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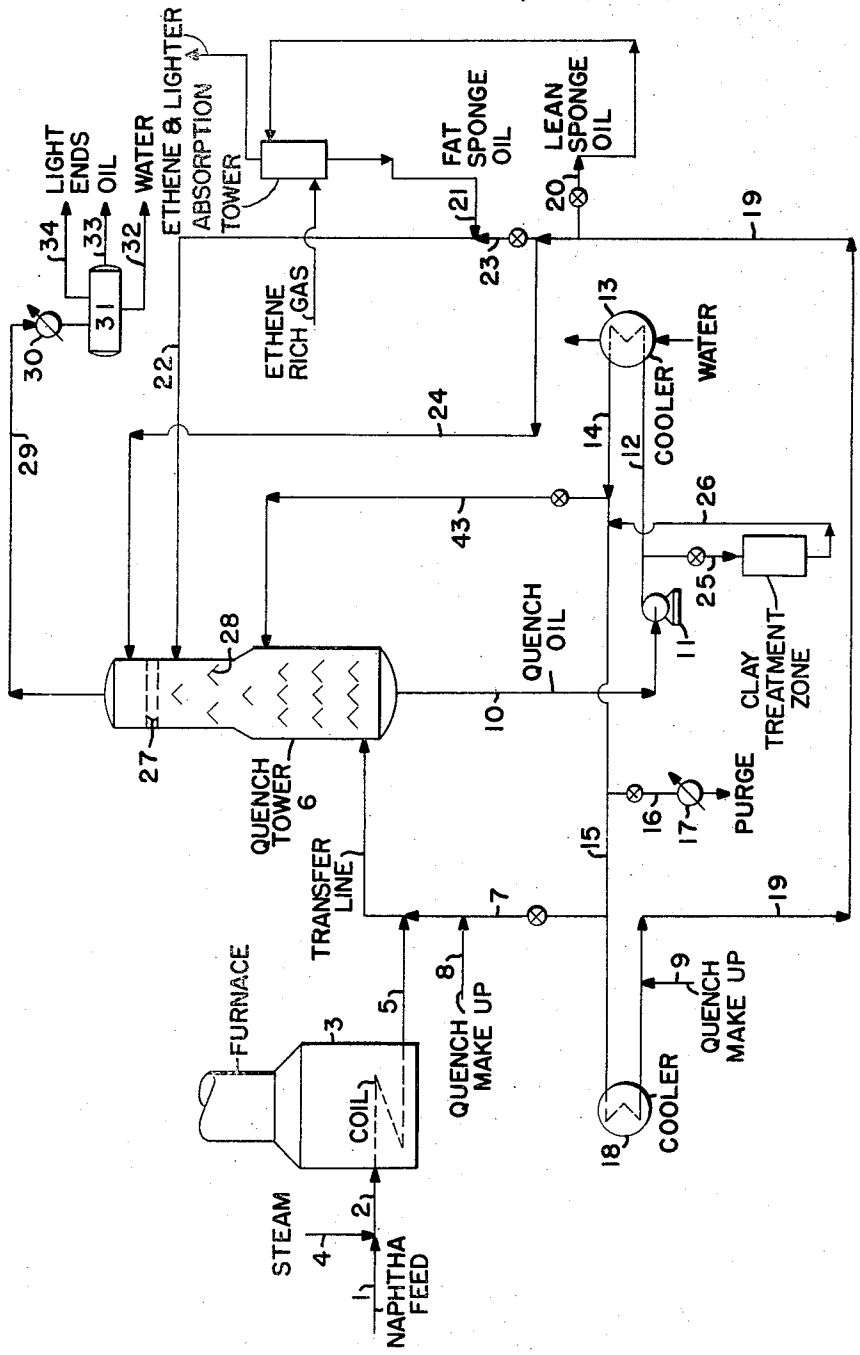

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NAPHTHA STEAM-CRACKING QUENCH

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This invention relates to a method of quenching hot gaseous effluent from steam-cracked naphtha products transferred from a cracking coil outlet into a quench tower for separation of the products into fractions. It deals wtih a simplified, efficient and economical method of quenching the cracked products as they are transferred to the quench tower and operating the quench tower for quick separation of gases and naphtha vapor from a residual fraction.

In steam-cracking virgin naphtha fractions to produce high yields of C_2 to C_5 olefins and diolefins using cracking conditions of high temperatures and low pressures, quick quenching and fast separation of products are necessary. The high temperatures and the high reactivity of the cracked products leaving the cracking coil are factors in the tendency toward polymer tar and coke formation.

Minimizing formation of the tar and coke to increase the yields of the low boiling olefinic hydrocarbons is an object of the present invention. Attainment of this object involves the use of a quench oil having suitable boiling characteristics and refractoriness to cracking under the quenching conditions, and the use of large quantities of the quench oil cooled and circulated to appropriate points in the quenching system.

Simultaneously with the quenching, it is important to effect a rapid separation of the volatile components to be recovered, especially the volatile and valuable C_2 to C_5 olefins and diolefins. For this reason, the quench tower is not constructed in the manner of conventional fractionating towers which have a large number of plates that cause holdup in the flow of liquid and vapors.

The manner of quickly quenching the high temperature steam-cracked naphtha products and obtaining the quick separation of these products into suitable fractions will be described with reference to the accompanying drawing.

In the drawing is shown a diagrammatic flow plan of means and steps found satisfactory for accomplishing the objects of the invention.

Referring to the drawing, a narrow cut virgin naphtha feedstock for the cracking starts from supply drum 1 and is passed by line 2 into a cracking coil located within the cracking furnace 3, where the cracking coil is exposed to high intensity radiant heat. The preferred feedstock for cracking is a naphtha containing principally a C_5 or C_6 to C_{10} saturated aliphatic hydrocarbons, i.e., paraffins and naphthenes, boiling principally in the range of 70° F. to 220° F. The feedstock may have a somewhat narrower or broader boiling range, e.g., in the range of 0° to 330° F.

A suitable proportion of steam is added to the hydrocarbon fed from line 4, generally to make the resulting cracking mixture contain 60 to 90 mole percent steam, thus lowering the partial pressure of the hydrocarbons to substantially less than half the total pressure. In the cracking coil located within the furnace 3, the naphtha hydrocarbons mixed in vapor phase with steam are

heated in the range of 1350° to 1500° F., preferably above 1400° F. The total pressure of the cracked reaction mixture is in the range of 1 to 5 atmospheres and preferably less than 30 pounds per square inch absolute. The cracked reaction mixture of steam and hydrocarbons passes through the cracking coil in furnace 3 in a fraction of a minute, then on leaving the outlet of the coil is transferred by transfer line 5 to the quench tower 6. A sufficient amount of relatively cool quench oil is injected from line 7 into transfer line 5 at one or more points to effect a rapid lowering of temperature in the cracked reaction products. This transfer line cooling from a coil outlet temperature that is above 1350° F. to a temperature in the range of 450° to 650° F. is effected in a few seconds in the stream passing through the transfer line.

The mixture of the cracked products and quench oil is preferably introduced to the bottom part of the quench tower at a temperature below 650° F. and preferably close to 500° F. The quench oil flow rate from line 7 into transfer line 5 has to be high with reference to the flow rate of the cracking coil effluent, e.g., from 3 to 6 parts by weight of quench oil per one part by weight of cracking coil effluent, the quench oil having a temperature in the range of 300° to 400° F.

To prevent excessive coking in the transfer line 5, the quench oil supplied from line 7 must be controlled in its polymer tar content, i.e., its content of materials which have a coke forming tendency. In using as a large proportion of the quench oil residual oil separated as bottoms in the quench tower 6, it is necessary to control the content of polymer tar by replacing a portion of the residual with an oil of lower polymer tar-forming reactivity, e.g., refractory oil from an extraneous source. This makeup oil may be added through line 8 to the quench oil line 7, but it is advantageously introduced into the residual oil recirculated to the quench tower 6 as by line 9.

A good refractory quench makeup oil is obtained by light cracking of gas oil, for example, a catalytic cracking or other kind of low temperature cracking, i.e., lower than used in steam-cracking. This oil is a distillate oil and preferably has an initial boiling point substantially above the end boiling point of the naphtha feed to the steam cracking coil and above the boiling range of vapors taken overhead from the quench tower 6, i.e., above 450° F. The upper end boiling point of the quench makeup oil is preferably no higher than 700° F. A preferred boiling range for the quench makeup gas oil is 500° or 525° to 660° F. The suitable gas oil makeup is stable in being less reactive under the quenching conditions than oil derived from the steam cracking.

When the quench makeup oil is added to recycled residual oil from quench tower 6 flowing through line 9, it becomes mixed with residual oil which is circulated to an upper part of the quench tower 6. The residual fraction withdrawn as bottoms from the quench tower 6 at a temperature of 450° to 600° F. through line 10 is passed by pump 11 through line 12 for cooling in heat exchanger 13. The partly cooled oil leaving the heat exchanger 13 at a temperature in the range of 300° to 400° F. through line 14 becomes divided into at least four streams. One stream of the partly cooled quench tower bottoms is passed through line 43 to a mid-portion of tower 6 for partial cooling of vapors flowing upwardly through tower 6. A purge stream of the quench tower bottoms is withdrawn from line 15, which is a continuation of line 14. A purge stream is withdrawn through line 16 and heat exchanger 17.

The transfer line quench oil stream is withdrawn from line 15 through line 7 which sends the quench oil into

the transfer line 5 at one or more points, as previously mentioned. A portion of the quench oil may be clay treated to remove polymer tars and then returned into circulation as quench oil. The remaining partly cooled residual oil continues in line 15 to be passed through heat exchange cooler 18 for cooling, and from there through line 19. Quench oil makeup, e.g., gas oil, is introduced into line 19 from line 9.

The quench oil flowing through line 19 is divided into two or more streams for particular purposes which will be further indicated. One part of the stream flowing through line 19 is diverted through line 20 to an absorption tower for use as a lean sponge oil which absorbs hydrocarbons higher boiling than ethene from an ethene-rich gas stream in processing the light ends. The resulting fat sponge oil containing absorbed hydrocarbons is returned through line 21 to be passed by line 22 into the quench tower 6 at a point intermediate the top of the tower and the point in which the stream from line 43 enters tower 6, and the absorbed hydrocarbons are released in said quench tower from said fat sponge oil. Valved connecting line 23 is useful for proportioning the amount of oil which is admixed from line 19 with the sponge oil that is returned to the quench tower. Another part of the main stream flowing through line 19 is passed through line 24 to a top part of the quench tower 6. This top quench stream introduced from line 24 has the relatively lowest temperature.

As an additional control of the polymer tar content in the residual oil circulated from the bottom of tower 6, a quantity of this oil is withdrawn from line 12 through line 25 for a clay treatment which removes polymer oils and the treated oil is returned to line 14 via line 26.

The interior of quench tower 6 is equipped with a few plates, 27, and with baffles 28, which may be in the form of inverted V-shaped sheds, for obtaining contact between liquid and vapor but allowing for fast flow of materials.

The necessary cooling is obtained in the upper part of the quench tower 6 by injecting each of the quench oil streams in suitable amounts and at proper temperatures at the several spaced points.

The temperature of the vapors at the top of the quench tower 6 is set to avoid condensation of water in the upper part of the tower. For the same reason, the quench oil flow in each of the several streams is controlled in temperature and flow rate to avoid water condensation in the upper part of the tower.

The gaseous stream that reaches the top of the quench tower to be taken overhead therefrom through line 29 contains steam-cracked hydrocarbon products boiling below 430° F., steam, and some hydrogen. This gaseous stream is passed via line 29 into cooling condenser 30 at a sufficiently low temperature to condense out water and hydrocarbons having more than five carbon atoms per molecule. The condensate is collected in the separating tank 31, wherein the liquid condensate is settled so that a lower water layer can be withdrawn through line 32 and condensed oil can be withdrawn from an upper liquid layer through line 33. Uncondensed gaseous hydrocarbon products containing principally olefins and diolefins having up to six carbon atoms per molecule are withdrawn from vessel 31 through line 34 to be subjected to light ends processing. The light ends processing steps are such as to recover ethene, propene, butenes, butadiene, etc.

As the present invention is principally concerned with the quenching operation, a more detailed explanation follows regarding the quench oil circuit.

The total flow rate of the main quench oil stream, i.e., residual oil from the bottom of quench tower 6, can be controlled by the circulating pump 11. Various temperature and pressure controlling means may be used.

Heat exchanger 13 lowers the temperature of the main quench oil stream from a temperature above 450° F., near 500° F., or higher to a temperature in the range of 300° to 400° F. A substantial part of the main quench stream thus lowered in temperature, e.g., about one-half or more, is led by line 7 to the transfer line 5 wherein a quick cooling of the cracking coil effluent is accomplished. The remaining part of the main quench stream is further cooled in heat exchanger 18 to lower its temperature from 300° F. or higher to a temperature in the range of 175° to 250° F. The heat exchangers extract large amounts of heat useful for producing steam.

A purged portion of the main quench stream withdrawn through line 16 is generally 1 to 10 percent of the main quench stream. To replace the purged amount, the fresh light gas oil quench makeup added through line 9 is approximately similar in amount.

The makeup quench oil may come from storage at a temperature about 100° F. or lower. This makeup oil is preferably blended with the hotter quench oil stream such as coming from the heat exchanger 18 so that the combined stream flowing through line 19 has a temperature in the range of 150° to 200° F., preferably close to 175° F. Thus, a portion of the oil flowing through line 19 is brought to a satisfactory temperature level for introduction to the top of quench tower 6 and therein gives adequate cooling without causing condensation of water.

A major portion of the stream flowing through line 19 is preferably passed into the quench tower through line 22 at a temperature 5 to 50 Fahrenheit degrees higher than the temperature of the top quench stream which flows through line 24. This intermediate stream will contain sponge oil, such as returned through line 21, and preferably has a temperature in the range of 175° to 200° F.

Line 43 introduces a third quench oil stream and this stream has a temperature preferably in the range of 350° to 400° F.

A favorable manner of proportioning the different quench streams sent into tower 6 is to have the intermediate quench oil stream from line 22 flow at a rate approximately three times that of the upper and lower quench streams sent into the upper part of tower 6, i.e., above the cracked product inlet. Altogether the total flow of quench oil from the streams to the mid-portion and upper part of quench tower 6 will amount to nearly half the flow rate of the main quench stream withdrawn from the bottom of tower 6, and this flow rate is in the order of 3 to 6 times the flow rate of hydrocarbons entering the cracking coils.

In the quench tower 6, the cracked vapors entering from the transfer line 5 pass up countercurrently to the successive quench oil washes to have their temperature lowered at a fast rate, for example, lowered from above 450° F. to a temperature in the range of 220° to 275° F., preferably close to 225° F. when the pressure is slightly above one atmosphere. A preferred mode of operation is illustrated further by the following example.

Example

Various virgin naphtha fractions may be used as the feedstocks of the steam-cracking. A preferred feed contains hydrocarbons boiling principally in the range of 70° to 220° F. The feed is cracked at temperatures close to 1400° F. in the presence of sufficient admixed steam to make the hydrocarbon partial pressure near 12 pounds per square inch absolute or less. The cracked products leaving the outlet coil at nearly 1400° F. are then contacted in a transfer line with quench oil having a temperature of 375° F., the proportion of quench oil being close to four times the weight of the admixed cracked hydrocarbon products which are quickly cooled to below 650° F. before they enter the bottom part of the quench tower.

The amount of quench oil injected into the transfer line is made adequate to bring about a lowering of the temperature of the cracked hydrocarbon products, to a

temperature of 500° F. to 525° F., within short periods, e.g., a fraction of a second up to about two seconds.

The quench oil which is injected into the transfer line is made up of residual oil from the quench tower supplemented with the light gas oil of refractory character, e.g., a catalytically cracked gas oil product boiling in the range of 525° to 660° F. A similarly useful supplemental quench oil may be obtained by chemical treatments of cracked gas oils to remove unsaturates. Various virgin light gas oil fractions may be used. Tests have indicated that the quench oil should not be made up only of recycled residual oil from the quench tower without the supplemental light gas oil if excessive cooking is to be avoided in the transfer.

In the combined quenching and fractionating zone of the quench tower 6, the gaseous products are cooled by being brought successively into contact with the quench oil streams that have lower temperatures as they are introduced at higher levels, the predominant amount of cooling being done by the quench oil introduced into the upper part of the tower at temperatures preferably in the range of 170° to 200° F.

With the type of system described, the quench tower can be used with several more than one cracking coil. The quench oil can be injected at more than one point at the outlet of the coil or in the transfer lines.

Several observations on effects and results are summarized as follows:

The use of residual oil with accumulated tarry polymer bottoms from the quench tower per se as a transfer line quench oil gives intolerable coke in the transfer line. Highly improved quenching from the viewpoint of low coke formation is obtained when a portion of the quench tower bottoms is purged and replaced by a makeup light gas oil that is preferably refractory and has low coking tendencies.

The recovery of the desired olefins and diolefins up to six carbon atoms per molecule is improved by having a fast flow of the steam with volatile hydrocarbons up through the quench tower, using large amounts of relatively cool quench oil to cool the vapor mixture.

The amount of residual oil withdrawn from the quench tower, then cooled and circulated to the upper part of the quench tower to act as a cooling reflux, has to be substantially larger in liquid flow rate than the liquid flow rate of the initial cracking feed, for example, three or four times greater on the basis of pounds per hour.

For the purpose of obtaining the desired high yields of ethylene, propylene, butylenes and butadienes, a narrow virgin naphtha fraction containing C_5 or C_6 to C_8 or to C_{10} hydrocarbons is used as the cracking feed. As the cracking temperature is raised to above 1400° F., the proportion of olefins and diolefins in the product increases.

The yield and quality of the desired products is also improved by improving the rapidity of quenching in the transfer line and the separation of the desired gaseous products in the quench tower quenching and fractionating zone.

Modifications may be made which come within the scope of the invention, as for example, a step of separating a heavy distillate fraction in a bottom part of the quench tower for circulating as a quench oil. There are some disadvantages, however, in separating an intermediate distillate in the quench tower, since such a separation causes liquid holdup and slows down the flow of vapor up through the tower. It is to be noted that in using a bottoms residual in the quench circuit, satisfactory results are obtained by purging a portion of this bottoms and replacing the purged portion by a light gas oil.

The invention as described is claimed as follows:

1. In a process of steam-cracking hydrocarbons at an elevated temperature and low hydrocarbon partial pressure to form unsaturated C_2 to C_6 hydrocarbons, the improvement which comprises mixing with cracked products leaving a cracking zone a quench oil in a sufficient amount to rapidly lower the temperature of the resulting mixture from above about 1350° F. to below about 650° F. as the mixture is passed to a quenching and fractionating zone, separating from the quench cracked products in said quenching and fractionating zone a residual fraction boiling above about 430° F. and lower boiling vapors which pass rapidly upwardly through the quenching and fractionating zone countercurrent to relatively cooler quench oil, said quench oil being mainly residual oil withdrawn from the quenching and fractionating zone below the point at which said mixture is passed into said quenching and fractionating zone, then cooled and a portion of the cooled quench oil circulated to the cracked products leaving the cracking zone and another portion of cooled quench oil passed to an upper part of said quenching and fractionating zone, a third portion of the thus circulated quench oil being purged and replaced by a more stable gas oil which lowers the tar content of the quench oil.

2. In a process of steam-cracking a virgin naphtha fraction at temperatures in the range of 1350° to 1500° F. and low hydrocarbon partial pressures, the improvement which comprises admixing cooled quench oil with steam-cracked product being transferred in a transfer line from a cracking zone to a quench tower in which cracked vapor products boiling below 430° F. are cooled by a downflowing cooled quench oil and are separated from higher boiling components that remain with the quench oil as a residual oil; withdrawing quench oil containing said residual oil from the bottom part of said quench tower; cooling, circulating and using a first portion of the withdrawn quench oil as the cooled quench oil admixed in said transfer line; further cooling and circulating a second portion of the withdrawn quench oil to the quench tower to form said downflowing cooled quench oil; purging a third portion of the withdrawn quench oil; and replacing the purged portion of the withdrawn quench oil with oil of relatively lower polymer-tar forming reactivity, thus giving the circulated withdrawn quench oil a lower tar content.

3. In a process as defined in claim 2, said oil of relatively low polymer-tar forming reactivity being a refractory gas oil fraction formed by cracking at lower temperatures than those used in the steam-cracking.

4. In a process as defined by claim 2, said quench oil passed to the transfer line being injected at more than one point into said line.

5. In a process as defined by claim 2, said quench oil pumped back from a bottom part of the quench tower to its upper part being from three to six times the weight of cracked hydrocarbons entering the tower.

6. In a process of steam-cracking a virgin naphtha fraction at temperatures in the range of 1350° to 1500° F. and low hydrocarbon partial pressures, the improvement which comprises admixing cooled quench oil with steam-cracked product being transferred in a transfer line from a cracking zone to a quench tower in which cracked vapor products boiling below 430° F. are cooled by a downflowing cooled quench oil and are separated from higher boiling components that remain with the quench oil as a residual oil; withdrawing quench oil containing said residual oil from the bottom part of said quench tower; treating at least a part of said withdrawn quench oil with clay to remove polymer tars and returning said part of withdrawn quench oil into circulation as cooled quench oil; cooling, circulating and using a first portion of the withdrawn quench oil as the cooled quench oil admixed in said transfer line; further cooling and circulating a second portion of the withdrawn quench oil to the quench tower to form said downflowing cooled quench oil; purging a third portion of the withdrawn quench oil and replacing the purged portion of the withdrawn quench oil with oil of relatively lower polymer-

tar forming reactivity, thus giving the circulated withdrawn quench oil a lower tar content.

7. In a process of steam-cracking a virgin naphtha fraction at temperatures in the range of 1350° to 1500° F. and low hydrocarbon partial pressures, the improvement which comprises admixing cooled quench oil with steam-cracked product being transferred in a transfer line from a cracking zone to a quench tower in which cracked vapor products boiling below 430° F. are cooled by a downflowing cooled quench oil and are separated from higher boiling components that remain with the quench oil as a residual oil; withdrawing quench oil containing said residual oil from the bottom part of said quench tower; cooling, circulating and using a first portion of the withdrawn quench oil as the cooled quench oil admixed in said transfer line; further cooling and circulating a second portion of the withdrawn quench oil to the quench tower to form said downflowing cooled quench oil; said further cooled quench oil being at a temperature in the range of about 150° to 200° F. and being circulated to an upper part of the quench tower at a rate to prevent condensation of water vapor in said upper part of said quench tower; purging a third portion of the withdrawn quench oil and replacing the purged portion of the withdrawn quench oil with oil of relatively lower polymer-tar forming reactivity, thus giving the circulated withdrawn quench oil a lower tar content.

8. In a process of steam-cracking a virgin naphtha fraction at temperatures in the range of 1350° to 1500° F. and low hydrocarbon partial pressures, the improvement which comprises admixing cooled quench oil with steam-cracked product being transferred in a transfer line from a cracking zone to a quench tower in which cracked vapor products boiling below 430° F. are cooled by a downflowing cooled quench oil and are separated from higher boiling components that remain with the quench oil as a residual oil; withdrawing quench oil containing said residual oil from the bottom part of said quench tower; cooling, circulating and using a first portion of the withdrawn quench oil as the cooled quench oil admixed in said transfer line; further cooling and circulating a second portion of the withdrawn quench oil to the quench tower to form said downflowing cooled quench oil; said second portion of the withdrawn quench oil being circulated to said quench tower being divided into two streams, one stream being circulated to the top part of the quench tower and the other stream being circulated to a place intermediate a middle portion of the quench tower and the top of the quench tower at a temperature higher than that of the stream circulated to the top part of the quench tower; purging a third portion of the withdrawn quench oil and replacing the purged portion of the withdrawn quench oil with oil of relatively lower polymer-tar forming reactivity, thus giving the circulated withdrawn quench oil a lower tar content.

9. In a process of steam-cracking a virgin naphtha fraction at temperatures in the range of 1350° to 1500° F. and low hydrocarbon partial pressures, the improvement which comprises admixing cooled quench oil with steam-cracked product being transferred in a transfer line from a cracking zone to a quench tower in which cracked vapor products boiling below 430° F. are cooled by a downflowing cooled quench oil and are separated from higher boiling components that remain with the quench oil as a residual oil; withdrawing quench oil containing said residual oil from the bottom part of said quench tower; cooling, circulating and using a first portion of the withdrawn quench oil as the cooled quench oil admixed in said transfer line; further cooling and circulating a second portion of the withdrawn quench oil containing residual oil to the quench tower to form said downflowing cooled quench oil; said second portion of withdrawn quench oil being divided into two streams, one stream at a temperature of about 350° to 400° F. being circulated to a middle portion of the quench tower and another stream at a temperature of about 150° to 200° F. being circulated to an upper part of the quench tower; purging a third portion of the withdrawn quench oil; and replacing the purged portion of the withdrawn quench oil with oil of relatively lower polymer-tar forming reactivity, thus giving the circulated withdrawn quench oil a lower tar content.

10. In a process of steam-cracking a virgin naphtha fraction at temperatures in the range of 1350° to 1500° F. and low hydrocarbon partial pressures, the improvement which comprises admixing cooled quench oil with steam-cracked product being transferred in a transfer line from a cracking zone to a quench tower in which cracked vapor products boiling below 430° F. are cooled by a downflowing cooled quench oil and are separated from higher boiling components that remain with the quench oil as a residual oil; withdrawing quench oil containing said residual oil from the bottom part of said quench tower; cooling, circulating and using a first portion of the withdrawn quench oil containing residual oil as the cooled quench oil admixed in said transfer line; further cooling and circulating a second portion of the withdrawn quench oil containing residual oil to the quench tower to form said downflowing cooled quench oil; a part of said second portion of withdrawn quench oil being used as a sponge oil absorbent to absorb hydrocarbons boiling higher than ethene, then being circulated with another part of said second portion of withdrawn quench oil to the upper part of the quench tower where the absorbed light hydrocarbons are released; purging a third portion of the withdrawn quench oil and replacing the purged portion of the withdrawn quench oil with oil of relatively lower polymer-tar forming reactivity, thus giving the circulated withdrawn quench oil a lower tar content.

11. In a process of steam-cracking a virgin naphtha fraction at temperatures in the range of 1350° to 1500° F. and low hydrocarbon partial pressures, the improvement which comprises admixing cooled quench oil with steam-cracked product being transferred in a transfer line from a cracking zone to a quench tower in which cracked vapor products boiling below 430° F. are cooled by a downflowing cooled quench oil and are separated from higher boiling components that remain with the quench oil as a residual oil; withdrawing quench oil containing said residual oil from the bottom part of said quench tower; cooling, circulating and using a first portion of the withdrawn quench oil as the cooled quench oil admixed in said transfer line; further cooling and circulating a second portion of the withdrawn quench oil to the quench tower to form said downflowing cooled quench oil; said second portion of the withdrawn quench oil being divided into three streams, two streams being at temperatures of about 170° to 200° F. and being circulated to the upper part of said quench tower and a third stream being at a temperature of about 350° to 400° F. and being circulated to a middle portion of the quench tower; purging a third portion of the withdrawn quench oil containing residual oil; and replacing the purged portion of the withdrawn quench oil with oil of relatively lower polymer-tar forming reactivity, thus giving the circulated withdrawn quench oil a lower tar content.

References Cited in the file of this patent

UNITED STATES PATENTS

2,358,912	Dimmig	Sept. 26, 1944
2,363,903	Smith	Nov. 28, 1944
2,366,521	Guichet	Jan. 2, 1945
2,672,489	Holland	Mar. 16, 1954
2,736,685	Wilson et al.	Feb. 28, 1956