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PRODUCTION OF AROMATICS AND UNSATURATED HYDROCARBONS

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2 Sheets-Sheet 1

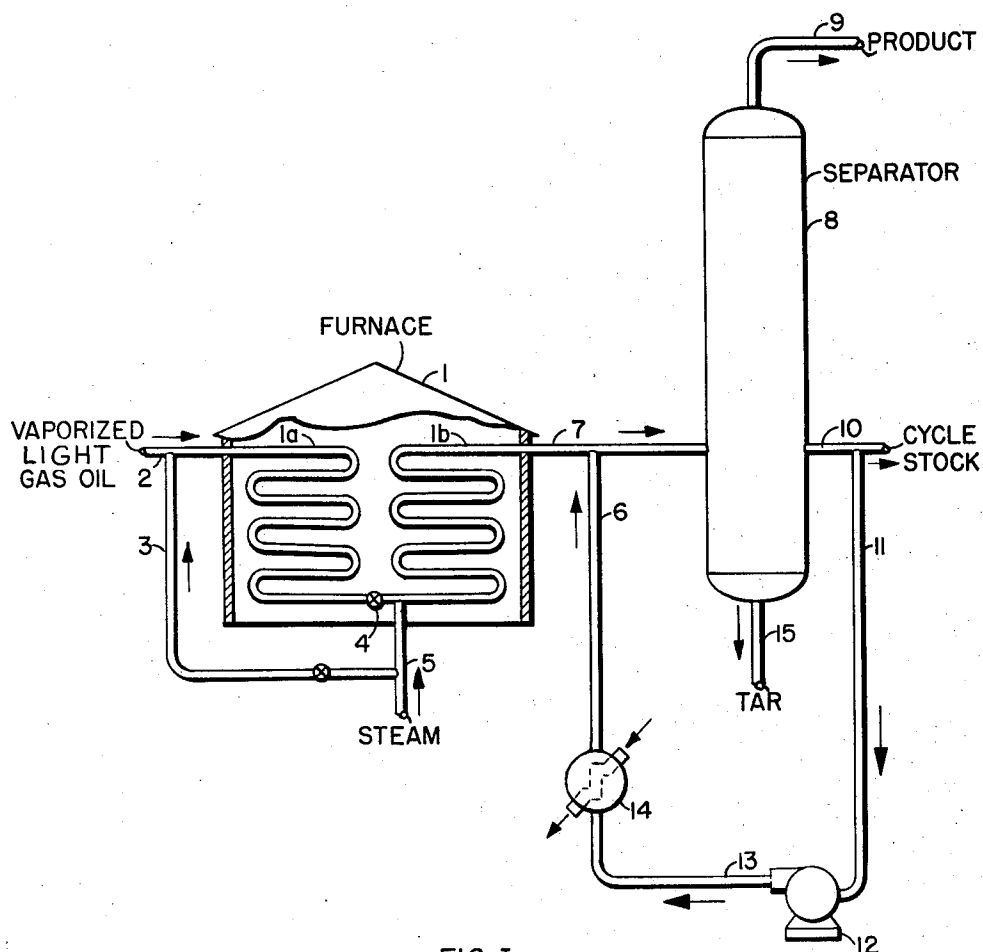


FIG. 1

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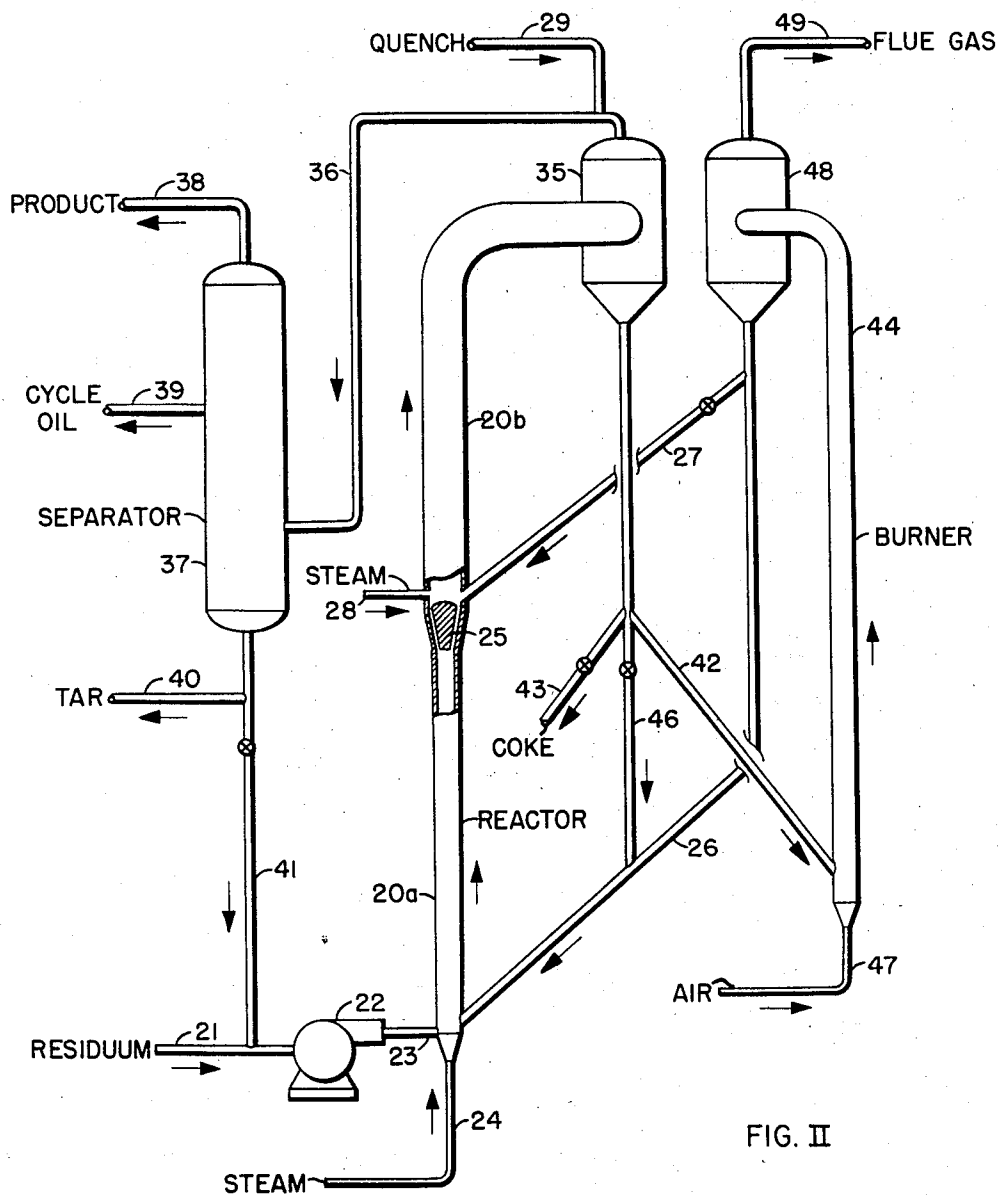
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2 Sheets-Sheet 2



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PRODUCTION OF AROMATICS AND UNSATURATED HYDROCARBONS

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11 Claims. (Cl. 196—49)

This invention relates to the art of converting petroleum oils to aromatics and unsaturated aliphatic hydrocarbons. More specifically, it pertains to a process for the simultaneous production of aromatics, olefins and diolefins by the high temperature cracking of hydrocarbon oils.

High temperature pyrolytic processes such as steam cracking, fluid coking, etc. for the conversion of normally liquid petroleum oils to chemical products and intermediates are generally quite well known. Usually such processes are carried out at relatively low hydrocarbon partial pressures, e. g., 10–25 p. s. i. a., in order to maximize the production of olefins and diolefins. For example, it has been customary to conduct steam cracking operations at about 1250° F. and 30 p. s. i. g. total pressure in the presence of 75 mol percent steam to secure approximately 12 wt. percent ethylene for tetraethyl lead production and about 2 wt. percent butadiene for synthetic rubber production.

Fairly recently, there has been a need for a cracking process that will produce a range of petrochemical intermediates. Specifically, there exists a concurrent demand for aromatics, e. g., benzene and toluene, and for unsaturated aliphatics, e. g., ethylene and butadiene.

The present invention proposes a process whereby maximum yields of both aromatics and unsaturated aliphatic compounds are produced by the pyrolysis and condensation of hydrocarbon oils, particularly of petroleum oils. By thermally cracking a gas oil in accordance with the teachings of this invention, yields are obtained that comprise 2 to 10 wt. percent benzene, 10 to 30 wt. percent ethylene and 2 to 6 wt. percent butadiene.

It has now been found that improved yields and product distributions can be obtained by conducting high temperature, e. g., 1200° to 1700° F., hydrocarbon oil cracking operations in two zones or in two steps. The first zone is operated at relatively high hydrocarbon partial pressures, e. g., 30–100 p. s. i. a. and the second zone at relatively low partial pressures, e. g., 2–20 p. s. i. a. In the first or high pressure zone, conditions are adjusted to obtain an intermediate conversion of the oil, preferably to yield greater than about 25 wt. percent C₃ and lighter products. This results in high aromatic yields and relatively low yields of unsaturates. The second or low pressure zone serves to dehydrogenate the saturated products formed in the first zone and to further convert the oil to form principally unsaturates. The conditions in the second zone are controlled to obtain an ultimate conversion of about 35 to 50 wt. percent of the oil to C₃ and lighter compounds. At least 5 wt. percent of said oil is further converted to C₃— products in the second zone.

In the first zone, the high hydrocarbon partial pressure favors the production of aromatics. The hydrocarbon compounds of the petroleum oil feed pyrolytically decompose and the decomposed products, under the influence of pressure, condense to form substantial amounts of aromatics.

The aromatics formed in the first zone are relatively stable products and having once been formed are relatively refractory and will pass through the second zone substantially unaltered. Yields of unsaturates, however, are determined principally by the pressure and temperature conditions at a cracking reactor outlet. Thus in the second zone, the remainder of the unconverted hydrocarbon oil feed is converted to the desired olefins and diolefins with perhaps some further production of aromatics.

Table I illustrates the opposite effects of partial pressure upon unsaturates and aromatics production during thermal cracking of a gas oil in a thermal cracking coil. It can be seen that an increase in hydrocarbon partial pressure greatly increases the amount of aromatics produced.

Table I

Temp., ° F.	1,255	1,280
HC PP, P. s. i. a.	4	31
Conf., Wt. percent C ₃ —	43.9	44.6
Products, Wt. percent of feed:		
Ethylene	18.6	11.0
Propylene	14.4	11.9
Butadiene	3.6	2.5
Benzene	0.5	6.0
Toluene	.1	5.0

It is, therefore, a principal object of this invention to secure maximum yields of aromatics, particularly benzene, and unsaturated aliphatics by thermally cracking hydrocarbon oils at high temperatures. A more specific object is to convert petroleum oils by a two-stage pyrolytic process to obtain substantial proportions of aromatics, olefins and diolefins.

These and other objects will more clearly appear as this description of the invention proceeds and the attached drawings, forming a part of the specification, are described in detail.

In the drawing, Figure I schematically presents a thermal cracking pipe coil with a product recovery system adapted to achieve the objects of the present invention.

There is depicted in Figure II a system wherein the oil being converted is contacted with high temperature particulate solids in a transfer line reactor arrangement operated in accordance with this invention.

Stocks suitable for use with this invention are principally gas oils and similar petroleum oils. Broadly, however, the invention is capable of cracking a wide range of charging stocks such as coal tars, shale oils, catalytic cycle stocks, aromatic extracts, whole crudes, distillate and residual fractions therefrom, or mixtures thereof, etc. It is preferred to use a relatively clean stock, such as a gas oil distillate boiling in the range of 430° to 1000° F., when the cracking is conducted in a pipe coil. However, by use of heat-carrying particulate solids as is hereinafter described, carbon-forming stocks such as vacuum residua may also be converted by the method of this invention to obtain petrochemicals and intermediates.

For convenience, the pertinent operating conditions applicable to the following example are summarized in Table II.

Referring now to Figure I, there is shown a thermal cracking furnace 1 constructed so as to have two banks of pipe coils, 1-a and 1-b. A light gas oil which can be suitably preheated to a temperature of about 300° to 750° F. is introduced into the furnace by line 2 under a pressure of about 50 to 300 p. s. i. g. Steam may be admitted by line 3 to line 2 such that the hydrocarbon partial pressure of the mixture at any point in coil 1-a is greater than 30 p. s. i. a. The diluted gas oil is contained in coil 1-a for a period of time sufficient to obtain the desired conversion corresponding to about 30 to 45% wt. C₃ and

lighter yields. The outlet temperature of the coil is maintained at a temperature in the range of 1200° to 1700° F.

The partially cracked gas oil then flows past valve 4 or other throttling means into coil 1-b. In coil 1-b, the pressure of the system is maintained at about 0 to 50 p. s. i. g. sufficient to obtain a hydrocarbon partial pressure of 0 to 30 p. s. i. a. The mixture is retained in coil 1-b at a temperature of 1200° to 1700° F. for a period of time sufficient to obtain an ultimate conversion of 35 to 50 wt. percent of the gas oil to C₃ and lighter hydrocarbons.

Alternatively, or in conjunction with valve 4, the gas oil entering coil 1-b can be diluted with about 5 to 400 wt. percent of steam to obtain the desired decrease in hydrocarbon partial pressure.

The temperature of each coil can, of course, be maintained at separate levels conducive to the formation of maximum yields of products and to good operability.

After being cracked, the material is removed from the furnace by line 7 and is suitably quenched to a temperature in the range of about 500° to 800° F. sufficient to arrest further reaction. For example, a cool recycle oil supplied by line 6 may be injected into the cracked mixture. Alternatively, a steam or a water quench or other means, such as an indirect heat exchanger, can be used. The quenched mixture is then introduced into a separator 8 or fractionating tower where the desired products are separated and removed overhead as gases through line 9. The specific aromatics, olefins, diolefins, etc. that are desired as products are then removed from the vapors overhead from the separator by conventional means, well known by the art, e. g., distillation, fractionation, absorption, crystallization, extraction, etc.

A more complete means of separating the effluent from the furnace can, of course, be used as desired. As shown, material boiling above the desired product boiling range, e. g., above about 400° to 500° F., is removed by line 10 as cycle stock. A portion of the cycle stock may be recycled to the furnace for further treatment. Part of the cycle stock is transferred by line 11, pump 12 and line 13 to heat exchanger 14, wherein its temperature is reduced sufficiently to serve as the aforementioned quench.

Bottoms from the separator, e. g., a highly aromatic refractory tar boiling above about 600° F. is removed by line 15 as product.

Table II presents the operating conditions for the apparatus shown in Figure I and presents a specific example of operating conditions. Table III presents the products and product distribution obtainable from the feed stock indicated when a process is operated in accordance with the example of Table II.

Table II

	Range		Example
	Broad	Preferred	
Outlet Pressure, P. s. i. g.:			
First zone.....	30 to 300	30 to 100	50
Second zone.....	0 to 50	0 to 30	5
Outlet Hydrocarbon Partial Pressure, P. s. i. a.:			
First zone.....	30 to 300	30 to 100	50
Second zone.....	0 to 30	2 to 20	12
Outlet Temperature, ° F.:			
First zone.....	1,200 to 1,700	1,250 to 1,500	1,250
Second zone.....	1,200 to 1,700	1,250 to 1,500	1,400
Vapor Residence Time, Secs.:			
First zone.....	0.1 to 20	0.1 to 5	3
Second zone.....	0.01 to 10	0.01 to 2	0.15
Conversion, Wt. Percent C ₃ -:			
First zone.....	25 to 50	30 to 45	40
Ultimate.....	35 to 60	35 to 50	45
Total Steam Rate, Wt. Percent on Oil:			
First zone.....	0 to 30	5 to 25	10
Second zone.....	0 to 400	5 to 100	25

Table III

Feed—East Texas light gas oil:

35° API gravity
430 to 650° F. boiling range
0 wt. percent Conradson carbon
80% paraffins
16% aromatics
4% naphthenes

Products, wt. percent of feed:

Fuel gas (C ₂ H ₆ , CH ₄ , H ₂).....	11.3
Ethylene	18.9
Propylene	14.1
Propane	0.7
Butadiene	3.6
Butylenes	6.0
Aromatic dist. (total C ₅ —500° F.)	30.6
Isoprene	1.0
Cyclopentadiene	1.0
Benzene	6.5
Toluene	6.7
Tar (500° F.+)	14.8

The principles of this invention may be applied or carried out in many forms and types of apparatus. The invention is, of course, particularly applicable to steam cracking processes. The thermal cracking zones that can be used in the practice of this invention include, however, fluidized solids zones, gravitating solids zones, and zones operating by the regenerative technique besides transfer line zones and steam cracking coils, furnaces, etc. In specific applications, different types of zones can be used for the high pressure and low pressure cracking. Thus, a steam cracking coil can be used to initially convert a charging stock under pressure. The partially cracked mixture can be discharged into a regenerative zone, e. g., a zone containing checker brick work to transfer heat, to be cracked under conditions of low hydrocarbon partial pressure. Or, when particulate solids are used as a heat-carrying medium, a transfer line zone can be the first zone and a fluidized solids zone can be used as the second zone. The principle of this invention may also be applied to the retorting of shale in that the retorting can be conducted in two zones and the conditions may be adjusted in accordance with this invention conducive to the formation of ethylene, butadiene and benzene.

Figure II illustrates an alternative method of practicing this invention wherein finely divided solids, e. g., particulate petroleum coke, are used as a heat-carrying medium. The two-step thermal cracking reaction is conducted in a transfer line reactor. High temperature particulate solids are conveyed by entrainment upwardly through the reactor at a velocity above 10 ft./second, e. g., 40–60 ft./second.

The oil to be converted, e. g., a vacuum residuum, is introduced into the base of the reactor by line 21, pump 22 and line 23. The residuum contacts particulate solids supplied by line 26 from a heater or burner 44, at the base of the reactor which solids have a temperature of about 1250° to 1800° F. The solids for a transfer line burner may be of any type, such as spent catalyst, sand, pumice, etc., but it is customary to use coke produced by the process. The solids may have a size of 0 to 2,000 microns. Preferably they have a size in the range of 70 to 800 microns (by screen analysis). The vacuum residuum upon contact with the high temperature coke undergoes pyrolysis evolving substantial portions of vapors and depositing carbonaceous residue on the solids.

Steam and/or C₂ or C₃ hydrocarbons are admitted to the base of the reactor by line 24 and supplement the vaporized residuum in supplying a sufficient volume of gas to convey the solids upwardly through the reactor.

Steam can, of course, be admitted to the base of the reactor and along the length of the high pressure zone 20a so as to adjust the hydrocarbon partial pressure between 30 and 100 p. s. i. a.

After having obtained the desired degree of conversion, the partially cracked residua and solids flow past a restriction 25 in the middle portion of the reactor to the low pressure zone 20-b. Zero to 400 wt. percent of steam can also be introduced in initial portions of the low pressure reactor by line 28 to adjust the hydrocarbon partial pressure within desired limits, e. g., 0-20 p. s. i. a. Hot solids from the burner hereinafter described may be supplied by line 27 such that the temperature in the low pressure zone may be independently controlled.

After the desired degree of conversion has been obtained, the mixture passes to a short-time cyclone separation system 35 where substantially all of the entrained heat-carrying solids are removed. The product vapors leaving the top of the cyclone 35 are immediately quenched. The quench liquid, e. g., water or cooled recycled product, can be introduced into line 36 at the proper point by line 29. The quenched product vapors and liquid are conveyed to a separator 37 by line 36.

Product vapors are removed from the separator by line 38 and are conveyed to a conventional recovery system to obtain the desired aromatics, olefins, etc. Aromatic tar boiling above 650° F. is removed from separator 37 by line 40. A portion or all of this tar can be recycled by line 41 for further treatment. A cycle oil sidestream 39 may be withdrawn from the separator to serve as a quench medium or as a product.

The solids separated in cyclone 35 are conveyed by line 42 to a conventional transfer line burner 44. A portion of the solids may be conveyed by line 46 to line 26 and thence into the base of the reactor for temperature control purposes. Product coke is withdrawn through line 43. The solids circulated to the burner amount to about 10 to 50 lbs. of solid per lb. of fresh feed.

Air or other oxidizing gas in the amounts of 0.3 to 3 ft.³ of air per lb. of solid is introduced into the base of the burner by line 47. The air entrains the solids and conveys them upwardly through the reactor and supports a partial combustion of them, whereby the temperature of the solids is raised to about 100° to 300° F. above the reactor temperature.

After combustion, the flue gases are separated from the solids by cyclone system 48 and are removed from the cyclone by line 49. The heat content of the flue gases may be utilized by conventional methods such as by a heat exchange with the feed to the process. High temperature solids are conveyed downwardly by line 26 to the base of the reactor to be contacted with residuum as before described. A portion of the heated solids may be conveyed by line 27 to the middle portion of the reactor for heat control purposes.

Other variations of this invention will be readily apparent to those skilled in the art. For example, the second low hydrocarbon partial pressure cracking zone can be operated at high severities to destroy C₃ to C₅ compounds and to maximize the yield of ethylene. The process can, accordingly, be made to produce primarily ethylene and benzene. Thus, an oil can be cracked in a tubular cracking coil at temperatures in the range of 1200° to 1700° F. and at partial pressures above 30 p. s. i. a. The effluent from the coil can then be reduced in hydrocarbon partial pressure by dilution or reduction of total pressure and be discharged into a zone containing heat-carrying particulate solids operated at temperatures in the range of 1400° to 1700° F. At high severities, coke yields are substantial and the use of heat-carrying solids is desirable as the solids readily remove the coke from the reaction zone. This second zone may be a gravitating solids bed heated cyclically or continuously supplied with high temperature solids, a transfer

line zone, or a zone containing the solids as a fluidized bed.

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

What is claimed is:

1. A non-catalytic process for cracking hydrocarbon oils to produce aromatics and normally gaseous, unsaturated aliphatic hydrocarbons comprising continuously heating petroleum oil to a cracking temperature in the range of 1200° to 1700° F. while maintaining a hydrocarbon partial pressure of 30-300 p. s. i. a. for a period of time sufficient to convert 25-50 wt. percent of said oil to C₃ and lighter hydrocarbons, thereafter reducing the hydrocarbon partial pressure below 30 p. s. i. a., maintaining the oil so reduced in pressure within said cracking temperature range for a period sufficient to obtain a total conversion of said oil of 35 to 60 wt. percent C₃ and lighter hydrocarbons, said total conversion being at least 5% greater than the conversion obtained in the first zone, cooling the cracked products and separating from the cooled products aromatics and unsaturated aliphatic hydrocarbons.

2. The process of claim 1 wherein the reduction of said hydrocarbon partial pressure is secured by injecting a substantially inert gasiform diluent into the partially cracked mixture.

3. The process of claim 1 wherein the reduction of said hydrocarbon partial pressure to below 20 p. s. i. a. is obtained by reducing the total pressure on the partially cracked mixture.

4. The process of claim 1 wherein said process is conducted in a narrowly confined, elongated conduit and the heat necessary to create and maintain said cracking temperature is supplied by conduction through the walls of said conduit.

5. The process of claim 1 wherein said cracking occurs in contact with high temperature, substantially catalytically inert, particulate solids, having a particle size in the range of 0 to 2000 microns.

6. The process of claim 1 wherein said cracking is carried out by contact with particulate coke having an initial temperature in the range of 1250° to 1800° F. in a transfer line reactor, said coke being conveyed by entrainment through said reactor at a velocity above 10 ft./second.

7. A non-catalytic process for cracking petroleum oils to produce aromatics and normally gaseous, unsaturated aliphatic hydrocarbons comprising continuously heating a petroleum oil boiling in the range of 430° to 1000° F. in a narrowly confined elongated conduit to a cracking temperature in the range of 1250° to 1500° F. while maintaining a hydrocarbon partial pressure of 30-100 p. s. i. a. for a period of 0.1 to 5 seconds sufficient to convert 30 to 45 wt. percent of said oil to C₃ and lighter hydrocarbons, thereafter reducing the hydrocarbon partial pressure below 20 p. s. i. a., maintaining the oil so reduced in pressure at said cracking temperature for a period of 0.01 to 2 seconds, sufficient to ultimately convert 35 to 50 wt. percent of said oil to C₃ and lighter hydrocarbons, cooling the cracked products and separating from the cooled products aromatics and unsaturated aliphatic hydrocarbons.

8. The process of claim 7 wherein said cool products comprise 2 to 10 wt. percent benzene, 10 to 30 wt. percent ethylene and 2 to 6 wt. percent butadiene.

9. The process of claim 7 wherein said reduction of hydrocarbon partial pressure is obtained by injecting 5 to 100 pounds of steam per 100 pounds of said oil into said conduit.

10. A non-catalytic hydrocarbon conversion process for obtaining maximum yields of benzene and ethylene by thermally cracking a petroleum oil, which comprises heating a petroleum oil in a first cracking zone to a temperature in the range of 1200° to 1700° F. while maintaining a hydrocarbon partial pressure in the range of 30-

to 100 p. s. i. a. for a period of time sufficient to convert 30 to 45 wt. percent of said oil to C_3 and lighter hydrocarbons, thereafter reducing the hydrocarbon partial pressure below 20 p. s. i. a., maintaining the partially cracked oil so reduced in pressure in a second cracking zone at a temperature in the range of 1400° to 1700° F. to ultimately convert up to 60 wt. percent of said oil to C_3 and lighter hydrocarbons and withdrawing and separating the cracked oil from said second zone.

11. The process of claim 10 wherein said first cracking zone comprises a tubular cracking coil and said second cracking zone comprises a zone containing heat-carrying, substantially inert particulate solids.

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