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COMBINED PROCESS FOR MANUFACTURING ENRICHED WATER-GAS AND AROMATIC HYDROCARBONS

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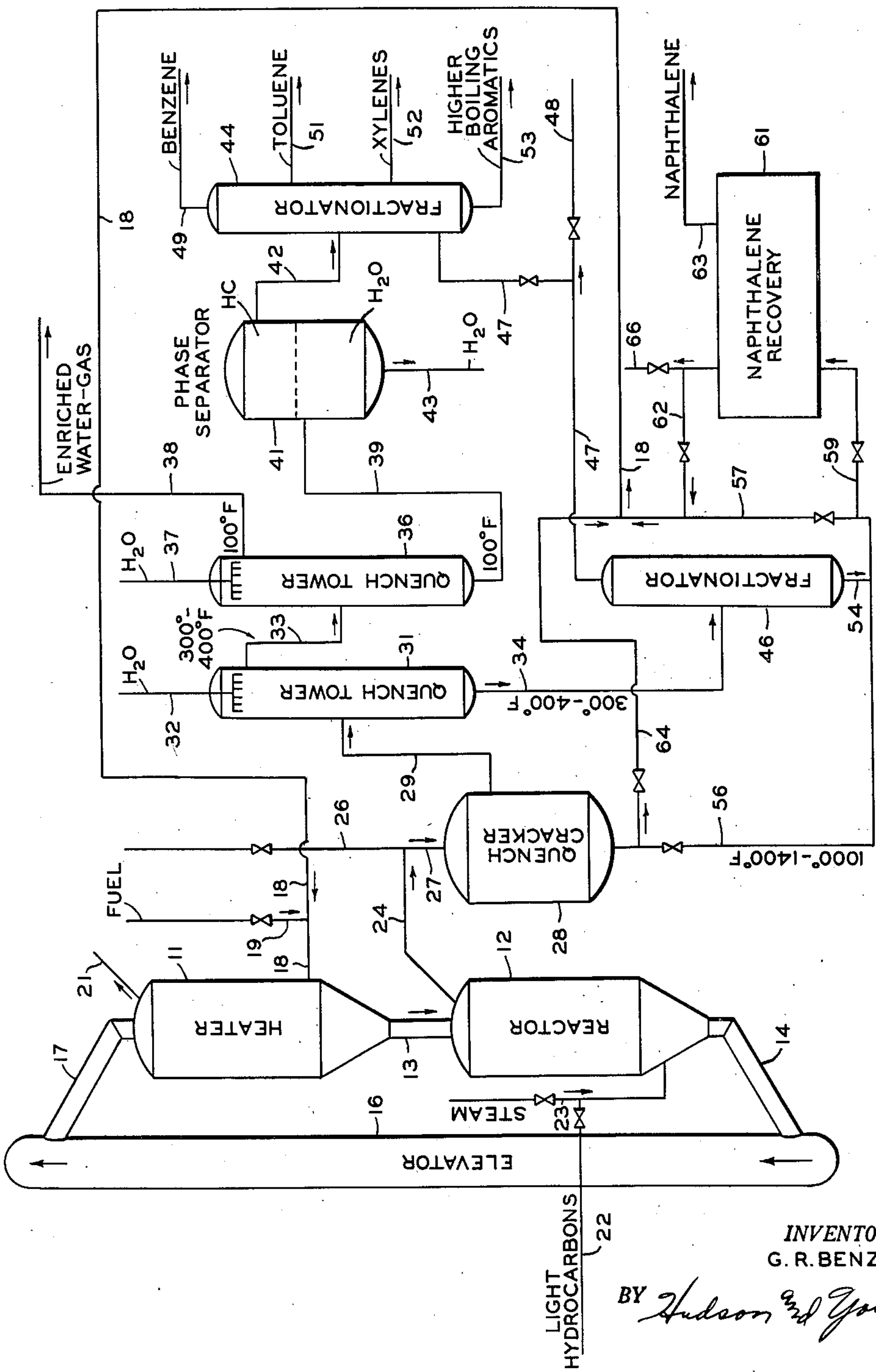

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COMBINED PROCESS FOR MANUFACTURING ENRICHED WATER-GAS AND AROMATIC HYDROCARBONS

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The invention described herein pertains to a process for manufacturing enriched water-gas and aromatic hydrocarbons. The process utilizes pebble heater type apparatus to effect a water-gas reaction and a combination quench-cracking chamber to produce aromatic hydrocarbons from atomized heavy hydrocarbon oil.

Pebble heat-exchange apparatus has been applied to a wide variety of processes where rapid heating of gases to high temperatures is desirable, including heating of air, nitrogen, steam, and gaseous reactants. In this type of operation, a continuous compact mass of highly refractory pebbles descends by gravity through a series of heat-exchange chambers, absorbing heat from a hot gas, usually combustion gas, in an upper chamber and delivering the heat required for heating and/or chemical reaction in a lower chamber by direct contact with the feed gas therein.

The pebbles utilized in the process may be any of the conventional pebbles of the art. The term "pebble" as used throughout this specification denotes any solid refractory contact material, either catalytic or non-catalytic with respect to the process in which it is used, of flowable form and size, and sufficiently rugged and abrasive resistant for use in cyclic heat-exchange processes. Pebbles are preferably substantially spherical and relatively uniform in size in a given process, but may be of other shapes, either regular or irregular and non-uniform in size. Spheres of about ⅛ inch to 1 inch in diameter function desirably in pebble heat-exchange processes and those in the range of ¼ inch to ⅝ inch are most practical. Since pebble heat-exchange apparatus has its greatest utility in processes requiring gas heating and/or reaction temperatures upwards of about 1500° F., pebbles must be formed of material that will withstand extremely high temperatures. In some hydrocarbon cracking processes, pebbles must withstand temperatures of 3000° F. or even higher. Serviceable heat and abrasive resistant pebbles have been compacted from alumina, mullite, alumina-mullite, zirconia, magnesia, beryllia, thoria, periclase, natural and synthetic clays, and mixtures of these materials. Spheres formed of high temperature alloys and metals have also been found practical in some processes.

One of the problems of the petroleum industry is the utilization of heavy hydrocarbon oils such as heavy fuel oils and residual hydrocarbons from various refinery processes conventionally termed "heavy residuum." Due to the abundance of this type of hydrocarbon and the relatively small demand for the same, it is desirable to convert as much as possible into lighter, more valuable hydrocarbons by cracking, but cracking such material to produce lighter hydrocarbons involves difficulties which have been hard to overcome. The process of this invention offers a simple and effective method of cracking heavy hydrocarbons to lighter hydrocarbons, particularly normally gaseous hydrocarbons and aromatics.

The water-gas reaction has long been used to produce large quantities of CO and H_2 which can be effectively utilized as fuel or as synthesis gas for the synthesis of hydrocarbons useful as motor fuel. In many instances it is desirable to up-grade the water-gas so as to increase the B. t. u. content of the same and render it more valuable as a fuel gas. The present invention provides a process which effectively produces an enriched water-gas and simultaneously produces valuable aromatic hydrocarbons.

The principal objective of the invention is to provide an improved process for producing an enriched water-gas. It is also an object of the invention to provide a combined process for producing enriched water-gas while simultaneously producing valuable aromatic hydrocarbons from relatively inexpensive raw material. Another object of the invention is to afford better utilization of heat and greater efficiency in a process for producing enriched water-gas. Other objects of the invention will become apparent from a consideration of the disclosure.

The invention entails the reaction in a pebble heater reactor of a mixture of steam and hydrocarbon in vapor form under water-gas producing conditions, whereby an effluent containing large proportions of CO and H_2 at a temperature in the range of 1700 to 2500° F. is produced and immediately quenched with atomized heavy hydrocarbon oil in a combination quench-cracking chamber which is maintained under conditions effective in cracking the atomized oil to hydrogen, light olefins, and aromatic hydrocarbons ranging from benzene to naphthalene and heavier. The gaseous effluent from the quench-cracking chamber containing the water-gas and hydrocarbons produced from the cracking of the heavy oil boiling below the temperature maintained in the quench-cracking chamber is separated into a normally gaseous fraction comprising the enriched water-gas and a normally liquid fraction comprising principally the aromatic hydrocarbons. The normally liquid fraction from the cracking step is then fractionated to recover the lighter aromatics boiling below about 400° F. leaving a bottoms fraction containing heavier aromatics such as naphthalene, heavier alkalated benzenes, and other heavy hydrocarbons. This heavy fraction is then utilized as fuel for supplying the hot combustion gas required for heating the pebbles in the pebble heating chamber as taken from the fractionator or after passing through a naphthalene recovery system where the naphthalene is extracted as a product of the process. The bottoms from the oil cracking step may be combined with the bottoms from the fractionator before or after naphthalene recovery from the fractionator bottoms.

For a more complete understanding of the invention reference may be had to the drawing which shows a diagrammatic arrangement of apparatus particularly adapted for effecting the process of the invention. The drawing shows a typical pebble heater apparatus comprising a pebble heater chamber **11** and a reaction chamber **12** connected by throat **13** so as to provide for gravitation of the pebbles in a compact mass from the pebble inlet in the heater to the pebble outlet in the reactor. A pebble chute **14** connected with the pebble outlet of reactor **12** carries pebbles by gravity flow to the bottom of elevator **16** which may be of the bucket type or of any other conventional lifting type of device suitable for transferring pebbles from chute **14** to chute **17** from which the pebbles flow by gravity into the top of heater **11**. The flow of pebbles through the heater and reactor is controlled by a pebble feeding device, not shown, in chute **14**.

In processing hydrocarbons, suitable fuel is burned in the lower section of heater **11** or in an adjacent burner and the hot combustion gas is passed upwardly through the void spaces between the pebbles and is taken off through stack **21**. In the process of the invention the principal or sole source of fuel is the heavy bottoms product from the cracking of the heavy hydrocarbon used in quenching the hot effluent from reactor **12**. Auxiliary fuel line **19** is used to provide light liquid or gaseous fuels to supplement the heavy fuel in line **18**, where desired or necessary to expedite the burning of the heavy fuel. The pebbles in heater **11** are heated to a temperature of at least 100° F. above the desired reaction temperature to be maintained in reactor **12** which is in the range of 1700 to 2500°, thereby requiring an entrance pebble temperature in the range 1800 to 2600° and higher, depending principally upon pebble and feed flow rates. The hot pebbles in reactor **12** are contacted with a mixture of hydrocarbon in vapor form and steam introduced to the bottom of the reactor through line **22**, the steam being introduced to line **22** through line **23**. As the hydrocarbon-steam mixture passes upwardly through reactor **12** the temperature of the gas is rapidly increased to reaction temperature, and water-gas comprising CO and H_2 is formed in the upper section of the reactor. The hot effluent taken off through line **24** is passed through line **27**, which may be an expanded conduit, in admixture with atomized heavy fuel oil or other heavy hydrocarbon mixture introduced through line **26**. The amount of atomized fuel oil is regulated in proportion to the amount and temperature of the effluent passing through line **24** so as to maintain a temperature in quench-cracking chamber **28** in the range of 1000 to 1400° and effectively crack the atomized oil to hydrogen and lighter hydrocarbons comprising olefins and aromatics. Uncracked and other hydrocarbons boiling above the temperature maintained in quench-cracking chamber **28** collect in the bottom of the chamber while the vaporized fraction including the water-gas and lighter products of the cracked-quench oil pass through line **29** to quench chamber **31** where this stream is quenched with water spray admitted through line **32** to a temperature in the range 300 to 400° F., preferably about 300° F. This quench knocks out the aromatics and other hydrocarbon oils boiling above the quench temperature and these are withdrawn through line **34** and processed as hereinafter set forth. The gaseous effluent from quench tank **31**, including the H_2O together with the enriched water-gas, is passed through line **33** to quench tank **36** where practically all of the water and products boiling above approximately 100° F. are knocked out. The gaseous effluent from quench tank **36** passes out through line **38** as the enriched water-gas product of the process and may be further dried or processed in any other desirable manner preparatory to using the same as fuel in a city gas system or other application. The condensate from quench tank **36** is passed through line **39** to a phase separator **41** from which the hydrocarbons are withdrawn through line **42** and passed to fractionating tower **44**. Water introduced to the process in the pebble heater reactor through line **23** and through lines **32** and **37** to the quench tanks, settles to the bottom of phase separator **41** and is withdrawn through line **43** for disposal or recycling as quench water or steam.

The liquid bottoms from quench tank **31**, containing principally the olefins, aromatics, and other hydrocarbons boiling between a temperature in the range of 300 to 400° F. is passed through line **34** to a fractionator or other separation means **46**, in which the lighter more valuable aromatics, such as those boiling below about 400° F., are taken off overhead through line **47** and passed to fractionator **44** for separation together with the effluent from line **42** into various aromatic products such as benzene, toluene, and xylene for recovery through lines **49**, **51**, and **52**, respectively. The higher boiling aromatics and other hydrocarbons in the overhead from fractionator **46** and phase separation **41** are recovered through line **53**.

The liquid bottoms from fractionator **46**, including heavy aromatics such as naphthalene, are withdrawn through line **54** and mixed with the liquid bottoms from

quench-cracking chamber **28** passing through line **56** and the admixture is passed through line **57** either directly to pebble heater fuel line **18** or indirectly thereto through line **59**, naphthalene recovery system **61**, and effluent line **62**. Naphthalene recovery system **61** may be of any conventional type or design from which the naphthalene is recovered through line **63**.

It is desirable in some instances to pass the heavy liquid product from quench-cracking zone **28** through line **64** directly to fuel line **18** without mixing this fuel with the bottoms product from fractionator **46** prior to the recovery of naphthalene from the material in line **37**. It is, of course, feasible to utilize the heavy hydrocarbon in line **64** as the sole source of fuel where its quantity is sufficient. In this case the residual hydrocarbon from the naphthalene recovery can be withdrawn through line **66** for any suitable use or process.

The hydrocarbon raw material for the water-gas may comprise any hydrocarbon in vapor form but is preferably made-up of normally gaseous hydrocarbons and particularly propane. The hydrocarbon feed is mixed with steam in a ratio of hydrocarbon to steam in the range of 1:1 to 1:10 and the reaction temperature is maintained in the range of 1700 to 2500° F. and preferably above 2000° F. in order to produce maximum quantities of CO and H_2 and also to provide the maximum amount of heat for cracking the oil atomized into the hot water-gas effluent. It has been found that 87 lbs. of heavy oil can be cracked for each 100 lbs. of hydrocarbon feed passed into the pebble heater reactor. The amount of atomized oil mixed or sprayed into the hot water-gas stream and reacted in the quench-cracking chamber is regulated so as to maintain a suitable temperature within the range of 1000 to 1400° F. and preferably at least 1100° F. so as to produce maximum amounts of aromatics in the cracking step.

When converting propane and steam to water-gas without the use of an oil quench for enriching the water-gas, for each hundred pounds of propane fed to the process there is produced 8,462 $ft.^3$ of water-gas having a B. t. u. value of 310/$ft.^3$ and a specific gravity of 0.343 as compared with the process of the invention in which approximately 87 lbs. of oil is cracked for each hundred lbs. of propane feed and there is produced 9,177 $ft.^3$ of enriched gas having a B. t. u. value of 390/$ft.^3$ and a specific gravity of 0.380. This comparison which shows a valuable up-grading of the gas and greater yield thereof from a given amount of propane feed, is based upon a reaction temperature of 2500° F. in the pebble heater, a quench-cracking temperature of 1100° F., a heavy fuel oil-quench oil, and a ratio of 100 lbs. of propane to 163.6 lbs. of steam.

Of the 87 lbs. of oil cracked per hundred pounds of propane, 19.5 lbs. of gas of the composition shown in Table I is produced.

Table I

	Mol percent
H_2	17.9
C_1	27.3
C_2	38.8
C_3	10.8
C_4	5.2
	100.0

The products in Table I appear in the enriched water-gas and are a part of this product of the process. The remaining 67.5 lbs. of the oil converted is in the form of normally liquid aromatics of different weights together with olefins and some paraffins. Approximately 16 lbs. of this liquid product from the cracking step is made-up of aromatics boiling up to 400° F. The 400° F. end point fraction is an aromatic concentrate comprising, principally, benzene, toluene, and xylenes with the benzene in major proportion. Approximately 15 lbs. of the oil cracked comprises aromatics and other hydrocarbons boiling in the range of 400 to 900° F. The balance of the liquid fraction comprises heavier hydrocarbons and coke.

The hot gaseous effluent from the quench-cracking chamber is water-quenched to approximately 300° F. so as to knock out the oil without condensing any appreciable amount of water and thereby avoiding the formation of oil emulsions which are difficult to break. This simplifies the separation of the liquid stream from the first quench comprising the aromatics boiling above 300° F. and allows the gaseous overhead from the first quench to be water quenched so as to condense the water entrained in the product stream. This procedure makes it relatively simple to separate the light aromatics from the water condensed in the second quench by passing the mixture to a phase separator where the hydrocarbon phase separates from the water phase and is drawn off the top or upper section of the phase separator for separation in fractionator 44 into its various constituents together with the overhead from the heavier aromatic separation in fractionator 46.

It should be evident from the disclosure that the process described is particularly effective in efficiently producing an enriched water-gas in maximum amounts with extremely high utilization of heat and improved efficiency. The quenching of the water-gas effluent from the pebble heater reactor with a heavy fuel oil or residuum utilizes the sensible heat of that stream in a highly efficient manner by heating and cracking the heavy hydrocarbon to more valuable products which are recovered in the process as aromatic hydrocarbons and as light fuel gases in the enriched water-gas product. In addition, the practically valueless heavy hydrocarbon residuum from the process is utilized in the heating of the pebbles in the pebble heater so as to reduce fuel costs and thereby aid in the economics of the process. As further evidence of the efficient heat utilization of the process it should be noted that a substantial portion of the sensible heat of the water-gas effluent from the pebble heater is imparted to the heavy residual hydrocarbon from the cracking step and from fractionator 46, and this heavy hydrocarbon is passed in hot condition to the pebble heater as fuel, thereby utilizing its sensible heat in producing higher temperatures in the pebble heating chamber than would be produced with the same amount of cold fuel. It should also be noted that the quenching and cracking of heavy oil utilizes valuable heat of the effluent water-gas to simultaneously enrich the water gas and produce valuable aromatic hydrocarbons.

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.

I claim:

1. A continuous process for cracking hydrocarbon to produce enriched water-gas and aromatic hydrocarbons which comprises heating a gravitating compact mass of pebbles in a heating zone to a temperature at least 100° F. above the hereinafter specified reaction temperature; contacting the resulting gravitating hot stream of pebbles in a reaction zone with a gaseous stream comprising hydrocarbon and steam in a weight ratio of hydrocarbon to steam in the range of 1:1 to 1:10 at a reaction temperature in the range of 1700 to 2500° F. so as to produce water-gas; passing the water-gas-containing effluent into a combination quench-cracking zone and quenching same with a heavy liquid hydrocarbon having an initial boiling point above 600° F. in such an amount as to maintain a cracking temperature in the range of 1000 to 1400° F. thereby vaporizing and cracking a substantial portion of said liquid hydrocarbon to H_2 and lighter hydrocarbons including aromatics solely by the sensible heat of said effluent; separating the gaseous effluent from said quench-cracking zone into a normally gaseous fraction comprising water-gas enriched with H_2 and normally gaseous hydrocarbons produced in the quench cracking step and a heavier fraction comprising aromatic hydrocarbons by first water-quenching said effluent to a temperature in the range of 300 to 400° F. and then water-quenching the remaining gaseous effluent to knock out light liquid hydrocarbons and water therefrom; fractionating said heavier fraction so as to recover an overhead fraction boiling below a temperature in the range of 350 to 400° F. containing aromatic hydrocarbons and a bottoms fraction containing naphthalene; recovering naphthalene from said bottoms fraction to form a residual bottoms fraction; recovering a liquid fraction from said quench-cracking zone and combining same with said residual bottoms fraction to form a mixed heavy hydrocarbon fraction; burning at least a portion of said combined heavy hydrocarbon fraction in said heating zone to heat said pebbles; and recycling pebbles from said reaction zone to said heating zone for reheating.

2. The process of claim 1 in which the hydrocarbon feed to said reaction zone is a propane-rich gas.

3. A continuous process for cracking hydrocarbons to produce enriched water-gas and aromatic hydrocarbons which comprises heating a gravitating compact mass of pebbles in a pebble heating zone to a temperature at least 100° F. above the hereinafter specified reaction temperature; contacting the resulting gravitating hot stream of pebbles in a reaction zone with a mixture of propane and steam in a weight ratio of hydrocarbon to steam in a range of 1:1 to 1:10 at a reaction temperature in the range of 2000 to 2500° F. so as to produce water-gas; passing the water-gas containing effluent into a combination quench-cracking zone and quenching same with a heavy liquid hydrocarbon having an initial boiling point above 600° F. in such an amount as to maintain a cracking temperature of 1100 to 1400° F. thereby vaporizing and cracking a substantial portion of said liquid hydrocarbon to H_2 and lighter hydrocarbons including aromatics solely by the sensible heat of said effluent; passing the gaseous effluent from said quench-cracking zone into a first water-quench zone and quenching the effluent to a temperature of 300° F. so as to knock out the hydrocarbon oil boiling above said temperature while passing the uncondensed fraction comprising steam and hydrocarbons boiling below said temperature to a second water-quench zone; water-quenching said uncondensed fraction in said second water-quenching zone to a temperature of 100° F. so as to recover a gaseous effluent therefrom containing enriched water-gas and a condensate containing essentially all of the H_2O and hydrocarbons boiling in the range of 100 to 300° F.; separating said condensate by phase separation into a hydrocarbon fraction and a water fraction; passing said hydrocarbon fraction comprising principally aromatic hydrocarbons, into a first fractionating zone together with a second aromatic fraction derived as hereinafter described and separating a combined aromatic feed into separate fractions consisting essentially of benzene, toluene, and xylenes, respectively; passing the condensate from said first water-quenching zone to a second fractionating zone and separating same into an aromatic overhead fraction boiling below 400° F. and bottoms fraction including naphthalene; passing said overhead aromatic fraction to said first fractionator; recovering naphthalene from said last-named bottoms fraction and burning the residual hydrocarbon therefrom in admixture with the bottoms from said quench-cracking zone in said pebble heating zone so as to heat said pebbles; and recycling pebbles from said reaction zone to said heating zone for reheating.

4. A continuous process for cracking hydrocarbon to produce enriched water-gas and aromatic hydrocarbons which comprises heating a gravitating compact mass of pebbles in a heating zone to a temperature at least 100° F. above the hereinafter specified reaction temperature; contacting the resulting gravitating hot stream of pebbles in a reaction zone with a gaseous stream comprising hy-

drocarbon and steam in a weight ratio of hydrocarbon to steam in the range of 1:1 to 1:10 at a reaction temperature in the range of 1700 to 2500° F. so as to produce water-gas; passing the water-gas containing effluent into a combination quench-cracking zone and quenching same with a heavy liquid hydrocarbon having an initial boiling point above 600° F. in such an amount as to maintain a cracking temperature in the range of 1000 to 1400° F. thereby vaporizing and cracking a substantial portion of said liquid hydrocarbon to H_2 and lighter hydrocarbons including aromatics solely by the sensible heat of said effluent; passing the gaseous effluent from said quench-cracking zone into a first water-quench zone and quenching the effluent to a temperature in the range of 300° to 400° F. so as to knock out hydrocarbon oil boiling above said temperature while passing the uncondensed fraction comprising steam and hydrocarbons boiling below said temperature to a second water-quench zone; water-quenching said uncondensed fraction in said second water-quenching zone to a temperature of about 100° F. so as to recover a gaseous effluent therefrom containing enriched water-gas and a condensate containing essentially all of the H_2O and hydrocarbons boiling in the range of 100 to 300° F.; passing said hydrocarbon fraction comprising aromatic hydrocarbons, into a first fractionating zone together with a second aromatic fraction derived as hereinafter described and recovering therefrom benzene, toluene and xylenes; passing the condensate from said first water-quenching zone to a second

fractionating zone and separating same into an aromatic overhead fraction boiling below 400° F. and a bottoms fraction including naphthalene; passing said overhead aromatic fraction to said first fractionator; recovering naphthalene from said last-named bottoms fraction and burning residual hydrocarbon therefrom in admixture with the bottoms from said quench-cracking zone in said pebble heating zone so as to heat said pebbles; and recycling pebbles from said reaction zone to said heating zone for reheating.

5. The process of claim 4 including the step of separating by phase separation the condensate from said second water-quenching zone into a hydrocarbon fraction and a water fraction.

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