HEAT RECOVERY IN THERMAL CONVERSION PROCESS

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ABSTRACT OF THE DISCLOSURE

In the high temperature thermal conversion of hydrocarbon feed wherein the effluent from the conversion zone is partially quenched and then passed thru a waste-heat boiler to recover heat resulting in the deposition of tar in the tubes of the boiler, a hydrocarbon oil is injected into the quenched effluent upstream of the waste-heat boiler to wash off any tar tendency to deposit in the heat exchange tubes.

This invention relates to a high temperature thermal hydrocarbon conversion process involving quenching of the converted product stream to preserve valuable products and an arrangement of apparatus for effecting the process.

The high temperature thermal conversion of hydrocarbon feed stocks ranging from methane to naphtha to produce substantially less saturated hydrocarbons such as ethylene and acetylene is conventional in the petroleum refining art. The type of process referred to is disclosed in U.S. Patents 3,018,309 and 2,945,075. In such processes, a small amount of heavy tar is produced amounting to about 2 weight percent of the hydrocarbon feed. Reaction products are quenched in the reactor quench section with water to a temperature in the range of about 100 to 1300° F., the temperature being selected so as to stop the thermal conversion and preserve the less saturated product, usually acetylene and/or ethylene. The water-quenched effluent is then cooled further in cooling pipes and quench systems with no heat recovery. The use of a waste-heat boiler has been precluded by the knowledge that the tar present in the quenched product stream would foul the tube surfaces in the waste-heat boiler or exchanger and would turn to coke at these high temperatures.

This invention is concerned principally with a process and arrangement of apparatus which permits substantial heat recovery in the foregoing process.

Accordingly, it is an object of the invention to provide a process and arrangement of apparatus for the recovery of heat in a high temperature thermal conversion process so as to permit the conversion of more saturated to less saturated light hydrocarbons such as those ranging from methane to naphtha. Another object is to prevent tar deposition and coking in a waste-heat boiler used in recovering from a product stream from a high temperature thermal conversion in which said tars are formed. Other objects of the invention will become apparent to one skilled in the art upon consideration of the accompanying disclosure.

A broad aspect of the invention comprises injecting a hydrocarbon oil into the quenched reactor effluent from a high temperature thermal conversion process and passing the quenched oil-containing effluent thru a waste-heat boiler to recover a substantial amount of heat from the quenched effluent, the oil in the quenched stream washing off any tar tendency to deposit in the heat exchange tubes of the boiler. The oil may be injected with the initial quench water or in a separate stream into the product stream intermediate the reactor and the waste-heat boiler.

Hydrocarbon conversion processes to which the invention is applicable, include various hydrocarbon feed stocks at temperatures in the range of about 1500 to 1500° F. to more valuable, less saturated hydrocarbons. The hydrocarbon product stream is then quenched to a temperature at which further reaction does not occur which is usually in the range of about 1000 to 1300° F. When producing acetylene from various feed stocks ranging from methane to naphtha, the conversion temperature is preferably controlled in the range of 2000-2500° F. and the reaction effluent water quenched down to a temperature in the range of 1150 to 1250° F. Usually a quench temperature of 1200° F. is most desirable because quenching at this temperature stops the reaction, preserves the acetylene and ethylene in the product stream, and provides a maximum temperature for heat recovery in the waste-heat boiler.

The amount of oil injected into the quenched product stream, or during the initial quenching, is controlled within the range of about 2 to 10 times the weight of the tar produced in the reaction. Usually an amount of oil equal to about 5 times the weight of the tar is satisfactory. When the amount of tar formed amounts to about 2 weight percent of the feed, the amount of oil injected into the product stream is in the range of 4 to 20 weight percent of the hydrocarbon feed.

The quench oil employed in the practice of this invention is substantially any heavy oil, paraffinic or aromatic, which will flow and can be sprayed at the lowest temperatures involved. Oils which are preferably employed include benzene, toluene, anthracene, predominantly aromatic kerosenes having, for example, a boiling point in the range of 200° F. to 500° F. and predominantly aromatic gas oil, such as oil having a boiling range of 400° F. to 700° F. A preferred oil is a heavy aromatic oil which is produced in the cracking operation and permitted to accumulate in the process. A suitable oil which can be used for quenching according to this invention has the following specification:

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific gravity at 60°/60° F.</td>
<td>1.0655</td>
</tr>
<tr>
<td>Kinematic viscosity at 100° F.</td>
<td>14.38 centistokes</td>
</tr>
<tr>
<td>Kinematic viscosity at 210° F.</td>
<td>2.86 centistokes</td>
</tr>
<tr>
<td>Bureau of Mines Correlation Index</td>
<td>133</td>
</tr>
<tr>
<td>ASTM distillation, corrected to 760 mm. Hg.</td>
<td>5 - 540° F.</td>
</tr>
<tr>
<td>10</td>
<td>50° F.</td>
</tr>
<tr>
<td>20</td>
<td>40° F.</td>
</tr>
<tr>
<td>30</td>
<td>39° F.</td>
</tr>
<tr>
<td>40</td>
<td>32° F.</td>
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</tbody>
</table>

A more complete understanding of the invention may be had by reference to the accompanying schematic drawing which is a flow or arrangement of apparatus for effecting the process of the invention.

Referring to the drawing, a reactor 10, preferably of the type shown in U.S. Patent 5,018,309, is provided with an axial feed line 12 for the selected hydrocarbon feed and steam, a tangential feed line 14 for fuel gas O₂ and steam, a water quench line 16 and a product effluent line 18. Fuel and air are supplied thru line 20 and steam thru line 22 from a source described below. A waste-heat boiler 24 provided with heat exchange tubes 26, a water feed line 28, and a steam outlet line 30 is positioned in effluent line 18 so that the partially quenched product enters indirect heat exchange with the water having heat exchange headers 32. Line 30 connects with tangential feed line 14 thru line 22.
Effluent line 34 leads from waste-heat boiler 24 into the lower section of quench tower 36 which is an upright cylindrical tower provided with spray means 38 for spraying quench oil into the ascending gas and vapor streams from line 34. The quench oil collects in the bottom of the tower and is withdrawn thru line 40. The quenched vapors and gases are withdrawn from the top of the tower thru line 42 and are passed to conventional recovery means, not shown, for separation of the hydrogen and recovery of the selected hydrocarbons from the resulting stream. These recovery steps are conventional and will not be described further.

Oil is supplied to sprays 38 from an oil tank or reservoir 44 thru line 46 under the impetus of pump 48. Oil from the bottom of the quench tower is circulated thru line 40 by means of pump 50 thru an air fin type cooler 52 thru line 54 back to tank 44.

Oil for injection into the product stream is obtained from line 40 downstream of pump 50 and is conveyed by line 56 either into line 18 directly, or thru line 58 into line 16 for injection with the quench water. It is also feasible to inject separate portions of the quench oil with the quench water and directly into line 18.

The injected quench oil vaporizes at the injection point but also partly condenses on the colder surfaces of the waste-heat boiler tubes and, in this manner, washes any tar or pitch settling on the heat exchange surfaces, thereby preventing coking and carbon deposition with attendant fouling of the heat exchange tubes. It is to be understood that the hydrocarbon product stream may be passed either thru the tubes as shown in the drawing or thru the exchanger so as to contact the outer surfaces of the tubes while the water passes thru the tubes. In the manner described, the condensing liquid actually improves the heat transfer coefficient in the waste-heat boiler. The steam produced in waste-heat boiler 24 is utilized in reactor 10, being fed thru lines 12 and/or 14.

In a typical process utilizing naphtha as the hydrocarbon feed in an air-stream injected thru line 12 and a fuel-O₂ steam mixture injected thru line 14, a temperature of about 2300° F. is maintained in reactor 10 and the reaction product stream is quenched to a temperature of 1200° F. by injecting water and oil thru line 16. The product stream is then cooled to a temperature of about 600° F. when passing thru waste-heat boiler 24 and enters quench tower 36 at this temperature where it is quenched to a temperature of about 200° F. in contact with the quench oil. Thus, the quenched effluent in line 42 at a temperature of 200° F. and containing sprayed 38 at a temperature of about 140° F. is heated to about 300° F. as it passes thru line 40. When the quench oil is injected directly into line 18 from line 56 and water quench from line 16 drops the temperature to about 1200° F., the product stream temperature is reduced to about 1185° F. downstream of the oil injection point.

Waste-heat boiler 24 is operated to reduce the temperature of the quenched stream in line 18 to the range of about 500 to 750° F. Quench tower 36 is operated to reduce the temperature of the effluent in line 42 to a temperature in the range of about 195 to 215° F.

Certain modifications of the invention will become apparent to those skilled in the art and the illustrative details disclosed are not to be construed as imposing unnecessary limitations on the invention.

We claim:

1. A process for the thermal conversion of hydrocarbon material ranging from methane to naphtha to less saturated hydrocarbons which comprises the steps of:

   (1) feeding said hydrocarbon material into a thermal conversion zone in admixture with steam and O₂ containing gas of less than stoichiometric O₂ content for burning all of said material and burning a portion of said material so as to heat said material to a conversion temperature in the range of 1500 to 3500° F. and convert another portion of said material to less saturated hydrocarbons;

   (2) water-quenching the spent product stream produced in step (1) to a temperature in the range of 1000 to 1300° F. to terminate conversion;

   (3) passing the quenched product stream from step (2) thru a waste-heat boiler containing indirect heat exchange tubes and heat exchange same with water therein to cool same and reduce the product stream temperature to a temperature in the range of 500 to 750° F., tars formed in step (1) having a tendency to deposit on the walls of said tubes;

   (4) dispersing a stream of oil into the product stream of step (2) so as to wash off any tars which condense on the tubes in step (3) and prevent tar deposition thereon;

   (5) oil quenching the product stream from step (3) to a substantially lower temperature; and

   (6) recovering product hydrocarbon material from the stream of step (5).

2. The process of claim 1 wherein the conversion temperature is in the range of about 2000° F. to 2500° F. and a substantial concentration of acetylene is formed in the conversion zone and preserved by quenching step (2) and the product is quenched to a temperature in the range of 1500 to 1250° F. in step (2).

3. The process of claim 1 wherein at least a portion of the oil of step (4) is introduced in the water quench of step (2).

4. The process of claim 1 wherein steam from step (4) is introduced as at least a substantial portion of the steam in step (1).

5. A process for producing acetylene comprising the steps of:

   (1) a stream of hydrocarbon material in the range of methane to naphtha in a thermal conversion zone in admixture with steam and less than the stoichiometric ratio of air and burning a substantial portion of said material so as to maintain a conversion temperature in the range of about 2000 to 2500° F. to form a substantial amount of acetylene;

   (2) water-quenching the product stream formed in step (1) to a temperature in the range of about 1150 to 1250° F. to preserve said acetylene;

   (3) passing the quenched stream from step (2) in contact with heat exchange tubes in a waste-heat boiler in indirect heat exchange with water to form steam and further quench said steam to a temperature in the range of about 500 to 750° F., heavy tars formed in step (1) tending to deposit on the walls of said tubes;

   (4) passing the quenched stream from step (3) thru an oil-quench zone and quenching same with oil therein to a temperature in the range of about 195 to 215° F.;

   (5) dispersing a stream of oil into the product steam upstream of step (3) so as to prevent tar deposition on said tubes; and

   (6) recovering acetylene from the product stream from step (4).

6. The process of claim 5 wherein at least a portion of the oil in step (5) is dispersed in the water in step (2).

7. Apparatus comprising in combination:

   (1) a thermal reactor having inlet means for hydrocarbons, steam, and air, and an outlet for a reaction product stream;

   (2) a water quench line leading into the downstream end of the reactor of (1);

   (3) a reaction product line leading from the product outlet of (1);

   (4) a waste-heat boiler having heat exchange tubes connected in the line of (3) for passage of the reaction product stream in contact with one side of said tubes;

   (5) conduit means for passing water thru the boiler of
(4) in contact with the opposite side of said tubes to produce steam and cool said product stream;
(6) an oil quench tower in the line of (3) downstream of the boiler of (4) having oil dispersion means in its upper end, a product stream inlet in a lower section connected with said line, a quenched product stream outlet in its top section, and a quench oil outlet in its bottom section; and
(7) an oil injection line leading into the product stream upstream of the boiler of (4).

8. The apparatus of claim 7 including:
(8) an oil recycle line connecting the oil outlet of (6) with the oil dispersion means of (6) having a pump therein; and
(9) a conduit connecting the oil injection line of (7) with the oil recycle line of (8) downstream of the pump therein.

References Cited
UNITED STATES PATENTS
2,179,378 11/1939 Metzger 260—679
2,179,379 11/1939 Metzger 260—679
2,899,475 8/1959 Davison 260—683
2,945,075 7/1960 Scofield 260—679
3,018,309 1/1962 Krejci 260—679

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J. D. MYERS, Assistant Examiner.
UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,347,949

Robert E. Dollinger et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 4, line 35, after "(1)" insert -- passing --.

Signed and sealed this 31st day of December 1968.

(SEAL)
Attest:
Edward M. Fletcher, Jr.
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents