

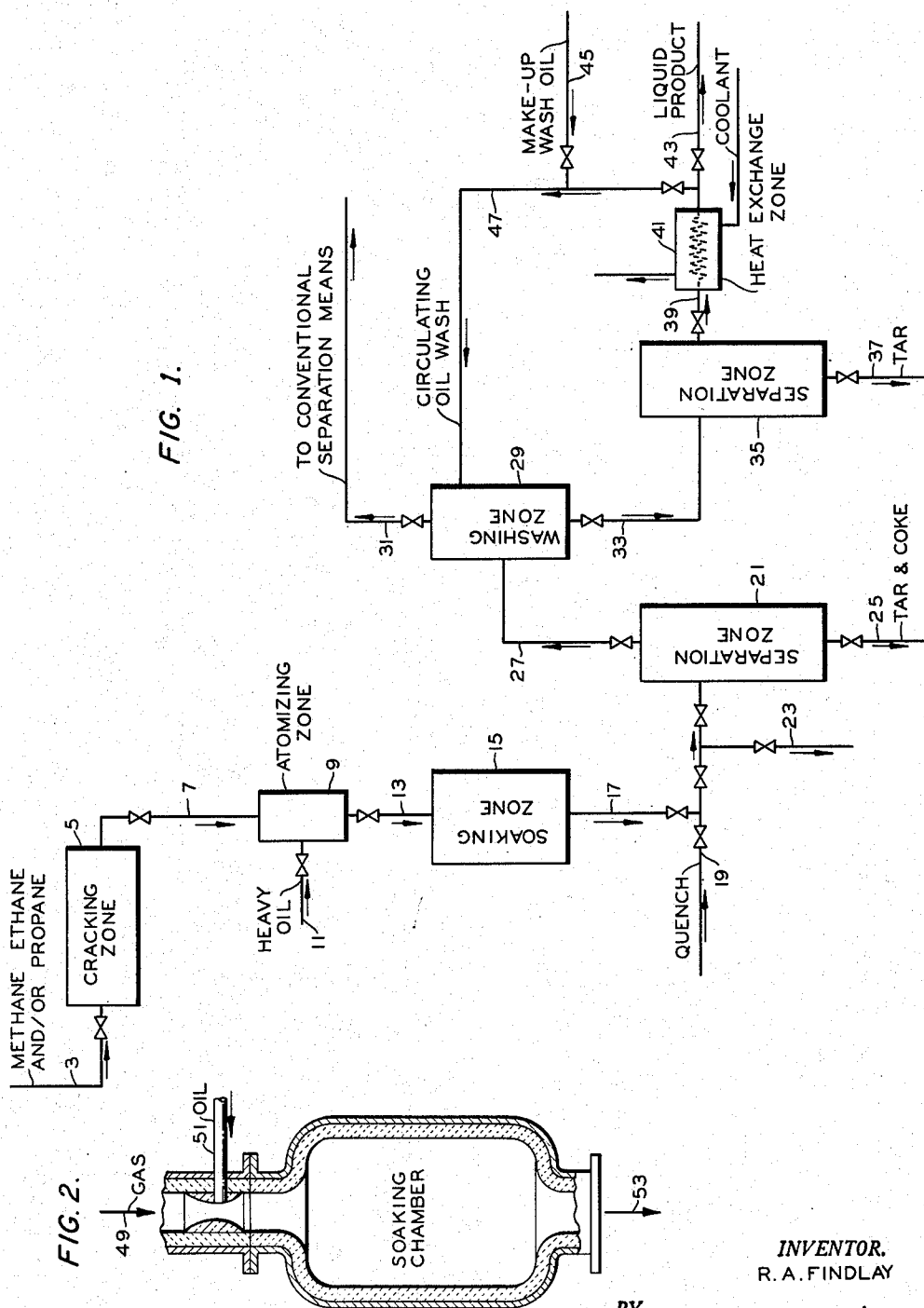
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CONVERSION OF HYDROCARBON MATERIALS

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CONVERSION OF HYDROCARBON MATERIALS

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This invention relates to treating hydrocarbon materials. In one of its more specific aspects it relates to a process for converting low-boiling normally gaseous hydrocarbon materials and higher boiling normally liquid hydrocarbon materials. In another of its more specific aspects this invention relates to a combination thermal conversion process for converting low-boiling normally gaseous paraffinic hydrocarbons, such as methane, ethane, propane and butanes, and high-boiling normally liquid hydrocarbon materials, such as gas oils, fuel oils and crude residuum. In still another of its more specific aspects this invention relates to a combination thermal conversion process and an effluent separation process for thermally converting low-boiling normally gaseous hydrocarbon materials and higher boiling normally liquid hydrocarbon materials and separating desired products of such conversions from tar and coke formed during such conversions.

It is old in the art to thermally convert low-boiling normally gaseous hydrocarbon materials, such as methane, ethane, propane, and butanes. Also, it is old in the art to thermally convert normally liquid hydrocarbon materials, such as high-boiling hydrocarbon fractions, such as gas oils, fuel oils and crude residuum. However, the petroleum industry is always striving to perform such thermal conversions more economically and more efficiently. It is advantageous to produce olefin hydrocarbons, such as ethylene, propylene and butylenes, which are used as starting materials in the synthesis of many hydrocarbon compounds as well as other organic compounds. Aromatic hydrocarbons and hydrocarbon-type materials normally have very good fuel ratings and their production is sought after in petroleum conversion processes. New thermal conversion processes for the production of olefinic hydrocarbons and aromatics which are economical, efficient and which give a high yield are valuable steps forward in the art.

I have invented a combination process for converting low-boiling normally gaseous hydrocarbon materials and higher-boiling normally liquid hydrocarbon materials. In the process of my invention, low-boiling normally gaseous hydrocarbon materials are converted in a first conversion zone. The effluent resulting from this first conversion is utilized in a second conversion zone to at least partially vaporize and convert higher boiling normally liquid hydrocarbon materials by directly transferring heat from the effluent from the first conversion operation to

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the higher boiling normally liquid hydrocarbon materials. The resulting effluents from both conversion operations are withdrawn in admixture with each other and subsequently treated to separate and recover the desired products resulting from these conversions.

I find that the process of my invention is particularly adaptable to the combination conversion of low-boiling normally gaseous hydrocarbon materials, such as methane, ethane, propane and/or butanes, and high-boiling normally liquid hydrocarbon materials, such as gas oils, fuel oils and crude residuum. In the conversion operation of the process of my invention, wherein the higher boiling normally liquid hydrocarbon materials are converted, I prefer to use a very advantageous and unique atomizing operation, that is, the effluent from the conversion of the low-boiling normally gaseous hydrocarbon materials is directly contacted with the high-boiling normally liquid hydrocarbon materials to partially vaporize a portion and to atomize a remaining portion of the high-boiling normally liquid hydrocarbon materials. The resulting vapors and atomized high-boiling normally liquid hydrocarbon materials are allowed to soak or remain for the necessary contact time at conversion temperatures so that the high-boiling normally liquid hydrocarbon materials are converted. During the atomizing operation the effluent from the low-boiling normally gaseous hydrocarbon conversion operation is quenched to a temperature below conversion temperature due to the transfer of heat to the high-boiling normally liquid hydrocarbon materials. Subsequent to the second conversion operation in which the high-boiling normally liquid hydrocarbon materials are converted, the mixed effluent resulting from both conversion operations is quenched to a temperature below the conversion temperature of the high-boiling normally liquid hydrocarbon materials, and the resulting quenched effluent is treated to remove tars and coke formed during the conversion operations. For removing such tars and coke I find it desirable to employ a centrifugal separation operation followed by a washing step, which is used to remove finely entrained coke particles. Aromatics are recovered from the wash oil used to remove the fine coke particles and resulting products from the washing operation are separated and recovered in conventional separation means, if desired.

I find that the process of my invention is very economical and efficient. Relatively high-temperature cracking at relatively low pressures of

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both low-boiling normally gaseous hydrocarbon materials and heavy hydrocarbon oils produces large quantities of olefins, such as ethylene and propylene, and aromatics, and in the process of my invention I find that the heavy oil cracking or conversion is obtained substantially without cost, since the effluent from the low-boiling normally gaseous hydrocarbon material conversion is quenched with heavy oils which are thereby converted. Since quenching is necessary in all cases, the heat recovery scheme of the process of my invention is very advantageous. Relatively large amounts of heavy oils can be processed at very low cost. In addition, the atomizing procedure used on the high-boiling hydrocarbons in the process of my invention is found to be very advantageous in that tars and coke which are formed are kept in fluid state thus making their removal relatively easy in the separation procedure of my process.

It is an object of this invention to provide a method for the treatment of hydrocarbon materials.

It is another object of this invention to provide a combination thermal conversion process for the conversion of low-boiling normally gaseous hydrocarbon materials, such as methane, ethane, propane and butanes, and higher boiling normally liquid hydrocarbon materials, preferably high-boiling hydrocarbon materials, such as gas oils, fuel oils and crude residuum.

It is another object of this invention to provide a combination thermal conversion and separation process for the conversion of low-boiling normally gaseous hydrocarbon materials, such as methane, ethane, propane and butanes, and higher boiling normally liquid hydrocarbon materials, preferably high-boiling hydrocarbon materials, such as gas oil, fuel oils and crude residuum, and the separation of tars and coke from desired products formed during such conversion.

It is a further object of this invention to provide a very efficient and economical combination thermal conversion process for performing the above-mentioned thermal conversions and for removing tars and coke from the effluent resulting from such conversions.

Other objects and advantages of the process of my invention will become apparent, to one skilled in the art, upon reading this disclosure.

The drawings which accompany and are a part of this disclosure diagrammatically set forth a preferred specific embodiment of the process of my invention. Figure 1 depicts a flow scheme to show how the process of my invention is carried on and includes a preferred means of separating tars and coke formed during the conversions from the combined effluent resulting from both conversion operations. Figure 2 diagrammatically depicts a combination atomizing and soaking zone unit which I find suitable for carrying on the atomizing step of the process of my invention and the conversion of high-boiling normally liquid hydrocarbon materials.

The process of my invention can be used to convert low-boiling normally gaseous hydrocarbon materials and higher boiling normally liquid hydrocarbon materials in a single combination process. Effluent from a low-boiling normally gaseous hydrocarbon conversion process which contains heat is used to directly furnish heat to higher boiling normally liquid hydrocarbons to heat them to conversion temperature. As a result of this heat exchange, the effluent from the low-boiling normally gaseous hydrocarbon con-

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version process is cooled to a temperature below its conversion temperature. Some examples of low-boiling normally gaseous hydrocarbons which can be converted or cracked in the process of my invention and which are preferred are paraffinic hydrocarbons having from 1 to 4 carbon atoms per molecule such as methane, ethane, propane and butanes. Ethane and/or propane can readily be converted to ethylene at high temperature, low pressure and short contact time, and propane can readily be converted to ethylene and propylene at high temperature, low pressure and short contact time. Methane conversion to produce hydrogen at high temperature, low pressure and short contact time is readily accomplished. These conversion operations give particularly advantageous results when used in the combination process of my invention. The process of my invention can be used to convert normally liquid hydrocarbons, generally C_5 and higher boiling hydrocarbons, preferably light gas oils and high-boiling hydrocarbon materials, such as heavy gas oils, fuel oils, crude residuum, and the like. I find that heavy gas oil, fuel oil and crude residuum give particularly good results when converted or cracked in the normally liquid hydrocarbon conversion step of the combination process of my invention. Olefins, particularly ethylene, and aromatics production are particularly good when ethane and/or propane are converted and used to partially vaporize, atomize, and convert heavy gas oils, fuel oils or crude residuum by the method of the process of my invention.

Referring now to Figure 1, which diagrammatically sets forth a preferred specific embodiment of the process of my invention, the following discussion is directed at my combination of thermal conversion processes for converting methane, ethane and/or propane, and a heavy oil, such as heavy gas oil, fuel oil or crude residuum. Also, a preferred separation scheme for removing tars and cokes formed during such conversions, from the combined effluent resulting from such conversions is discussed. A methane, ethane and/or propane stream is passed via line 3 into cracking zone 5 wherein the light paraffinic hydrocarbon stream is thermally converted at a relatively high temperature, a relatively low pressure and for a relatively short contact time. Cracking zone 5 can be any suitable thermal conversion process, but it is preferably a thermal conversion process carried out by utilizing pebble heater apparatus, that is, pebble heater apparatus utilizing a contiguous moving bed of refractory pebbles. Normally, the refractory pebbles are heated in a pebble heating zone and flow by gravity into the thermal conversion zone wherein they heat the light paraffinic hydrocarbon stream to conversion temperature.

The effluent resulting from the thermal conversion carried on in cracking zone 5 is withdrawn via line 7 and is passed into an atomizing zone 9. In atomizing zone 9 the hot effluent from cracking zone 5 is directly contacted with heavy oil passed into atomizing zone 9 via line 11, thereby partially vaporizing the heavy oil and atomizing the remainder. Atomizing zone 9 can be any suitable device that is so designed to bring the heavy oil into direct contact with the hot effluent from cracking zone 5. I prefer to use a Venturi section, forcing the heavy oil into the gas stream as it passes through the Venturi throat. Figure 2, which is discussed hereinafter, depicts a preferred Venturi atomizing zone which

exhausts directly into a soaking chamber wherein the heated heavy oils, in vapor and atomized form, are held for the desired length of time prior to quenching so that thermal conversion of the heavy oils can proceed to the desired degree of completion.

Resulting vapors and atomized heavy oils are withdrawn from atomizing zone 9 via line 13 and passed into soaking zone 15, which can be any suitable chamber or series of chambers for holding the heavy oils at conversion temperature for a desired length of time.

As the result of contacting the effluent from cracking zone 5 and the heavy oil in atomizing zone 9, the effluent from cracking zone 5 is cooled to a point below its conversion temperature and the heavy oils are heated to conversion temperature. I find it desirable to control the temperature by regulating the amount of heavy oils passed into atomizing zone 9.

The mixture resulting from both conversions is withdrawn from soaking zone 15 via line 17, quenched in a suitable manner, preferably by directly contacting the combined effluent with a quenching medium introduced via line 19, and a resulting mixture is passed into separation zone 21. The effluent mixture from the conversion which has been quenched can be withdrawn, if desired, via line 23 for treatment and suitable separation means. However, I find that the separation process which I have depicted in Figure 1 is very satisfactory for the desired separation process. I prefer that separation zone 21 be a centrifugal separator. The combined quenched effluent is passed tangentially into centrifugal separation zone 21. Centrifugal force throws the greater quantity of the tar and coke formed during the thermal conversion operations to the walls of the centrifugal separator. The tar and coke remain in fluid state because I keep the walls at a temperature high enough to prevent the tars and cokes from setting up. Resulting separated tar and coke are withdrawn from the bottom portion of the centrifugal separator via line 25.

A resulting stream from which the greater portion of tar and coke has been removed is withdrawn from separation zone 21 via line 27 and is passed into a washing zone 29 which can conveniently be a bubble-tray or packed wash column. Within washing zone 29 the said resulting stream is contacted with a circulating wash oil stream. The wash oil stream is compatible with fine coke particles which pass through the centrifugal separator, washing the fine coke particles and removing them from the desired effluents of the thermal conversion processes. Resulting products of the thermal conversion processes are withdrawn from washing zone 29 via line 31 and are passed to conventional separation means wherein the products are separated and recovered as desired.

Wash oil containing fine coke particles removed in washing zone 29 is withdrawn via line 33 and is passed into separation zone 35, preferably a settling zone, wherein the fine coke particles are removed from the wash oil and are withdrawn via line 37. Resulting wash oil is removed from separation zone 35 via line 39 and is passed into heat exchange zone 41 wherein it is cooled prior to recirculation to washing zone 29.

Normally, as the result of the washing in washing zone 29, aromatics are absorbed by the wash oil. Therefore, a portion of the wash oil from heat exchanger 41 is desirably withdrawn via line 43 and treated with any suitable equipment, con-

ventional fractionation equipment being desired, to separate and recover aromatics. A portion of the wash oil from heat exchange zone 41, with make-up wash oil introduced via line 45, is recirculated to the upper portion of washing zone 29 via line 47 for further contacting.

Figure 2 depicts a preferred combination atomizing zone and soaking zone which I find is desirable to use as atomizing zone 9 and soaking zone 15. The effluent from the low-boiling paraffinic hydrocarbon conversion operation enters as indicated by arrow 49 into a ceramic venturi. Heavy oil is passed into the throat of the Venturi section via line 51 wherein it is directly contacted with the hot gases, thus vaporizing a portion and atomizing a remaining portion of the heavy oil. The resulting vapors and atomized heavy oils are discharged directly into a soaking chamber wherein a conversion of the heavy oil takes place. The venturi is formed of a suitable ceramic material, such as heat resistant fired clays, or it can be formed of known heat resistant metallic alloys. The soaking chamber is preferably lined with heat resistant material, such as insulcrete or the like materials, since the combined stream is maintained at relatively high temperatures.

The soaking chamber is so designed that the heavy oils are held at conversion temperature for a desired length of time and the combined effluent resulting from the conversions is withdrawn from the soaking chamber as indicated by arrow 53. Rapid quenching, as discussed hereinbefore, is carried out following the heavy oil conversion in the soaking chamber.

In the process of my invention I prefer to carry on ethane or methane cracking, or methane and ethane cracking, at a pressure of from 5 to 40, preferably 5 to 25, pounds per square inch absolute, a temperature of from 1300-2500° F., preferably 1500-2000° F., and for a contact time of from 0.001 to 1 second, preferably 0.05 to 0.2 second. If propane, or propane and ethane are converted in carrying out the process of my invention, I prefer to carry on such conversions at a pressure of from 5 to 40, preferably 5 to 25, pounds per square inch absolute, at a temperature of from 1200-2400° F., preferably 1400-1900° F., and for a contact time of from 0.002 to 1.5 seconds, preferably 0.07 to 0.5 second. In the heavy oil conversion step of the process of my invention, I prefer to carry on the heavy gas oil, fuel oil, or crude residuum conversion at a pressure of from 5 to 40, preferably 5 to 25 pounds per square inch absolute, at a temperature of from 950-1450° F., preferably 1050-1350° F., and for a soaking time of from 0.2 to 3.5 seconds, preferably 1 to 2 seconds. I find that it is desirable to quench the combined effluents from the conversion processes to a temperature of 900° F. or less, preferably to a temperature of from 525-725° F. Maintenance of the wall temperature in centrifugal separation zone 21 at the temperature at which the combined conversion effluents are quenched, is suitable to maintain the tars and coke in fluid state within the centrifugal separator so that they will not set up on the walls.

In the washing operation performed in washing zone 29, I prefer to use a liquid washing medium, such as a mineral seal oil, a light gas oil or the like. Steam or water can be used, if desired, as the quenching medium. However, I prefer to use a thermally stable quench oil, such as a cycle oil from a product fractionator employed in the conventional separation means used to separate and recover the products resulting from the con-

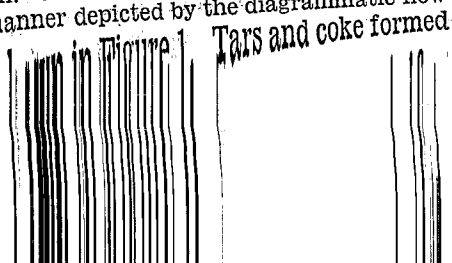
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versions, for instance, a fairly refractory cycle oil having, for example, a boiling range of from 500-600° F. A quench oil, if an extraneous oil stream, is desirably a fairly refractory oil with not too low a boiling range to result in substantial vaporization of the quench oil.

It is to be understood that the above set forth preferred specific direction of my invention, setting forth materials, such as feed streams to the conversion operation, quenching mediums, wash oils, etc., temperatures, pressures, etc., is not to unduly limit the scope of my invention.

Following is an example of the process of my invention. The following example is carried out in the manner depicted by the diagrammatic flow



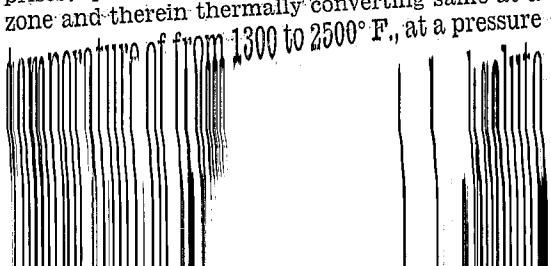
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I find that by decreasing the heavy oil feed rate, larger amounts of olefinic hydrocarbons and smaller amounts of liquid products are produced.

As will be evident to those skilled in the art, various modifications of this invention can be made, or followed, in the light of this disclosure and discussion, without departing from the spirit or scope of this disclosure or from the scope of the claims.

I claim:

1. A process for converting ethane and liquid high-boiling hydrocarbon materials selected from the group consisting of heavy gas oil, fuel oil, crude residuum and mixtures thereof, which comprises: passing ethane into a first conversion zone and therein thermally converting same at a



high-boiling hydrocarbon materials from said second conversion zone and directly contacting same with a quench medium, thereby quenching to a temperature below 900° F.

3. A process for converting paraffinic hydrocarbons selected from the group consisting of methane, ethane, propane and liquid mixtures thereof and high-boiling hydrocarbon materials selected from the group consisting of heavy gas oil, fuel oil, crude residuum and mixtures thereof, which comprises: passing such a paraffinic hydrocarbon into a first conversion zone and therein thermally converting same at conversion temperature and pressure; withdrawing resulting products of conversion from said first conversion zone and passing same into an atomizing zone; passing such a liquid high-boiling hydrocarbon material into said atomizing zone; directly contacting said resulting products of conversion from said first conversion zone and said liquid high-boiling hydrocarbon material in said atomizing zone, thereby vaporizing a portion, atomizing a remaining portion and heating to conversion temperature said high-boiling hydrocarbon material, and quenching said resulting products of conversion from said first conversion zone below conversion temperature; directly passing a resulting mixture of vapors and atomized high-boiling hydrocarbon materials into a second conversion zone and therein thermally converting said high-boiling hydrocarbon materials at conversion temperature and pressure; and withdrawing resulting vapors and atomized high-boiling hydrocarbon materials from said second conversion zone and directly contacting same with a quench medium, thereby quenching to a temperature below conversion temperature.

4. The process of claim 3 wherein said quench medium is water.

5. The process of claim 3 wherein said quench medium is a thermally stable quench oil.

6. A process for converting paraffinic hydrocarbons selected from the group consisting of methane, ethane, propane and mixtures thereof and high-boiling hydrocarbon materials selected from the group consisting of heavy gas oil, fuel oil, crude residuum and mixtures thereof which comprises: passing such a paraffinic hydrocarbon into a first conversion zone and therein thermally converting same at conversion temperature and pressure; withdrawing resulting products of conversion from said first conversion zone and passing same into an atomizing zone; passing such a high-boiling hydrocarbon material into said atomizing zone; directly contacting said resulting products of conversion from said first conversion zone and said high-boiling hydrocarbon material in said atomizing zone, thereby vaporizing a portion, atomizing a remaining portion and heating to conversion temperature said high-boiling hydrocarbon material, and quenching said resulting products of conversion from said first conversion zone below conversion temperature; passing a resulting mixture of vapors and atomized high-boiling hydrocarbon materials into a second conversion zone and therein thermally converting said high-boiling hydrocarbon materials at conversion temperature and pressure; withdrawing resulting vapors and atomized high-boiling hydrocarbon materials from said second conversion zone, directly contacting same with a quench medium, thereby quenching to a temperature below conversion temperature but at least high enough so that tars and coke

formed in said conversion remain in a fluid state; passing resulting quenched vapors and high-boiling hydrocarbon materials, containing said tars and coke in fluid state, into a centrifugal separation zone and therein separating tars and coke from said vapors and high-boiling hydrocarbon materials; withdrawing resulting tars and coke from said centrifugal separation zone; withdrawing resulting vapors and high-boiling hydrocarbon materials, containing fine particles of coke, from said centrifugal separation zone, passing same into a washing zone and therein directly and countercurrently contacting same with a wash oil, thereby wetting said fine coke particles and removing them from said resulting vapors and high-boiling hydrocarbon materials passed into said washing zone; withdrawing resulting wash oil from said washing zone, removing coke particles and aromatic hydrocarbons from same and recycling resulting wash oil to said washing zone; and withdrawing resulting overhead vapors from said washing zone.

7. The process of claim 6 wherein said quench medium is a thermally stable quench oil, and said wash oil is a mineral seal oil.

8. The process of claim 7 wherein the said first conversion zone is a pebble heater.

9. A process according to claim 6 in which ethylene is produced and in which the conditions in the first conversion zone are: a temperature in the range 1300-2500° F., a pressure in the range 5 to 40 pounds per square inch absolute, and a contact time in the range 0.001 to 1 second and wherein the conditions in the second conversion zone are: a temperature in the range 950-1450° F., a pressure in the range 5 to 40 pounds per square inch absolute, and a contact time in the range from 0.2 to 3.5 seconds, and wherein the effluent vapors and atomized high boiling hydrocarbon materials from said second conversion zone are quenched to a temperature below approximately 900° F.

10. A process for converting low-boiling normally gaseous hydrocarbon materials and high-boiling normally liquid hydrocarbon materials, which comprises: converting a low-boiling normally gaseous hydrocarbon material at conversion temperature and pressure in a first thermal conversion operation; passing resulting products of said first thermal conversion into an atomizing zone, therein directly contacting same with such a high-boiling normally liquid hydrocarbon material which is passed into said atomizing zone, thereby vaporizing a portion, atomizing a remaining portion and heating to conversion temperature said high-boiling normally liquid hydrocarbon materials, and quenching said resulting products from said first thermal conversion operation to a temperature below conversion temperature; directly converting resulting atomized and vaporized high-boiling normally liquid hydrocarbon material at conversion temperature and pressure while in admixture with said resulting products from said first thermal conversion operation in a second thermal conversion operation; and quenching a resulting mixture of products of said first and second thermal conversion operations to a temperature below conversion temperature.

11. A process for converting low-boiling normally gaseous hydrocarbon materials and a reduced crude, which comprises: passing said low-boiling normally gaseous hydrocarbon material into a first conversion zone and therein converting same at conversion temperature and pres-

pressure, withdrawing resulting products from said first conversion zone, passing same into an atomizing and conversion zone and using same therein to vaporize a portion, atomize a remaining portion and convert at conversion temperature and pressure such a reduced crude which is passed directly into said atomizing and conversion zone, by directly transferring heat from said resulting products withdrawn from said first conversion zone to said reduced crude passed into said second conversion zone, and withdrawing a resulting mixture from said second conversion zone.

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