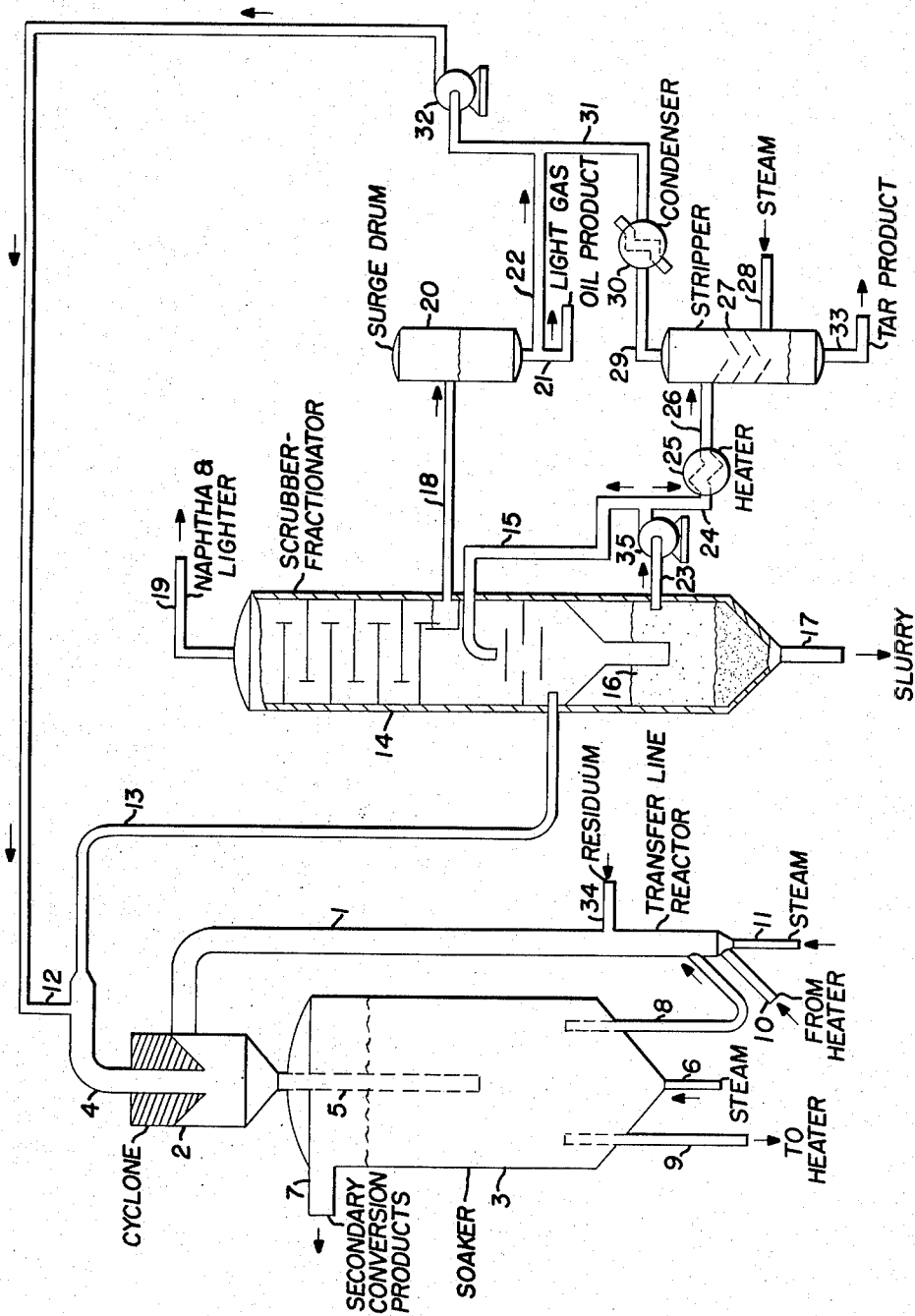


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**IMPROVED QUENCH OIL FOR HIGH TEMPERATURE COKING OF RESIDUA**

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This invention relates to an improved high temperature fluidized solids process for the coking of heavy oils. It is particularly concerned with an improved method for quenching the high temperature vapors obtained by coking of heavy oils.

In brief compass this invention is concerned with an improved fluidized solids, transfer line, heavy oil coking process for the production of chemicals and chemical intermediates such as low molecular weight unsaturates and aromatics. The transfer line coking process comprises contacting a heavy oil in a transfer line coking zone with flowing fluidized particulate solids maintained at a temperature above 1200° F., to produce vaporous product and carbonaceous residue which is deposited on the particulate solids. The particulate solids are separated by conventional means, such as by cyclone, from the vaporous product.

The improvement of this invention is concerned with the quenching of this vaporous, high temperature product. This improvement comprises injecting into the vaporous product, after the solids are separated, a liquid quench medium obtained in a particular manner. This quenching quickly lowers the temperature of the vapors below about 700° F., and forms a liquid-vapor mixture.

To obtain the liquid quench medium, this liquid-vapor mixture is separated to obtain at least a naphtha product, a light gas oil fraction boiling in the range of 430° to 650° F., and a tar bottoms having an initial boiling point immediately above the end boiling point of the light gas oil fraction. The heavy tar bottoms is then stripped to obtain an overhead fraction having a final boiling point below about 800° F. This overhead fraction obtained by the stripping is condensed and combined with a portion of the light gas oil fraction to obtain the liquid quench medium.

It is known to convert hydrocarbon oils, particularly heavy hydrocarbon oils such as residua, by contacting the oils with highly heated fluidized particulate solids unidirectionally flowing in a narrowly confined, elongated, conversion chamber or transfer line conversion zone. In this process, solids having a temperature above about 1200° F. are flowed through a transfer line zone by means of a fluidizing gas, e.g., steam, at a density of about 5 to 50 lbs./cu. ft. The oil to be converted is injected into the flowing solids and, upon contact with the solids, undergoes pyrolysis forming vaporous conversion products and carbonaceous residue or coke which is deposited on the solids. After a relatively short contact time, i.e., usually 0.15 to 1.0 second before quench, the solids are separated from the vaporous products thus formed, and the vaporous products are quickly cooled to arrest further conversion and avoid undesirable secondary reactions. The thus cooled vapors are then further separated as desired to recover the desired products such as low molecular weight unsaturates, as ethylene and butadiene, and aromatics.

Any suitable, relatively finely divided solid can be used

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in this process. The coke particles produced in the process can themselves be used. Materials such as metal particles, ceramic beads, kieselguhr, and the like can also be used. These solids, along with the deposited coke, after being separated from the conversion products, are usually heated in some manner in an external heating zone. This can comprise a transfer line zone similar to the transfer line conversion zone, or can be a fluid bed or gravitating bed unit wherein the solids are contacted with a free oxygen-containing gas and burned to remove coke deposits and to raise their temperature 50° to 400° above the conversion temperature. Indirect means can also be used to heat the solids, or an extraneous gaseous, liquid or solid fuel can be injected into the burning zone. After being so heated, the solids are recycled to the reaction zone to supply the requisite heat for the pyrolysis.

In the previous coking designs, the vaporous reactor products are quenched normally by injecting a cool liquid directly into the vapors. The liquid used is preferably a hydrocarbon oil and can comprise material separated from the reactor products. In this arrangement, however, severe coking has been experienced at the quench point. The reactor products contain an appreciable amount of tarry materials or coke precursors. In being cooled from the high reaction temperature to a relatively cool temperature, these tarry materials have an opportunity to condense on surfaces at intermediate temperature near the quench point, which temperature is still sufficiently high to allow further conversion. These tarry materials or coke precursors, when condensed, rapidly cause appreciable coke deposits which can cause fouling or complete shutdown of the equipment.

A large quantity of liquid diluent in the line downstream from the quench point will dilute and wash away coke and heavy condensation products. In previous designs, however, where a stream separated from the reaction products is recycled as the liquid quench medium, there is normally not enough material available to supply any large amount of liquid wash at the quench point and beyond.

The present invention proposes an improved method for obtaining the required quantity of liquid diluent or quench medium from the reaction products to overcome this specific problem.

In the present invention, the products are separated in a conventional manner to obtain naphtha and lighter materials, a light gas oil fraction and a heavier tar bottoms. In the past, the light gas oil fraction having a boiling range of about 430–650° F. would normally be used as the liquid quench medium. When this light gas oil fraction is so used, however, at the temperature of quenching, practically all of it vaporizes without leaving sufficient liquid to wash away the coke deposits, i.e., the amount of higher boiling material normally available in the vaporous reaction products is not sufficient to supply the desired quantity of wash liquid in the liquid quench medium.

This invention proposes that a narrow fraction, within a boiling range of about 650–800° F., be separately removed from the reactor products and recycled back to the quench point along with a portion of the liquid gas oil fraction, to provide the necessary washing action and thus prevent coking. This narrow fouling diluent or liquid wash fraction is separated by steam stripping the heavy tar bottoms, followed by condensation before it is returned to the quench point.

Stated somewhat differently, this invention proposes that two separate fractions be recovered from the vaporous reaction products from the coking zone to permit both rapid cooling of the high temperature vaporous products by vaporization of the liquid quench medium, and

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washing of the heavy condensation products from the vaporous products.

In the specific manner of this invention, the separate recovery of the liquid wash component of the quench medium permits recirculation of enough of it to overcome the problem of coking after quench or beyond the quench point. By the present method, the circulation of the liquid wash diluent can be varied as required by the process. Thus, the problem of insufficient production of intermediate boiling range material boiling at a temperature of about 650–800° F. is satisfactorily overcome.

The following description of the drawing attached to and forming a part of this specification will serve to make this invention clear.

Illustrated is a transfer line chemicals coking apparatus for the conversion of heavy oils to chemicals and chemical intermediates. A wide range of feed stocks can be used in this process, such as naphthas, light and heavy gas oils, residua or even whole crudes. This invention is most applicable to heavy oils such as residua, shale oils, tars, asphalts, coal tars, and the like that contain an appreciable proportion of materials non-vaporizable at atmospheric pressure without degradation, i.e., contain more than 10% of such materials. These extremely heavy constituents in oils of this type account for the coke precursors or tarry materials in the conversion products from the coking zone. It is, therefore, with this type of feed that coking of the quench point is most pronounced and thus, this invention is most applicable to this type of feed. With lighter feeds such as naphthas and gas oils, the problem is not so severe.

Referring to the drawing, there is shown a transfer line coking zone 1, a solids recovery system or cyclone 2, and an associated soaker or solids reservoir chamber 3. A heavy oil, e.g. a residuum, is injected into this transfer line zone 1 by line 34 and contacts therein flowing particulate solids maintained at a temperature above 1200° F. The density of the solids may range from 2 to 15 lbs./cu. ft. The solids pass up through the transfer line zone at a velocity above about 30–60 ft./sec. Upon contact with the solids, the residuum undergoes conversion depositing coke on the solids and evolving lighter vaporous conversion products. The conversion products are separated from the solids in cyclone 2.

This cyclone differs somewhat from the standard cyclones. In the conventional cyclones, an internal outlet pipe or duct extends down into the cyclone barrel and is exposed to the gas stream both inside and outside. For operation above the softening temperature of structural metals, which in this case may be as high as 2000° F., this outlet pipe must be internally cooled or alternatively made of unsupported refractory material. In the present case, the top of the cyclone is made in the shape of a truncated cone (apex down) as shown in the drawing. The basic cyclone flow pattern is retained but the outlet pipe is eliminated, allowing the entire cyclone to be made of supported refractory material. Thus the problem of erosion and weakening of the outlet duct is avoided.

The vaporous products separated in the cyclone are recovered overhead from the outlet duct by line 4. The separated solids pass downwardly through dipleg 5 to the soaking zone 3. The separated solids contain some residual tarry and tacky material. The solids are, therefore, retained in the soaking zone to complete the conversion of this material and to strip out the vapors. Solids are maintained in soaking zone 3 in a fluidized condition, in a manner well known in the art. To do this, steam or other suitable fluidizing and stripping gas is supplied to the base of zone 3 by line 6. The secondary conversion products formed in the soaking zone are removed overhead by line 7 and may be further treated as desired. If desired, a portion of the solids from the soaking zone can be recirculated to the inlet of the transfer line zone

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by line 8, although this is not mandatory. Another portion of the solids in the soaking zone is transferred by line 9 to an external heating zone, not shown, as previously described. Heated solids are returned from the heating zone by line 10 to the inlet of the transfer line zone. The solids are conveyed in these lines by aeration or conveying gas such as steam, inert gases, and the like in a manner known in the art.

The solids injected in the base of the transfer line zone are picked up by a suitable conveying gas, such as steam, nitrogen or light hydrocarbons, supplied by line 11. The amount of gas used is sufficient to give the required velocity in the transfer line zone, density of solids, and hydrocarbon vapor partial pressure. When steam is used, the amount of steam may vary from 0.01 to 0.05 lb./lb. of fresh feed.

The apparatus so far described illustrates one form of transfer line coking of residual oils to produce chemicals and forms no particular part of the present invention. Other forms of coking will occur to those skilled in the art.

The present invention is concerned with the treatment or quenching of the high temperature vaporous products in line 4. After emerging from cyclone 2, the products are immediately quenched by a liquid quench medium supplied to line 4 by line 12. The temperature and amount of this liquid quench medium is sufficient to cool the vapors below 700° F., preferably below 600° F. In normal operations, the vapors are quenched in this manner within 0.15 to 1.0 sec. from the time of feed injection into reactor. The quench material is transferred by line 13 to scrubber-fractionator 14.

In the scrubber-fractionator, the quench vapors are met with a recycled scrubbing oil supplied by line 15. Condensed material passes down into a settling zone 16 wherein coke particles, not removed by cyclone 2, are allowed to settle out from the tar bottoms. A slurry of these coke particles is withdrawn by line 17 and can be disposed of as desired. This slurry may be recycled to the transfer line coking zone.

There is condensed from the vapors passing up through the scrubber-fractionator, a light gas oil product which is withdrawn by line 18. The remainder of the vapors, comprising naphtha and lighter material, is withdrawn overhead by line 19 and may be further treated as desired, such as by distillation, fractionation, settling, crystallization, absorption and adsorption. The separated light gas oil product is collected in a surge drum 20 and the product is withdrawn by line 21. A portion of the light gas oil is recirculated to the quench point by line 22.

According to this invention, an addition to the light gas oil which is recycled as a quench medium, the tar bottoms collected in zone 16 have stripped therefrom an intermediate boiling range fraction which will remain liquid at the temperature resulting after quenching. To do this, the temperature of the separation is carefully controlled. The temperatures of the various liquid fractions given herein refer to the flash vaporization temperature.

Thus, according to this invention, the light gas oil product has an initial boiling point of about 430° F. and a final boiling point of about 650° F. The tar bottoms have an I.B.P. of about 650° F. and include all material heavier than the light gas oil product. The tar bottoms are withdrawn from zone 16 by line 23 via pump 35. A portion of the bottoms are recycled by line 15 as the previously described scrubbing oil. The remainder of the withdrawn tar bottoms is passed by line 24 through a heater 25 and then is injected by line 26 into a stripper 27. The stripper is supplied with a suitable stripping medium, in this case, steam, by line 28. There is recovered overhead from the stripper, an intermediate boiling range fraction having an I.B.P. contiguous to that of the light gas oil product, and a final boiling point below 800° F.,

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preferably below 700° F. This intermediate fraction recovered by line 29 is condensed in condenser 30 and mixed by line 31 with the contents of line 22. The combined mixture is passed to a pump 32, which recirculates the quench medium through line 12 to the quench point.

The remainder of the tar product is withdrawn from stripping zone 27 by line 33. It can be withdrawn as product or can be recycled to the transfer line conversion zone 1, to be further converted.

#### Example

The feed stock comprises an 1100° F. I.B.P. South Louisiana residuum, having a Conradson carbon of 17 wt. percent, a sulfur content of 0.74 wt. percent, a gravity of 10.7° API, and amounting to 2.4 wt. percent of crude. The average coking temperature in transfer line zone 1 is 1400° F. The average residence time before quench is 0.75 sec. The pressure at the cyclone outlet is 8 p.s.i. 5 wt. percent total steam on fresh feed is used to convey the solids to the transfer line zone. The C<sub>3</sub>—conversion of the feed is 30 wt. percent based on fresh feed. The temperature of the vapors after quench is 500° F. The ratio of liquid to vapor after the quench is 1.0 lb./lb.

The quenched vapors are separated to obtain 26.8 wt. percent on fresh feed of 430° F. minus naphtha and lighter products, a 430 to 650° F. light gas oil fraction and a heavy tar bottoms boiling immediately above this. 20 wt. percent of this tar bottoms is recycled as a slurry to return entrained solids. The remainder of the tar bottoms is stripped with steam to remove a 650 to 700° F. intermediate boiling range fraction. 230 wt. percent on fresh feed of the light gas oil fraction is combined with this intermediate boiling range fraction, which amounts to 45.0 wt. percent on fresh feed, and the combined mixture is recycled to the quench point at a temperature of 240° F. as a liquid quench medium. The remainder of the light gas oil fraction, amounting to 7.6 wt. percent on fresh feed, and of the stripped tar bottoms amounting to 30 wt. percent on fresh feed, are withdrawn as products.

Having described this invention, what is sought to be protected by Letters Patent is succinctly set forth in the following claims.

What is claimed is:

1. In a process wherein hydrocarbon vapors having a temperature above 1200° F. are produced and the vapors are quenched with a liquid quench medium, the

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improved method of providing a liquid quench medium which comprises separating the vapors after quenching to obtain at least a naphtha product, a light gas oil fraction boiling below about 650° F., and a tar bottoms having an I.B.P. above about 650° F. and which includes substantially all quenched vapors heavier than said light gas oil fraction; stripping from said tar bottoms an overhead fraction having a final boiling point below 800° F., and condensing and combining said overhead fraction with a portion of said light gas oil fraction to obtain said liquid quench medium.

2. An improved fluidized solids transfer line heavy oil coking process for the production of chemicals and chemical intermediates which comprises contacting a heavy oil in a transfer line coking zone with flowing fluidized particulate solids maintained at a temperature above 1200° F. to produce vaporous product and carbonaceous residue which is deposited on said particulate solids, separating particulate solids from said vaporous products, thereafter injecting a liquid quench medium obtained as described below into said vaporous product to quickly lower the temperature thereof below at least 700° F. and form a liquid-vapor mixture, separating said mixture to obtain at least a naphtha product, a light gas oil fraction boiling in the range of 430–650° F., and a tar bottoms having an initial boiling point immediately above said light gas oil fraction and including substantially all vaporous product boiling above said light gas oil fraction, stripping said tar bottoms to obtain an overhead fraction having a final boiling point below 800° F. and condensing and combining said overhead fraction with a portion of said light gas oil fraction, and returning the combined material as said quench medium.

3. The process of claim 2 wherein the heavy oil comprises a heavy residua containing at least 10% of constituents non-vaporizable at atmospheric pressure without degradation.

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