of the separator tower.

The amount of naphtha mixture passing to the cracking step was reduced. The cycle oil used as a quench make-up for the heavy naphtha feed was unsatisfactory for use in the quenching of the cracked products from the mixed naphtha feed and on subsequent operations when using light naphtha feed.

Increasing the rate of quench make-up did not alleviate the problem. However, on changing the quench make-up from the light catalytic cycle oil (boiling range 400–630° F.) to aromatic concentrate, the operators were able to increase the feed rate to the cracking furnaces from about 10,500 b./d. to 12,500 b./d. A section of the unit was subsequently shut down for cleaning, and, following the start-up using aromatic concentrate for quench make-up, no further difficulty was encountered.

After much experimentation and research it was discovered that satisfactory quenching could be obtained by using an aromatic hydrocarbon concentrate as quench make-up having a high boiling point. As a result of continued recycling of quench oil from the separator tower to the transfer line and back to the separator tower, unsaturated hydrocarbons formed in the cracking zone and which remain liquid in the separator tower are polymerized to form high boiling highly condensed pitch bodies which are difficultly soluble in the quench oil. These are the materials which cause fouling of the separator tower,

2

quench oil lines, feed heat exchanger and reflux liquid cooler. The important characteristics of aromatic concentrate are (1) it remains as a liquid in the separator tower and in part at the quench point or points and (2) it dissolves the highly condensed pitch bodies mentioned above.

The aromatic hydrocarbon concentrate of the present invention has been used as a quench make-up in high temperature thermal or steam cracking and has been working satisfactorily without fouling or deposition of solids in the separator tower, quench lines, heat exchanger or reflux liquid cooler. Improved separator tower operation and overhead product have resulted. In addition the capacity of the cracking unit has been increased over that originally possible using the light catalytic cycle oil.

The aromatic hydrocarbon concentrate is an improved quench make-up when cracking mixtures of light and heavy naphthas, light naphthas alone or heavy naphthas alone to permit a greater throughput of hydrocarbon feed than heretofore when using other quench make-up. In addition, deposition of solids as a result of coking or polymerization of the cracked products at the quench point or points or beyond is eliminated so that the cracking runs can be extended.

Another advantage results from the high boiling point of the aromatic concentrate so that if for some reason water is present or collects in the separator tower, as occurs in a plant start-up, the quench medium is not lost as a result of steam distillation in the bottom of the separator tower. This has been the case when using light catalytic cycle oil and has resulted in fouling of the quench point or points.

In the drawing the FIGURE diagrammatically shows one form of apparatus adapted for carrying out the present invention but the invention is not limited to the exact apparatus shown as changes and modifications may be made in the apparatus without departing from the spirit of the invention.

Referring now to the drawing, the reference character 10 designates a line through which the hydrocarbon feed, for example, is introduced at a rate of between about 10,000 and 14,000 barrels per day. The hydrocarbon may be a light naphtha fraction or a heavy naphtha fraction or may be a wide cut naphtha fraction. The naphtha feed may be a virgin feed and when using a light naphtha fraction the boiling point is between about 60° F. and 220° F. and when using a heavy naphtha fraction the boiling range is between about 290° F. and 440° F. The naphtha or other feed is passed through heat exchanger 12 to preheat the naphtha feed to a temperature between about 275° F. and 305° F. and the preheated hydrocarbon material is then passed on through line 10 into cracking furnace or furnaces 14. Before being introduced into the cracking furnace the hydrocarbon feed is mixed with steam heated to a temperature of about 340° F. and 360° F. The amount of steam used is between about 70 and 85 mol percent of the oil feed plus steam.

The cracking furnace (or furnaces) is one which contains a heating coil 18 and the naphtha is heated to a high temperature in the furnace between about 1200° F. and 1500° F. and the time of reaction or time of residence of the naphtha at the high temperature is maintained from a few seconds such as two seconds to a fraction of a second as, for example, 0.5 second depending on the temperature used, the longer times being used with the lower temperatures. The pressure during cracking is between about 17 p.s.i.g. and 20 p.s.i.g.

The cracked products at the high temperature leave the cracking furnace through line 22 and are immediately quenched to a temperature of between about 600° F. and

700° F. by the introduction into line 22 of a quenching medium through spaced lines 24 or 26 or 28, but preferably line 24 and the quenched mixture is introduced into the bottom portion of separator tower 30. With the present invention fouling of and coking in the transfer outlet line 22 and in the bottom of tower 30 are prevented. The quench lines 24, or 26 or 28 are fed from a manifold from line 27 and all the quench medium comes from line 32 controlled by valve 34. A single quench point is preferred although a greater number of quench lines may be used. The quench lines 24, 26 and 28 are spaced horizontally along the outlet transfer line 22 leading from the cracking furnace 14 to the separator tower 30.

The quench make-up, which will be specifically described hereinafter, forms part of the quench medium which is withdrawn from the bottom of separator tower 30 along with tar or bottoms and heavy oils produced in the cracking process through line 38 at a temperature between about 400° F. and 450° F. and passed by pump 42 through line 44 provided with a valve 45. The aromatic concentrate quench make-up forms about 75 to 90% by volume of the bottoms fraction withdrawn through line 38 which serves as a quench medium and as cooling liquid to the top of tower 30. Liquid withdrawn from the bottom of separator tower 30 through lines 38 and 44 forms the quench and reflux medium, part is passed through line 32 and to the quench lines 24, or 26 or 28. A portion equivalent to the tar and heavy oil produced plus quench make-up is purged via line 68 and the rest is passed through line 44 and valve 45 through the indirect heat exchanger 12 and thence through cooler 46 for cooling the stream to a temperature between about 200° F. and 250° F. to form the reflux medium for the top of tower 30.

In passing through the heat exchanger 12, the hydrocarbon feed is preheated and the liquid reflux medium is cooled to between about 370° F. and 385° F. Before the aromatic concentrate was adopted for use as a quench make-up and as reflux for the tower 30, fouling of the heat exchanger 12 and cooler 46 occurred by the reflux liquid. Use of the aromatic concentrate eliminated this fouling of the exchanger 12 and cooler 46.

Separator tower 30 is provided with horizontally arranged vertically spaced perforated plates 43 such as bubble tower plates, pierced plates, or the like, in the upper portion thereof to effect a rough fractionation of the cracked and quenched products and between the tar plus quench make-up and lower boiling materials. During fractionation in the tower 30, high boiling tar plus high boiling aromatic hydrocarbons plus quench make-up boiling above about 400–450° C. are separated and withdrawn as part of the bottoms through line 38.

The cracked products from the furnace or furnaces 14 are introduced into the bottom portion of the separator tower 30 below the lowermost plate 43. The pressure in tower 30 is between about 14 p.s.i.g. and 15 p.s.i.g. Also introduced into the process and into the bottom portion of the separator tower below the lowermost plate 43 is quench make-up of the aromatic concentrate which is used in the quenching medium and this quench make-up is introduced continuously through line 52 at a rate between about 400 and 800 barrels per day. Other points of introduction may be used.

The aromatic concentrate which is used as a quench make-up is a high boiling aromatic fraction which is extremely refractory or hard to crack so that substantially no cracking of it occurs during the quenching step and so high boiling that in and following the quenching step, a portion of the quenching medium remains liquid. The amount of quenching medium including quench make-up passing through line 32 may be between about 20,000 and 30,000 barrels per day when feeding between about 12,000 and 14,000 barrels of oil per day (or between about 1.5 and 2.5 barrels per day of oil feed).

The ratio of quench make-up to oil feed may be between 1/17 and 1/35. The amount of quenching reflux pass-

ing through line 44 and valve 45 may be between about 4.3 and 5.0 barrels per day of oil feed when feeding about 12,000 and 14,000 barrels of oil per day (or between about 50,000 and 70,000 barrels of oil quench reflux per day). The quenching oil remains liquid in the bottom of the separator tower 30 which is at a temperature between about 400° and 460° F.

The aromatic concentrate of the present invention is produced by treating a mixture of heavy catalytic cycle oil and heavy virgin gas oil with phenol extract from the treating of a lubricating oil of a mixture of phenol extracts from the treatment of lubricating oils. The spent phenol or extract phase from lube oil treating was obtained by phenol extraction of lubricating oils, such as solvent 100 neutral, solvent 150 neutral, solvent 250 neutral, solvent 280 neutral and solvent 450 neutral, the number between solvent and neutral indicating the average Saybolt Universal viscosity at 100° F. The lube oil fraction may also be Barossa 43 (43 SSU at 210° F.), Barossa 56 (56 SSU at 210° F.) or Bright Stock (SSU 160–170 at 210° F.) The spent phenol or extract phase from lube oil treating is preferred but spent phenol from other sources or fresh phenol may be used.

In one example, a heavy catalytic cycle or clarified oil having a boiling range between about 538° F. and 1047° F. at 96% recovery was mixed with a heavy virgin gas oil having a boiling range between about 655° F. and 1047° F. at 73.5% recovery and the proportions of the cycle oil (clarified oil) and virgin gas oil were in the ratio of 1.4/1 to 1/1.4. This mixture of heavy cycle oil and heavy virgin gas oil was treated with a phenol extract.

Phenol extract was obtained by extracting a lubricating oil with phenol in a liquid-liquid extraction unit. Fresh phenol was used in treating the lubricating oil in a solvent extraction step and following the extraction, the extract phase containing the phenol was separated from the raffinate phase. This extract phase containing the phenol was used for treating the mixture of catalytic cycle oil and heavy virgin gas oil to obtain the aromatic concentrate. About 1 volume of the mixture of the catalytic cycle oil and heavy virgin gas oil was treated with about 1.2 to 1.4 volumes of the spent phenol or phenol extract containing about 12.5% water and about 16% oil to obtain an extract phase and a raffinate phase. The extract phase was then separated into a phenol phase and a hydrocarbon phase by distillation. The latter is called aromatic concentrate which forms the quench make-up in the present invention. The phenol extract from the lube oil extraction step will contain about 16.5 vol. percent of the total oil in the feed to the heavy catalytic cycle oil-heavy virgin gas oil extraction.

The aromatic concentrate prepared as above described has the following typical physical characteristics:

° API gravity	40.5
Pour point	45° F.
Sulfur content	1.3 wt. percent
Saybolt Universal viscosity at 210° F.	77 seconds
Aniline point	42.4° F.
Asphaltenes	1.3 wt. percent
Aromatic rings	61.0 do.
Conradson carbon residue	7.4 do.

Boiling Points at 10 mm. Pressure	° F.	Range, ° F., Atmospheric Pressure
Initial	200	428
5%—	320	573
10%—	354	615
50%—	478	763
70%—	542	835
80%—		919
90%—		972
Above 90%—	too heavy to distill	1047

Instead of using only one phenol extract, a mixture of phenol extracts may be used. For example, in some re-

5

fineries there are two lubricating phenol extraction sections, one section being used for treating a low viscosity oil stock, such as solvent 150 neutral, and the other section being used for a high viscosity oil stock, such as solvent 450 neutral. The spent phenol or phenol extracts from the two sections are combined in about equal parts by weight prior to treating the mixture of the heavy catalytic cycle oil and the heavy virgin gas oil above referred to. The mixed phenol extracts are used in about 1.2 to 1.4 volumes to 1 volume of the mixture of heavy cycle oil and heavy virgin gas oil just described. The extract phase was separated from the raffinate phase and the extract phase was separated into a phenol phase and a hydrocarbon oil phase which forms the aromatic concentrate. The aromatic concentrate separated from the resulting phenol extract phase had about the same characteristics as those just specifically given for a typical aromatic concentrate useful in the present invention.

The fractionated and vaporous reaction products pass overhead from the separator tower 30 through line 56 and are introduced into the bottom of fractionating tower 62 which is provided with horizontally arranged, vertically spaced fractionating plates 64 of any conventional form. Line 56 opens into the bottom of tower 62 below the lowermost plate 64 therein. Fractionated gases and vapors pass overhead from the fractionating tower 62 through line 66 and are then passed through a condenser (not shown) to separate high boiling liquids (C_3 and heavier) including aromatic compounds such as benzene and toluene and olefins and diolefins such as isoprene, pentene, hexene etc. from normally gaseous hydrocarbon (C_3 and lighter) products which are further separated into desired fractions. These recovery steps are not shown in the drawing. Fractionating tower 62 is maintained at a pressure between about 10 p.s.i.g. and 12 p.s.i.g.

The bottom fraction from fractionating tower 62 is withdrawn through line 65 and returned to the bottom of the separator tower 30 below the lowermost plate 48 therein. Other points of introduction are also satisfactory. This bottom fraction serves as additional cooling liquid for the bottom of separator tower 30. The bottom portion of fractionating tower 62 is maintained at a temperature between about 315° F. and 320° F. The top of the fractionating tower 62 is maintained at a temperature between about 240° F. and 270° F.

A portion of the bottoms fraction withdrawn from the separator tower 30 is withdrawn from the process through valved line 68 as a purge liquid. Between about 500 and 900 barrels per day of bottoms (tars plus quench make-up) are withdrawn through line 68 when feeding between about 12,000 and 14,000 barrels of oil per day. This purging line or withdrawing line 68 removes aromatic concentrate equivalent to the addition rate but this does not result in downgrading the stream withdrawn, as the stream withdrawn from the bottom of the separator tower 30 normally goes to fuel oil or to carbon black production.

From the above description it will be seen that aromatic concentrate make-up is introduced into the bottom of separator tower 30 and the bottoms withdrawn from the tower 30 through line 38 will contain tar and the aromatic concentrate above described. The aromatic concentrate-containing stream withdrawn through line 38 is then used partly as a quenching medium by being passed through quench lines 24, or 26 or 28, but preferably line 24 while another portion is passed through line 44, valve 45, through indirect heat exchanger 12 and cooler 46. The stream withdrawn from the bottom of separator tower 30 through line 38 is in part withdrawn through line 68 and discarded from the process and this forms about 0.6% by volume of the total stream withdrawn through line 38. About 30 to 40% by volume of the total stream withdrawn through line 38 is passed through lines 44 and 32 as quench oil, and the rest passed through line 44 and valve 45 as reflux or cooling medium which is introduced into the upper portion of the separator tower 30. The

6

cooled aromatic concentrate introduced through line 44 after having passed through the cooler 46 passes downwardly through the tower 30 and scrubs out heavy ends from the cracked and quenched vaporous and gaseous products passing upwardly through the separator tower 30.

The quench oil or medium containing about 80–90% by volume of aromatic concentrate added through line 52 is continuously introduced into the transfer outlet line 22 from the cracking furnace through lines 24, or 26 or 28 so as to prevent coking of the outlet line 22 and to prevent fouling of the line 22. Fouling of the bottom portion of the separator tower 30 is also prevented. The other portion of the quenching and reflux medium containing the aromatic concentrate which is passed through line 44 and valve 45 is passed through indirect heat exchanger 12 and cooler 46 and with aromatic concentrate as quench make-up there is no fouling of the heat exchanger 12 and the cooler 46 or the internals of tower 30.

In a previous operation where a light catalytic cycle oil was used as the quenching medium, fouling of the bottom portion of the separator tower 30 and fouling of heat exchanger 12 and cooler 46 by the reflux liquid were experienced and required shut down of the unit after a relatively short run. The unit had to be shut down even though the amount of naphtha feed to the contacting unit was reduced in order to continue operation at a reduced rate of oil feed. After the process was changed to use the aromatic concentrate quench medium of the present invention there was no evidence of coking and fouling of the outlet line 22 from the furnace 14 and also there was no evidence of fouling of the bottom of the separator tower 30, the heat exchanger 12, the cooler 46 or the internals of tower 30. In addition, the naphtha feed to the cracking furnace 14 was increased over 1000 barrels per day over that used when the light cycle oil stock was used as a quenching medium.

In a specific example about 12,000 barrels per day of a mixture of 40–60% of light virgin naphtha and 60–40% of heavy virgin naphtha, the mixture having a boiling point range of between about 167° F. and 420° F., and about 68–70 mol percent of steam per day at a temperature of about 350° F. were introduced into and passed through the cracking furnace 14 under a pressure of about 18 p.s.i.g. and wherein the reaction mixture was maintained at a temperature of about 1300° F. for about 1 second. The cracked products were continuously and immediately quenched by the continuous introduction of about 25,000 barrels per day of bottoms from line 32 containing about 80–90% by volume of the aromatic concentrate quench liquid of the type above described to reduce the temperature of the cracked product stream to about 640° F.

Preferably the first quench point in the transfer line shown as quench point 24 in the drawing is used. About 400–800 barrels per day of the aromatic concentrate quench make-up liquid are introduced into the bottom of the separator tower 30 through line 52. The bottoms passing through line 32 contains about 80–90% by volume of aromatic concentrate.

The bottom of the separator tower 30 is at about 440° F. and the bottoms withdrawn through line 38 contain about 80–90 vol. percent of aromatic concentrate quench liquid of the type above described. About 500–900 barrels per day of the bottoms stream 38 is withdrawn from the process through line 68. About 60,000 barrels per day of the bottoms stream 38 which is passed through line 44 as reflux or cooling liquid is passed to the top of separator tower 30. The aromatic concentrate quenching and reflux liquid passing through line 44 and introduced into the top of the separator tower 30 is at a temperature of about 220° F.

The vaporous and gaseous products passing overhead through line 56 are at a temperature of about 340–360° F. and contains normally gaseous unsaturated hydrocarbons, olefinic acid aromatic hydrocarbons and some heavy ends boiling in the gasoline range and some low boiling aro-

7
matic gas oil boiling to about 800° F. These vaporous and gaseous products are introduced into the bottom of the fractionating tower 62 where the bottom of the tower is maintained at a temperature of about 315–330° F. and the top of the fractionating tower 62 is maintained at a temperature of about 240° F. The bottoms from fractionating tower 62 are withdrawn through line 65 and these bottoms contain about 10 vol. percent of material boiling from about 200° F. to 450° F. and about 90 vol. percent boiling from about 450° F. to 700° F., the total stream having a gravity of about 10° API. About 2000–3000 barrels per day of bottoms are passed through line 65 to the bottom of separator tower 30. The tower 62 is under a pressure of about 10–12 p.s.i.g.

The vaporous and gaseous products separated in the fractionating tower 62 and passing overhead through line 66 are further cooled and condensed and passed through conventional separating means to recover the usual olefins, diolefins, benzene, toluene etc. obtained in conventional steam or thermal cracking processes.

What is claimed is:

1. In a process wherein mixed naphtha feed is thermally cracked at a temperature above about 1200° F. in a cracking zone in the presence of 70 to 80 mol percent steam to produce unsaturated normally gaseous hydrocarbons and liquid aromatic, olefinic and diolefinic hydrocarbons, the improvement which comprises quenching the cracked products to a temperature below about 700° F. by injecting into the cracked products leaving said cracking zone a quenching medium consisting essentially of a high boiling aromatic refractory concentrate a portion of which remains in liquid form during and after the quenching step, said aromatic concentrate being made by treating a mixture which contains 40–60% by volume of heavy catalytic cycle oil which boils above about 530° F. and the rest heavy virgin gas oil which boils above about 655° F. with a phenol-containing liquid to obtain a phenol extract and recovering the aromatic concentrate from the phenol extract phase, said phenol-containing liquid comprising a phenol extract obtained when treating lubricating oil in a liquid-liquid extraction step.

2. In a process wherein hydrocarbons are thermally cracked at a temperature above about 1200° F. in the presence of steam in a cracking zone to produce unsaturated normally gaseous hydrocarbons and aromatic, olefinic and diolefinic hydrocarbons and the cracked products are quenched and separated in a separating zone into a bottoms liquid fraction and a vaporous fraction and the bottoms liquid fraction is used in part as quenching liquid and in part cooled by indirect heat exchange in a cooling zone and used as reflux liquid at the top of said separating zone and fouling of the quench region, the bottom of said separating zone and the cooling zone occurs, the improvement which comprises preventing fouling of the quenching region, the bottom portion of said separating zone and said cooling zone by using a quench-reflux liquid consisting essentially of a high boiling aromatic concentrate liquid which is refractory and at least in part remains liquid during and following the quenching step and which is made by treating a mixture which contains 40–60% by volume of heavy catalytic cycle oil which boils above about 530° F. and the rest heavy virgin gas oil which boils above about 655° F. with a phenol-containing liquid to obtain a phenol extract and recovering the aromatic concentrate from the phenol extract phase, said phenol-containing liquid comprising spent phenol separated from the raffinate

phase in treating a lubricating oil in a liquid-liquid solvent extraction step.

3. In a process wherein hydrocarbons are thermally cracked at a temperature above about 1200° F. in the presence of about 70–80 mol percent steam in a cracking zone to produce unsaturated normally gaseous hydrocarbons and aromatic, olefinic and diolefinic hydrocarbons and the cracked products are quenched and separated in a separating zone into a bottoms liquid fraction and a vaporous fraction and the bottoms liquid fraction is used in part as quenching liquid and in part cooled by indirect heat exchange in a cooling zone and used as reflux liquid at the top of said separating zone and fouling of the quench region, the bottom of said separating zone and the cooling zone occurs, the improvement which comprises preventing fouling of the quenching region, the bottom portion of said separating zone and said cooling zone by using a quench-reflux liquid consisting essentially of a high boiling aromatic concentrate liquid which is refractory and at least in part remains liquid during and following the quenching step and which has the following typical characteristics:

*API gravity	-----	0.5
Pour point	----- ° F.	45
Sulfur content	----- wt. percent	1.3
Saybolt Universal viscosity at 210° F.	----- seconds	77
Aniline point	----- ° F.	42.4
Asphaltenes	----- wt. percent	1.3
Aromatic rings	----- do	61.0
Conradson carbon residue	----- do	7.4

Boiling Points at 10 mm. Pressure	° F.	Range, ° F., Atmospheric Pressure
Initial	200	428
5%	320	573
10%	354	615
50%	478	703
70%	542	835
80%		919
90%		972
Above 90%	too heavy to distill	1047

4. A process according to claim 2 wherein the quench reflux liquid is withdrawn from the bottom portion of said separating zone and a portion thereof discarded and make-up high boiling refractory aromatic concentrate of the character defined is introduced into the bottom portion of said separating zone.

5. A process according to claim 3 wherein said aromatic concentrate liquid is obtained by treating a mixture which contains 40–60% by volume of heavy catalytic cycle oil which boils above about 50° F. and the rest heavy virgin gas oil which boils above about 655° F. with a phenol-containing liquid to obtain a phenol extract and recovering the aromatic concentrate liquid from the phenol extract phase.

References Cited in the file of this patent

UNITED STATES PATENTS

2,366,521	Guichet	Jan. 2, 1945
2,727,854	Brown et al.	Dec. 20, 1955
2,777,802	Peet	Jan. 15, 1957
2,889,265	Borey et al.	June 2, 1959
2,899,475	Davison	Aug. 11, 1959
2,910,428	Thomas et al.	Oct. 27, 1959
2,951,029	Johnston et al.	Aug. 30, 1960