

- [54] **PROCESS AND APPARATUS FOR
QUENCHING UNSTABLE GAS**
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Related U.S. Application Data

- [63] Continuation of Ser. No. 327,285, Jan. 29, 1973,
abandoned, which is a continuation-in-part of Ser.
No. 887,011, Dec. 22, 1969, abandoned.
- [52] **U.S. Cl.**..... **208/48 Q; 23/277; 260/679 R;**
260/683 R
- [51] **Int. Cl.²**..... **C10G 9/16**
- [58] **Field of Search**..... **260/679, 683; 23/277, 248,**
23/277 X, 259.5; 261/118; 208/48 Q

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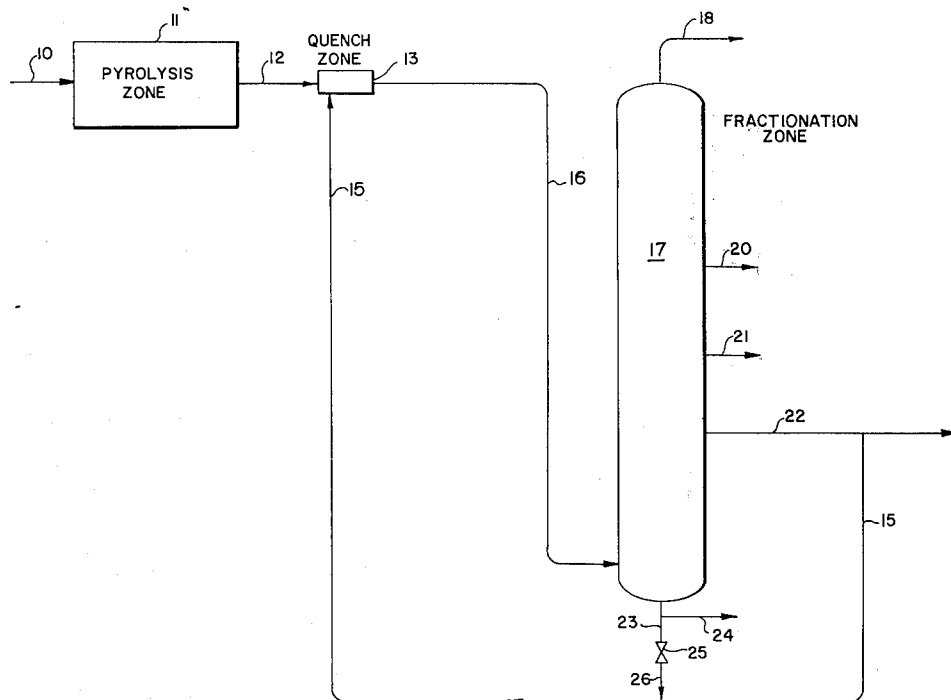
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[57]

ABSTRACT

There is disclosed a process for quenching pyrolysis product by passing it through a quench zone into which quench liquid is introduced in sufficient quantity and in a manner to form abruptly a continuous liquid film on the wall of the quench zone and to cool the pyrolysis product to a temperature at which it is stable; the quench liquid being refractory and highly aromatic. There is also disclosed an apparatus including a cylindrical quench zone having means for introducing quench liquid against the walls thereof to form a liquid film abruptly.

9 Claims, 7 Drawing Figures



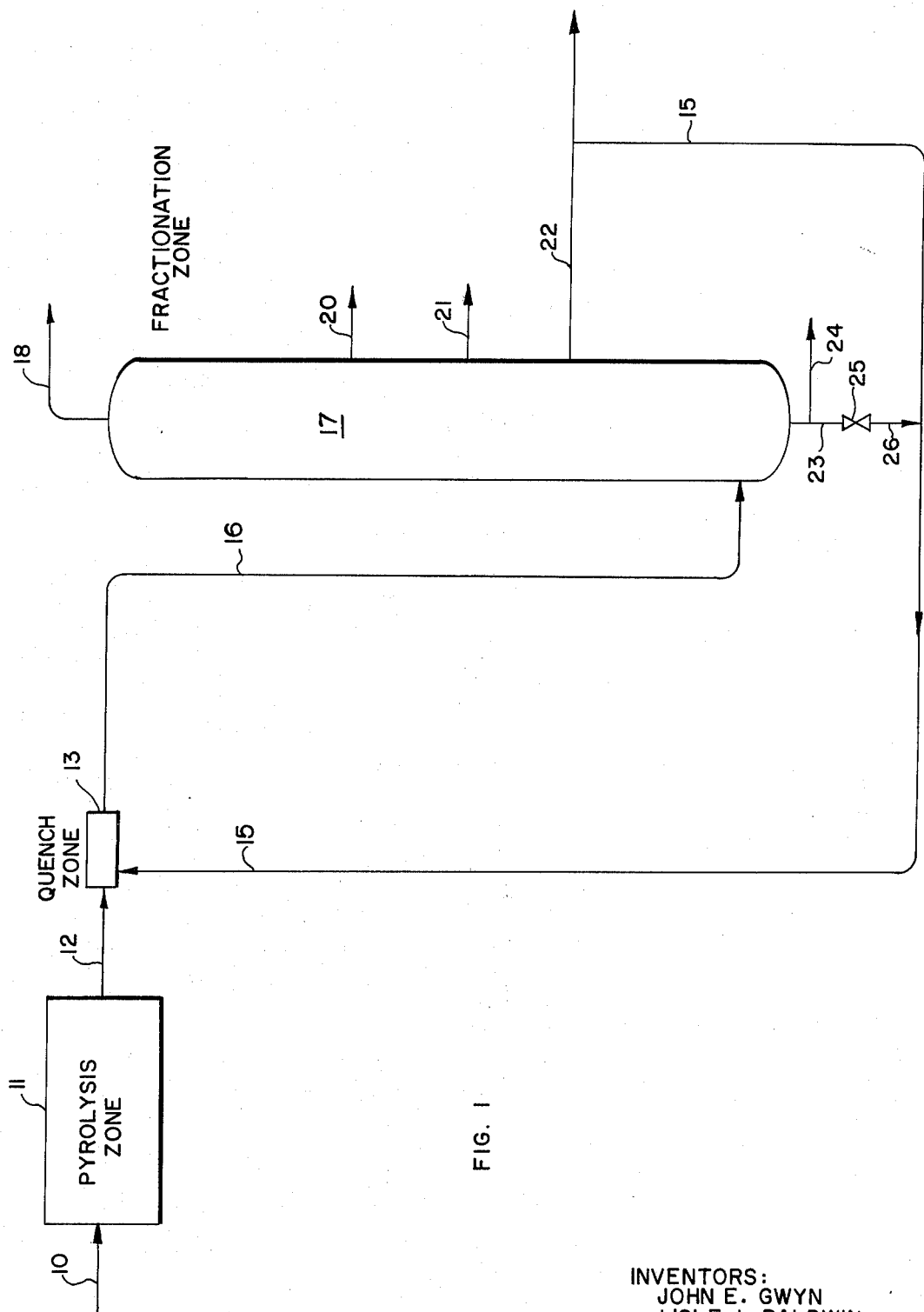


FIG. 1

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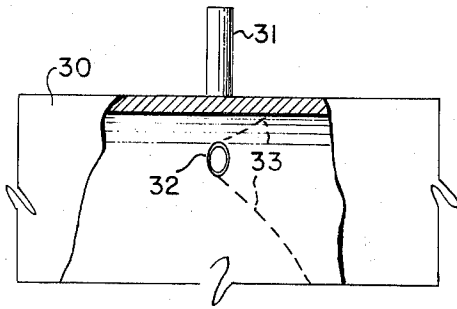


FIG. 2

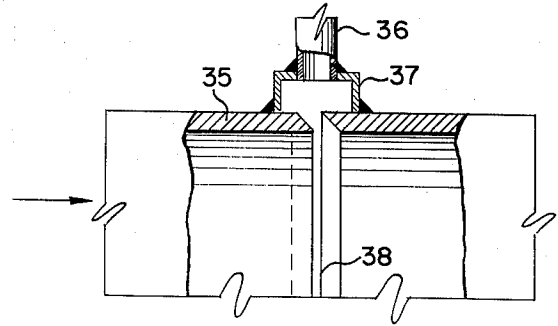


FIG. 3

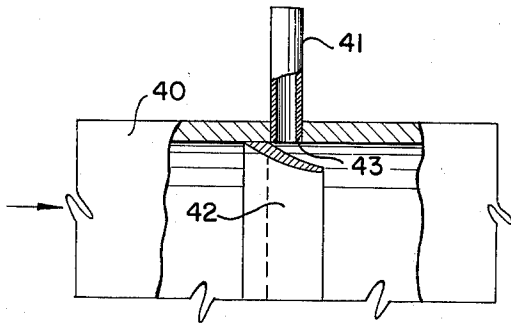


FIG. 4

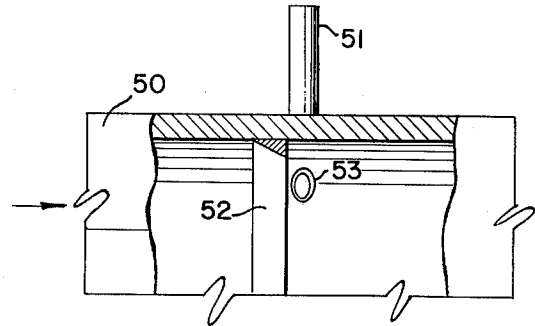


FIG. 5

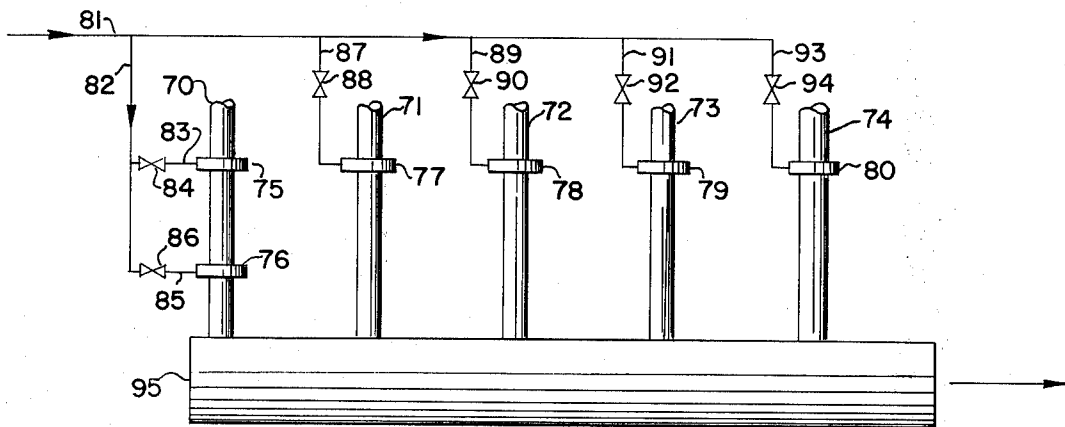


FIG. 7

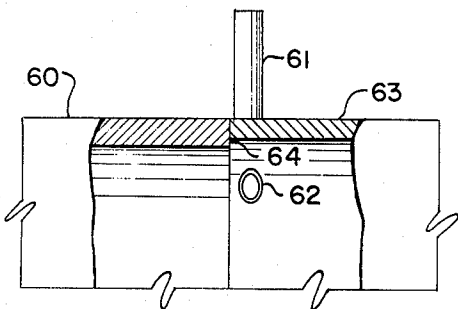


FIG. 6

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PROCESS AND APPARATUS FOR QUENCHING UNSTABLE GAS

This is a continuation, of application Ser. No. 327,285, filed Jan. 29, 1973 which in turn is a continuation of application Ser. No. 887,011 filed Dec. 22, 1969 both now abandoned.

BACKGROUND

Pyrolysis of a liquid hydrocarbon material is a well-known process that involves heating the material to a temperature that is high enough to cause thermal decomposition of larger molecules to form smaller molecules. Pyrolysis may be accomplished with a diluent, such as steam, to produce more favorable product distribution. A pyrolysis process produces a highly unsaturated and very unstable product, hereinafter called the effluent from the pyrolysis process, or simply the effluent.

The effluent is usually very rich in olefins, diolefins, acetylenes and other highly unstable compounds and there is a strong tendency for these materials to react to form high molecular weight products which are identified collectively as coke or tar or pitch. Such products are not desirable and to avoid forming them it is essential to reduce the temperature of the effluent quickly to a stable temperature, that is, to a temperature that is so low that rapid reactions of unstable compounds with each other do not take place. Typically, pyrolysis is effected above 1300°F and the effluent must be cooled to lower than about 700°F in order to be relatively stable. It is evident that if quenching of the effluent is accomplished quickly, more of the low boiling materials will be preserved.

Since rapid reduction of temperature is essential, quenching is normally effected by spraying a quench liquid directly into the effluent. The sensible heat of the quench liquid and its heat of vaporization quickly reduce the temperature of the effluent. However, it has been found that a severely cracked effluent tends to form deposits in the quench zone which are hereinafter referred to as coke, which cause a loss of useful product and increase the pressure drop across the quench zone and in severe cases clog the quench zone completely so that the process must be shut down. Even if the high pressure drop across the quench zone does not require shutting down the process, it produces a higher pressure in the pyrolysis zone which is expensive to maintain and which adversely affects the product distribution of the process.

THE INVENTION

This invention deals with a method and with an apparatus for quenching pyrolysis process effluent quickly and at the same time greatly diminishes the problem of coking in the quench zone. This invention is based on the observation that coking occurs in a quench zone at any point where the effluent is hotter than its stable temperature and where a dry wall below the dew point of the effluent exists, and this observation leads to a method of quenching that is contra-indicated by conventional methods of the prior art.

The method of this invention involves introducing quench liquid into the quench zone as a continuous film that begins abruptly with a sharp boundary on the wall of the quench zone rather than as a spray into the effluent stream. Surprisingly, it was found that contact

between the effluent and the wet wall is sufficient to effect a rapid temperature reduction of the effluent and thereby to preserve the desirable products in the effluent. Another advantage of the process is that the continuous liquid film on the wall of the quench zone not only prevents condensed products from sticking to the wall and thereby coking, but it even prevents many of the high boiling reaction products from forming at all.

Since it is an objective of this invention to avoid coking, the quench liquid preferably is refractory so that it does not form coke itself. By refractory it is meant that the quench liquid is stable at the conditions it experiences in the quench zone. For all practical purposes the quench liquid is a highly aromatic hydrocarbon fraction that is at least partly liquid at quench zone conditions. The preferred quench liquid is a heavy gas oil fraction recovered from the effluent, particularly material boiling above about 400°F separated from the effluent in a subsequent fractionation and returned to the process as a quench liquid. A particularly preferred quench liquid is a heavy gas oil separated from the effluent and blended with bottoms from the effluent fractionation, the bottoms being material boiling above 750°F. These fractions are highly aromatic in character and the blend of the fractions provides material that is light enough to vaporize thereby providing quick cooling of the effluent and heavy enough to maintain some liquid phase on the wall of the quench zone until the effluent is cooled below its stable temperature.

The manner of introducing quench liquid into the quench zone must meet the criteria set forth above, that is, the quench liquid must be introduced to provide an abruptly initiated continuous liquid film on any portion of the wall of the quench zone that is below the dew point of the effluent and above the stable temperature of the effluent. To obtain an abruptly formed continuous film on the wall of the quench zone it has been found that the quench liquid must be introduced through the quench zone wall in such a manner that the ratio of the radial component of the momentum of the liquid to the momentum of the gas is a maximum of unity. Preferably this ratio is less than 0.5.

Momentum of the fluid streams is the product of the density and the square of the velocity divided by twice the acceleration of gravity which cancels from the ratio. When the liquid is introduced at any angle to the radius of the quench zone, the square of the radial vector of velocity is employed to find the radial component of momentum. If the liquid is introduced axial with the gas, the radial momentum of the liquid is zero, and any liquid velocity may be employed. Any of many suitable methods for introducing quench liquid may be employed, several of which will be described below without limitation.

The simplest method for introducing quench liquid is to pump the quench liquid through a number of openings in the wall of the conduit through which the effluent is passing, but through openings that are so large that the momentum of the liquid does not exceed the momentum of the gas, so that the liquid does not spray into the conduit but rather tends to pass into the conduit as a slow-moving stream that is blown by the effluent stream into a flat film coating the entire inside surface of the quench zone. When the quench liquid passes into the quench zone through an opening in the wall, it is blown downstream as it spreads to meet the spreading film from an adjacent opening. In such a sys-

tem the abrupt beginning of the film is in the form of a zig-zag line. It has been found that coke formations spall off of the quench zone when they are heated to effluent temperature, and in this embodiment of the invention small deposits of coke can be removed by temporarily slowing the flow of quench liquid to form deeper V's in the zig-zag line. Spalling of coke may be done only as needed, or fluctuations in quench liquid flow rate may be made at regular intervals to avoid any buildup at all.

Another method for introducing quench liquid is to have the leading edge of the quench zone with respect to the direction of effluent flow in the form of a recessed chamber opening as a circumferential slit into the quench zone through which quench liquid is introduced. The slit may discharge liquid into the quench zone radially or at some angle to radial to reduce its radial momentum for any linear velocity. The quench liquid may also be introduced from beneath a Venturi-like ring insert into the quench zone, or from behind an internal ring having a wedge-shaped cross section, or from behind a ledge or shoulder in the conduit carrying the effluent.

This invention also includes an apparatus for quenching an effluent stream. The apparatus includes a cylindrical zone adapted to receive the effluent so that it passes through the quench zone to subsequent downstream processing. The quench zone includes a cylindrical wall and has at its leading edge with respect to the direction of effluent flow, a means for introducing liquid against the cylindrical wall.

The accompanying drawings are presented to illustrate the process and apparatus of the present invention and are intended to be illustrative rather than limiting on its scope.

FIG. 1 is a highly schematic flow diagram of a pyrolysis process including the quench zone of this invention.

FIGS. 2, 3, 4, 5 and 6 are partial sectional views of quench zones embodying this invention.

FIG. 7 is a schematic diagram illustrating a group of quench zones discharging into a common transfer line.

Referring first to FIG. 1, a line 10 supplies a suitable hydrocarbon feed such as gas oil to a pyrolysis zone shown schematically as zone 11 wherein the hydrocarbon is subjected to conditions that cause thermal decomposition with the production of a variety of unstable products. The pyrolysis product or effluent, passes from the pyrolysis zone through line 12 which is preferably very short and into quench zone 13. In quench zone 13 a liquid quench medium is introduced in a manner to maintain the walls of quench zone 13 wet, the liquid quench medium being supplied through line 15. As a result of being quenched, the effluent which is at a relatively stable temperature passes from quench zone 13 through line 16 into fractionator 17.

In fractionator 17, the stabilized effluent is separated into fractions according to boiling ranges, the lowest boiling materials being removed through line 18, intermediate boiling fractions being removed through lines 20 and 21, a heavy gas oil fraction being removed through line 22, and a bottom fraction being removed through line 23. At least part of the heavy gas oil from line 22 is passed into line 15 and returned to zone 13 as quench liquid. The bottom fraction may be recovered totally through line 24, or a portion of it may pass through valve 25 and line 26 to join the quench liquid in line 15.

In a typical pyrolysis process aimed primarily at producing ethylene and light olefinic hydrocarbons, a gas oil fraction from any suitable source is blended with about 8 pounds of steam for each 10 pounds of gas oil and the mixed stream is passed through line 10 into pyrolysis zone 11 where it is heated to a temperature in excess of 1400°F. As a result of the high temperature treatment, the gas oil fraction decomposes to form a variety of products, the total product being rich in low boiling olefins such as ethylene but containing hydrocarbons boiling through a wide temperature range. The effluent passes through line 12 at the temperature of the pyrolysis zone and is quickly quenched in zone 13 to below 700°F., preferably to 640°-660°F, which is a temperature where the pyrolysis product has enough liquid phase material to maintain the transfer line walls wet and to be stable. At the stable temperature, condensation and polymerization reactions occur at such a slow rate that the product created in the pyrolysis zone is preserved, and the stabilized effluent passes into fractionator 17 where it is separated into various fractions according to boiling range.

At least one, and preferably two, of the fractions separated in the fractionator 17 are the preferred quench liquids in that both are highly aromatic, extremely resistant to reactions at the conditions in the quench zone, at least partly liquid phase at quenching conditions, and available in abundance from the pyrolysis process. The heavy gas oil fraction removed through line 22 has an initial boiling point of about 550°F and contains material boiling through a wide temperature range, and this heavy gas oil fraction is the primary quench liquid. Heavy gas oil may be used alone as the quench liquid in that it can be supplied in sufficient quantity so that enough liquid phase will be in the quench zone at all times to maintain the walls of the quench zone wet. The heavy gas oil fraction additionally boils in a range where a large portion of it will vaporize at the temperature of the quench zone, thereby contributing to a rapid quench by absorbing heat of vaporization from the effluent. The preferred quench liquid will also contain a portion of the bottom fraction passing through line 23. This material has an initial boiling point of about 750°F and contains all higher boiling material in the effluent. A small amount of the bottom fraction in the quench liquid insures sufficient liquid phase to maintain the walls of the quench zone wet. The quench liquid may be cooled before being added to the quench zone so that heat may be extracted from the effluent by increasing the sensible heat of the quench liquid before it vaporizes.

Many different means may be employed to introduce quench liquid into the quench zone in a manner such that the walls of the quench zone are maintained wet. The simplest means is to introduce the liquid into the quench zone through holes in the wall of the conduit carrying pyrolysis product; however, the holes must be sufficiently large so that an adequate supply of quench liquid may be introduced into the quench zone at a velocity such that the radial momentum of the liquid does not exceed the momentum of the gas. Quench zones may be oriented vertically or horizontally, and when oriented vertically the gas flow is preferably downward.

FIG. 2 illustrates one embodiment of a suitable quench zone. In FIG. 2, effluent carried through line 30 in the direction indicated by the arrow is at a temperature in excess of 1400°F up to the portion of the con-

duit where quench liquid is introduced at various points around the circumference of the conduit, such introduction being effected through line 31, introduction enters line 30 through opening 32. Preferably, at least 3 such openings around the circumference of line 30 are employed.

The opening 32 must be large enough in diameter to permit the amount of quench liquid required to enter the quench zone as a slowly flowing stream, that is, as a stream which is diverted to flow against the wall of the quench zone by the vapor phase effluent passing through line 30. The quench liquid forms a continuous film which begins abruptly in a shape approximately as shown by broken lines 33. The quench liquid on the wall of the quench zone is vaporized and it is found that the turbulence of the effluent flowing through the quench zone is sufficient to cause cooling of the effluent quickly.

FIG. 3 illustrates another embodiment of the invention wherein the quench zone is constructed so that quench liquid is introduced uniformly around the circumference of the quench zone at its leading edge. In FIG. 3, line 35 represents the line carrying effluent from the pyrolysis zone in the direction indicated by the arrow. The quench zone begins where quench liquid is introduced into the conduit 35. Quench liquid is introduced through line 36 into a chamber 37 which discharges into a slit 38 formed by spacing adjacent segments of conduit making up line 35. As illustrated, the slit 38 is shaped so that fluid enters at an angle to the radius and against the wall of the conduit 35 whereby the quench zone, which is the area downstream of slit 38 at which the effluent is above the temperature of 700°F has a wet wall. Although FIG. 3 illustrates this embodiment with a circumferential chamber 37 and a diagonally oriented slit 38, many other arrangements may be employed to introduce quench liquid into the quench zone through a slit, for example, employing a slit where fluid flows perpendicular to the flow of pyrolysis product and where such slit is fed through a number of conduits or by other means.

FIG. 4 illustrates still another embodiment of the present invention. In FIG. 4 effluent flowing through line 40 in the direction of the arrow is quenched by quench liquid introduced through line 41 beneath the circumferential ring 42. Ring 42 is attached to the inside wall of conduit 40 at its leading edge and it is spaced slightly from the wall of the conduit 40 to form an opening 43 through which quench liquid is introduced against the interior wall of conduit 40 to produce a quench zone with wet walls. It is preferred that the circumferential ring 42 have a gradually tapering interior surface between its leading edge and trailing edge so that a smooth change in direction of effluent flow is produced. This venturi-like effect will minimize the pressure drop caused by the obstruction to the interior surface that ring 42 produces.

The embodiment shown in FIG. 4 permits quench liquid to be introduced at a higher velocity in that the ring 42 changes its direction of flow away from radial, and thereby maintains the radial momentum of the quench liquid well below the momentum of the effluent. However, the quench liquid tends to cool ring 42 so that coke sometimes will form on the cool portion of the ring. This coke can be removed by temporarily stopping the flow of quench liquid to cause the coke to spall.

The embodiment shown in FIG. 5 avoids a cool portion of the equipment where coke can form. In FIG. 5, effluent passes through the conduit 50 in the direction indicated by the arrow and it passes over a circumferential ring 52 that is shown with a cross section in the shape of a wedge with the point upstream. Quench liquid is introduced through line 51 into openings 53 spaced immediately downstream of ring 52. The turbulence in the effluent stream causes quench liquid to fill the entire circumference of conduit 50 behind the ring 52 so that quench liquid flows downstream in conduit 50 as a continuous film emanating from behind ring 52. Ring 52 does not have a large surface exposed to cool quench liquid and is substantially at the temperature of the effluent during operation so that cooling of the effluent begins abruptly substantially at the trailing edge of ring 52.

FIG. 6 illustrates still another embodiment of this invention. In the embodiment shown in FIG. 6 the advantages of the wedge-shaped insert illustrated in FIG. 5 are obtained without a pressure drop due to diminished cross section in the conduit carrying the effluent. As illustrated in FIG. 6, effluent passes into line 60 in the direction of the arrow and line 60 is connected to line 63 which has a larger inside diameter whereby a circumferential shelf or shoulder shown in cross section at 64, is formed. Line 61 introduces quench liquid through opening 62 which is immediately behind and downstream of the shelf 64. The turbulence of the effluent causes the quench liquid to fill line 63 circumferentially from the shelf so that the entire interior surface of line 63 is covered with a continuous liquid film.

In all the embodiments shown, the formation of coke in the quench zone is diminished if not completely eliminated. However, if small amounts of coke form they can be removed by turning off the quench liquid so that the coke deposits in the quench zone are subjected to the high temperature of the effluent passing into the quench zone. It has been found that thermal spalling of coke proceeds rapidly and small amounts of coke deposit can be removed by spalling with only brief interruptions in the flow of quench liquid.

FIG. 7 illustrates an embodiment of the invention wherein interruptions of quench liquid may be regularly accomplished without passing large quantities of uncooled effluent downstream of the quench zone. The effluent passes from the pyrolysis zone through a number of conduits illustrated as lines 70, 71, 72, 73, and 74. Obviously, any number of parallel conduits may be employed. The first conduit 70 is supplied with two quench rings illustrated as 75 and 76 while each of the other effluent conduits is supplied with one quench ring illustrated as 77, 78, 79, and 80. The quench rings are supplied with quench liquid through a header 80 which supplies lines 82, 87, 89, 91, and 93. Quench ring 75 is supplied with fluid through line 83 and valve 84 while quench ring 76 is supplied with quench liquid through line 85 and valve 86. Similarly, line 87 and valve 88 supply quench ring 77, line 89 and valve 90 supply quench ring 78, line 91 and valve 92 supply quench ring 79, and line 93 and valve 94 supply quench ring 80. All of the effluent eventually passes into transfer line 95 which carries it to downstream processing.

In operation, all quench rings except quench ring 76 will function so that the effluent passing through lines 70, 71, 72, 73, and 74 will be cool before it reaches transfer line 95. However, to ensure that clogged

quench zones will not interfere with the operation of the pyrolysis process due to slow accumulations of coke in normal operation, or rapid accumulations of coke when some upset in operation occurs, any one of the quench zones can be decoked by stopping the flow of quench liquid and permitting the coke to spall. Thus, if valve 94 were closed, quench liquid would no longer pass to quench ring 80 and hot pyrolysis effluent would raise the temperature of line 74 to the point where coke would spall from its walls. However, the high temperature effluent passing into line 95 is blended with cool effluent from lines 70-73 so that the effluent from line 74 does not raise the temperature of the material in transfer line 95 significantly. Similarly, any one of valves 88, 90 or 92 may be turned off to cause the coke to spall from the interior of lines 71, 72 or 73, respectively, without causing thermal damage to transfer line 95 or to downstream processing equipment. However, if the quench liquid in line 70 were turned off completely, transfer line 95 could be damaged by heat because there is no cooled effluent to dilute the effluent passing through line 70 where it enters the transfer line 95. To avoid thermal damage to this portion of transfer line 95, when it is desired to decoke line 70 valve 84 is closed but valve 86 is open so that quenching is accomplished in a different portion of line 70. When the normal quench zone, that portion of line 70 located immediately downstream of ring 75, is clean, then valve 86 may be closed and valve 84 opened so that quenching occurs normally.

What is claimed is:

1. A method for quenching the effluent from a hydrocarbon pyrolysis unit from a temperature in excess of 1400°F to a temperature at which the effluent is stable, which comprises:

- a. passing said effluent through a conduit, and
- b. introducing as the sole quenching fluid a refractory, highly aromatic hydrocarbon quench liquid

through the wall of said conduit in a manner such that the ratio of radial momentum of quench liquid to the momentum of the effluent passing through the conduit is less than unity, thereby abruptly forming a continuous liquid film on the conduit wall at a temperature below the dew point of the effluent, said quench liquid being introduced into the conduit in the form of the continuous liquid film in an amount sufficient to both cool the effluent to a temperature at which it is stable and to maintain a continuous liquid film on all portions of the conduit wall until the effluent reaches a stable temperature.

2. The process of claim 1 wherein the quench liquid comprises cracked heavy gas oil and the effluent is quenched to below 700°F.

3. The process of claim 2 wherein said quench liquid comprises heavy gas oil separated from the pyrolysis unit effluent.

4. The process of claim 2 wherein said quench liquid comprises a mixture of heavy gas oil and bottoms separated from the pyrolysis unit effluent.

5. The process of claim 1 wherein the effluent is quenched to 640°-660°F.

6. The process of claim 1 wherein quench liquid is introduced into the quench zone in contact with a continuous circumferential element.

7. The process of claim 1 wherein the ratio of the radial momentum of the liquid to the momentum of the gas is not more than 0.5.

8. The method of claim 1 wherein the conduit through which the pyrolysis effluent is passed is oriented horizontally.

9. The process of claim 1 wherein any coke deposits formed during the quenching process are removed by temporarily interrupting the flow of quench liquid introduced through the conduit wall.

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