

Sept. 25, 1956

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PRODUCTION OF AROMATIC TAR

2,764,527

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2 Sheets-Sheet 1

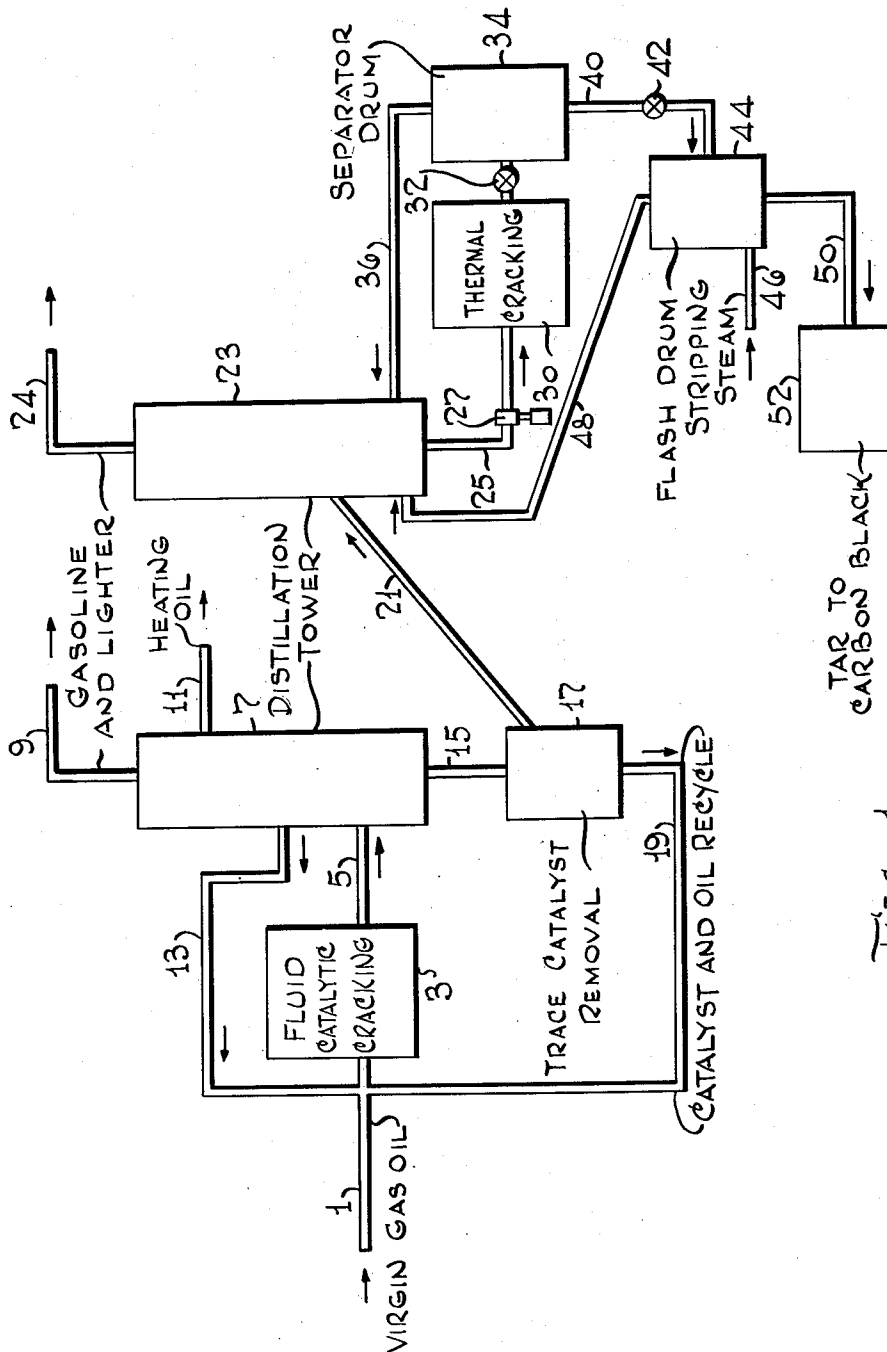


FIG.-1

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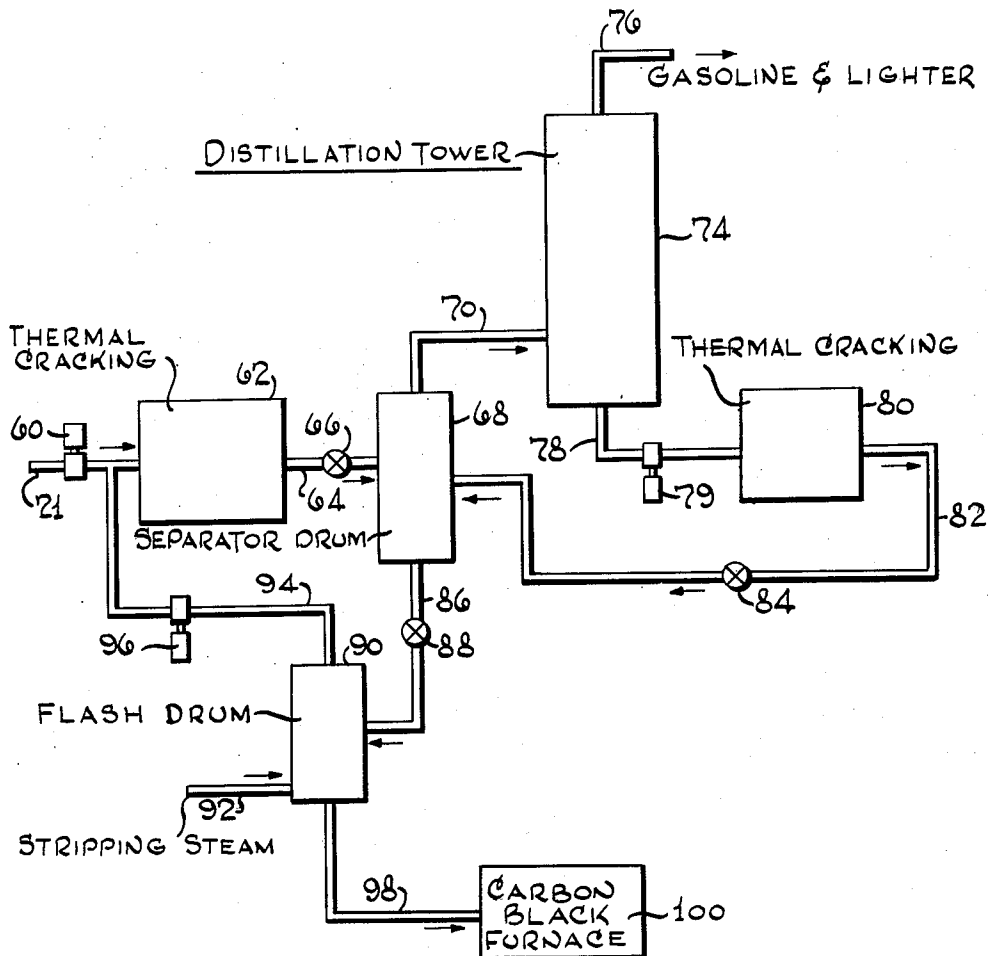


FIG.-2

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PRODUCTION OF AROMATIC TAR

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Application April 20, 1951, Serial No. 222,002

5 Claims. (Cl. 196—49)

The present invention relates to the conversion of hydrocarbon oils. More particularly, the invention pertains to the production of heavy tars rich in aromatic constituents suitable for the production of specialty products, such as furnace black of high quality. Briefly, the invention provides for a process involving catalytic cracking of gas oils followed by thermal cracking of a heavy catalytic oil fraction at conditions conducive to the formation of an aromatic tar having gravity and sediment characteristics suitable for the production of high quality furnace black useful in rubber compounding. The invention also contemplates the production of such high quality furnace black by means of this process.

In conventional petroleum refining the crude petroleum is first distilled to produce, in addition to other products, distillate fractions which may be converted into motor fuels by suitable refining processes. Catalytic cracking is the most important and most widely used of these refining processes because it produces high octane number gasoline from higher boiling crude distillates. The thermal and procedural requirements of catalytic cracking have been met most efficiently by the so-called fluid catalyst technique wherein finely divided catalyst is continuously circulated between a cracking zone and a combustion-regeneration zone. The catalyst is maintained in these zones in a dense highly turbulent state by the fluidizing action of upwardly flowing gases and vapors. In the regeneration zone, carbon formed in the reaction is burned off whereby the catalyst is regenerated and heated above cracking temperature so that heat required for cracking may be supplied in the form of sensible heat of hot regenerated catalyst returned to the cracking zone. The production capacity of plants of this type is limited by their carbon burning capacity and thus by the carbon-forming tendency of the feed stock. Feed stocks having a strong carbon-forming tendency are, therefore, undesirable.

While most virgin gas oils are unobjectionable in this respect, the situation is complicated by the fact that the cracking reaction yields, in addition to motor fuel range and lighter products, substantial proportions of up to about 30–50% on feed, of higher boiling fractions, such as gas oils and heavier materials boiling above 450° F. up to 800° F. or higher. These materials are of a considerably lower value than motor fuels and must be extensively further converted into motor fuels to maintain a sound economical balance of the process. Recycle to the cracking stage, though widely practiced, is only of limited value because these so-called "cycle oils" are quite generally much stronger carbon formers than virgin gas oils, their carbon-forming tendency being the stronger the higher their boiling range.

Heretofore, it has been proposed to alleviate these difficulties by subjecting cycle oils, particularly the higher boiling cycle oils to thermal cracking to produce additional amounts of gasoline and other valuable distillate fractions, in which coke formation is no serious problem. However, this procedure is complicated by other difficulties.

By far the largest proportion of the thermal cracking product is recovered in the form of a heavy tar of the fuel oil boiling range amounting to more than 70 vol. % on thermal cracking feed. It is essential that this high proportion of the product have a considerable commercial value to make the operation economically feasible. Since the commercial value of the lighter products, particularly the gasoline fractions, is by far higher than the value of the tar for any purpose known at present it is, however, necessary to reduce tar production in favor of gasoline production as much as possible. This may be accomplished by increasing the severity of the thermal cracking reaction, particularly with respect to temperature so as to convert more of the feed to lighter distillates. Thus, tar production may be reduced to 50 vol. percent or thereabout with a corresponding increase in distillate yields. However, the more severe the cracking reaction, the poorer is the quality of the tar as a fuel oil. In addition, it has not been possible heretofore to produce at these high severity thermal cracking conditions from a catalytic cycle oil a thermally cracked tar useful for the production of high quality furnace black suitable for rubber compounding, without a serious reduction in distillate yields. The present invention overcomes this difficulty.

It is, therefore, the principal object of the present invention to provide an improved process for the production of a high quality tar and relatively large amounts of distillate oils by thermal cracking of catalytic cycle oils. A more specific object of the invention is a process for producing high quality furnace black with the aid of a procedure of the type specified. Other and more specific objects and advantages of the invention will appear from the following description of the invention wherein reference will be made to the accompanying drawing in which

Figure 1 is a schematical flow plan of a system suitable to carry out a preferred embodiment of the invention; and

Figure 2 is a similar illustration of a modification of the system shown in Figure 1.

It has now been found that thermally cracked tars of excellent qualities, particularly for the purpose of high quality furnace black manufacture as well as high yields of distillate oils, may be produced by thermally cracking catalytic cycle oils, particularly so-called clarified oils which represent the heaviest fractions of catalytic cycle oils, at carefully controlled specific conditions, particularly at carefully controlled temperatures, in all sections of the thermal cracking unit. Such units normally comprise a fired cracking coil discharging into a vapor-liquid separator, bottoms of which are flashed and steam stripped in a flashing zone. Overhead from the separator and flashing zone represents the distillate product. Flash drum bottoms form the tar product. The cracking stage proper may include an expanded soaking zone following the cracking coil and maintained at similar conditions.

In systems of this type using cracking coils and soaking drums, conditions in accordance with the present invention include cracking coil pressures of about 300–600 p. s. i. g., cracking coil outlet temperatures of 935°–950° F., cracking zone throughputs of about 6–16 volumes of cold oil per volume of coil cracking space per hour v./v./hr.) which corresponds to about 0.5–1.2 v./v./hr. based on coil plus soaker space, separator pressures of about 80–100 p. s. i. g., separator temperatures of 800°–820° F. in the top and 790°–810° F. in the bottom, flash zone pressures of about atmospheric to 1.0 p. s. i. g. and flash zone temperatures of just about 730° F. in the top and 570° F. in the bottom. At these conditions about 45 vol. % of valuable distillate oils and 45 vol. % of tar are produced, on the basis of catalytic

cycle oil charged to the thermal cracking stage. The tar has the following inspections:

Gravity, °API	0-3.
Sediment by extraction (ASTM-D-473)	0.2 maximum.
H/C atomic ratio	1.0-1.1.
Viscosity, SSU at 210° F.	50-90.
Flash point, °F.	215 minimum.

The aromaticity of this tar is shown by its deficiency in hydrogen. This value is limited by the requirement of reducing coke formation in the cracking process. Coke so formed shows up in the tar as "sediment by extraction" which, in concentrations higher than those shown above, is a deleterious constituent in the final furnace black product.

More specifically, the gravity, sediment and H/C ratio must not appreciably deviate from the values given above if the tar is to be useful in the manufacture of furnace black for rubber compounding. Extensive tests have demonstrated that appreciable variations of the conditions specified above prevent the production of tars complying with these requirements. For example, if the oil is thermally cracked at more severe conditions, particularly at higher temperatures and flashed and stripped less completely, the resulting gravity of the tar will be satisfactory, but the asphaltene content will be too high. Asphaltenes are those constituents of the tar which are insoluble in low molecular weight paraffins. These materials are difficult to vaporize in conventional carbon black manufacture and appear in the product carbon black in the form of large size unconverted aggregates. If the oil is cracked less severely and flashed and stripped more completely, the gravity will be again satisfactory but the H/C atomic ratio will be too high, i. e., aromaticity will be too low. Other variations in the process conditions create different but equally prohibitive variations in the tar properties.

Having set forth its objects and general nature, the invention will best be understood from the following more detailed description thereof read with reference to the drawing.

Referring now to Figure 1 of the drawing, the system illustrated therein comprises a fluid catalytic cracking unit 3 and a single stage thermal cracking unit 30, both of essentially conventional design, details of construction having been omitted for the sake of simplicity. The function and coaction of these elements for the purpose of this invention will be forthwith described.

In operation, a virgin gas oil which may have a boiling range of about 620°-950° F. is passed through line 1 to catalytic cracking unit 3 wherein it is subjected to fluid-type catalytic cracking at conventional conditions in a manner known per se. Briefly, operations of this type involve the use of finely divided catalysts such as various activated clays or composites of silica gel with alumina, magnesia and/or boria, particularly silica gel-alumina composites containing about 13% of Al₂O₃ and having a particle size of about 50-400 mesh, mostly about 100-200 mesh. The catalyst is maintained in separate cracking and regenerating vessels in a dense, turbulent, fluidized state by gasiform media passing upwardly through the beds at linear superficial velocities of about 0.3-2.5 ft. per second. The catalyst circulates continuously between the reactor and regenerator, heat for cracking being generated by burning carbon from the catalyst in the regenerator. Conventional conditions include cracking temperatures of about 800°-1000° F., regeneration temperatures of about 950°-1200° F., but higher than the cracking temperature, pressures from subatmospheric to 100 p. s. i. g. or higher, total oil feed rates of about 4-5 lbs. of oil per lb. of catalyst per hour, catalyst to oil ratios of about 6-10 and oil recycle to fresh feed ratios of up to about 0.5 on a weight basis.

Cracked vapors containing small amounts of entrained catalyst are passed from the cracking reactor of unit 3

through line 5 to a conventional product distillation tower 7 from which catalytic gasoline and heating oil fractions may be recovered via lines 9 and 11, respectively. A light cycle oil having a boiling range of about 620°-700° F. and amounting to about 15-35 vol. percent, on virgin gas oil feed may be recycled via line 13 to the cracking reactor of unit 3. Tower bottoms boiling above 700° F. and amounting to about 2.0-10 vol. percent on virgin gas oil feed, are withdrawn via line 15 to a settler 17 wherein this oil is separated into a lower layer containing a slurry of catalyst fines in oil and an upper layer of "clarified oil." The lower layer together with the slurred catalyst may be recycled in line 19 to the cracking reactor of unit 3 at a rate of about 0.8-4.0% on fresh feed. The upper layer, i. e. the clarified oil, is withdrawn through line 21. This oil which may have a gravity of about 17-20° API is further treated in accordance with the invention as follows.

Line 21 discharges into an intermediate portion of a product distillation tower 23 which serves the work-up of the thermally cracked distillate oils as will appear more clearly hereinafter. Distillate products including gasoline and amounting to about 0.3-0.5 vol. per vol. of feed through line 21 are recovered through line 24 at a temperature of about 380°-400° F. Bottoms from tower 23 including thermally cracked recycle bottoms and amounting to about 1-3 vol. per vol. of feed through line 21 are withdrawn through line 25 at a temperature of about 570°-590° F. This material which may have an API gravity of about 17°-19° is supplied by means of pump 27 to conventional thermal cracking unit 30. This unit may consist of two conventional furnace coils operated in parallel and discharging into a soaking drum. The oil feed is cracked in these two coils and the soaking drum at a pressure of about 510-520 p. s. i. g., a coil outlet temperature of 935°-950° F. and a total residence time corresponding to a throughput of about 0.5-1.2 v./v./hr. through coil and soaker cracking space. Cracked effluent from unit 30 is transferred through pressure release valve 32 to a vapor-liquid separator 34 maintained at a pressure of about 90-110 p. s. i. g., a top temperature of 800°-820° F. and a bottom temperature of about 790°-810° F. The overhead vapors from separator 34 may be passed through line 36 to a lower portion of tower 23. This distillate may amount to about 1.3-3.5 liquid vol. per vol. of feed through line 21.

The bottoms of separator 34 representing the remainder of the thermally cracked product are withdrawn via line 40 and release valve 42 and flashed into flash drum 44 at about atmospheric pressure. Flash drum 44 is maintained at a temperature of about 730° F. in the top and about 570° F. in the bottom. Stripping steam is introduced through line 46 into the bottom of flash drum 44 in amounts of about 1.5-3 lbs. per bbl. of tar to remove light products which are vaporized and withdrawn overhead to be condensed in line 48 and passed to a lower portion of tower 23 after water removal in any conventional manner (not shown). Light products so removed may amount to about 0.1-0.3 vol. per vol. of feed in line 21. The bottoms of flash drum 44 are recovered through line 50. This material, amounting to about 0.4-0.6 vol. per vol. of feed in line 21, is an aromatic tar which complies with the specifications set forth above for the purposes of producing furnace black suitable in rubber compounding.

The conversion of the tar into furnace black may be carried out in unit 52 in any conventional manner, for example, by burning the tar with a combustion-supporting gas using a deficiency of oxygen based on carbon in the tar, and collecting finely divided product carbon from the flue gases by means of centrifugal and electrostatic gas-solids separation.

The system shown in Figure 1 permits of certain modifications. For example, the flash drum overhead in line 48 may be processed in a different manner to be used as such for fuel blending after water removal.

A system similar to that of Figure 1 except for the fact that two thermal cracking stages 62 and 80 are used in a recycle type of operation in place of cracking unit 30 is shown in Figure 2 in which the catalytic cracking stage which is identical with that described with reference to Figure 1 has been omitted in the interest of brevity.

Referring now in detail to Figure 2, the clarified catalytic heavy oil flowing through line 21 is pumped by pump 60 to thermal cracking unit 62 which may be of the same construction as unit 30 of Figure 1. The cracking temperature in unit 62 is preferably held at about 900° F. at the coil outlet and a cracking pressure of about 500 p. s. i. g. is used at a total oil residence time in coil and soaker corresponding to that specified for unit 30 of Figure 1. The cracked effluent is transferred through line 64 and release valve 66 to separator 68 wherein product vapors and liquid are separated substantially as described with reference to separator 34 of Figure 1, overhead from separator 68 being passed via line 70 to distillation tower 74 from which distillate products may be recovered via line 76 at about 380°–400° F. Bottoms from tower 74 are removed at a temperature of about 610°–630° F. and a pressure of about 80–100 p. s. i. g. through line 78 and pumped by pump 79 to the second stage thermal cracking unit 80. This unit which may be of the same design as unit 62 is preferably operated at a coil outlet temperature of about 950 F., a pressure of about 500 p. s. i. g. and the same oil residence time as specified for unit 62. Effluent from unit 80 is passed via line 82 and release valve 84 to separator 68 to be treated therein together with the effluent from unit 62.

Separator bottoms amounting to about 0.5–0.8 vol. per vol. of feed in line 21 are withdrawn via line 86 and flashed through release valve 88 into flash drum 90 at atmospheric pressure. Flash drum 90 is operated at the conditions specified with reference to flash drum 44 of Figure 1, stripping steam being admitted via line 92. The

vaporous overhead from flash drum 90 is withdrawn via line 94 and recycled by pump 96 after suitable conventional water removal to the first thermal cracking unit 62 which it enters together with the feed supplied through line 21. Alternatively these vapors may be transferred to tower 74 or they may be removed for separate processing and usage as pointed out with reference to vapors flowing through line 48 of Figure 1. The tar recovered from flash drum 90 through line 98 is of adequate quality to be converted in carbon black furnace 100 into furnace black suitable for rubber compounding.

The beneficial effects of the invention will be further illustrated by the following comparative example.

Example

To illustrate the superiority of the process of the invention over conventional type operations and to demonstrate the criticality of a close control and correlation of the reaction conditions within the limits of the invention, there are reported below the conditions and results of three thermal cracking runs which are representative for three types of operations each carried out for a considerable length of time on a commercial scale in a coil-and-soaker system. Run I is representative for an operation carried out in a two-stage system of the type of Figure 2 yielding a tar of relatively high API gravity. Runs II and III are representative for operations carried out in a single-stage system with recycle of the type illustrated in Figure 1, run II yielding a low API gravity tar and run III a tar of intermediate gravity, the latter run being typical for operations in accordance with the invention. The feed stock to all three runs was a clarified oil recovered from the product fractionator of a commercial fluid-type catalytic cracking plant operated as described above with reference to unit 3 and tower 7 of Figure 1. The essential reaction conditions of the thermal cracking stages and the results are summarized in the table below.

Run No.	I Figure 2		II Figure 1		III Figure 1	
Type of Operation						
Conditions:						
Coil Outlet Temp., ° F.:						
Unit 62	895					
Unit 80	880		950		945	
Unit 30						
Coil Outlet Pressure, p. s. i. g.:						
Unit 62	500					
Unit 80	500		510/530		510/520	
Unit 30						
Throughputs, v./v./hr.:						
(Coil+Soaker) (Total Feed to Coil)	0.9		1.0		0.8	
	Top	Bottom	Top	Bottom	Top	Bottom
Separator Temp., ° F.	792	800	820	805	810	800
Distillation Tower, ° F.	390	620	360	670	390	580
Flash Drum, ° F.	645	590	640	470	730	570
Cat. Cracking Distillation Tower Bot- toms, ° F.	720		713		725	
Separator Bottoms:						
Gravity, ° API	13.5		-4.7		6.6	
Viscosity, SUS @ 210	40		158		1386	
Inspections:						
Flash Drum Bottoms:						
Gravity, ° API	10.1		-6.8		0.5	
Viscosity, SUS @ 210° F.	50		191		179	
Sediment (ASTM-D-473)	<0.2		<0.2		<0.2	
H/C Atomic Ratio, ca.	1.5		0.85		1.1	
Flash Drum Overhead:						
Gravity, ° API	22.4		10.8		15.7	
10% ASTM Distillation, ° F.	481		444		548	
50% ASTM Distillation, ° F.	622		636		686	
90% ASTM Distillation, ° F.	720		88.5 @ 752		87.0 @ 750	
Feed to Thermal Cracking Units:						
Gravity, ° API	22.4		19.5		18.0	
10% 10 mm. Vacuum Dist., ° F.	264		339		357	
50% 10 mm. Vacuum Dist., ° F.	440		439		442	
90% 10 mm. Vacuum Dist., ° F.	540		555		571	
Viscosity SUS @ 100° F.	63		90.5		95	
Yields:						
Gas, wt. percent	2.17		9.99		5.5	
Distillate, Vol. percent	19.30		35.53		45.7	
Flash Drum O. H., Vol. percent	20.73					
Tar, Vol. percent	57.80		54.48		54.7	

¹ SUS @ 100.

The above data show that run III which was carried out at the conditions of the present invention yielded substantially larger amounts of valuable distillate products and about equivalent amounts of a tar of far superior quality with respect to gravity and H/C atomic ratio or aromaticity, as compared with runs I and II which were carried out using a similar feed stock at conditions which, prior to the present invention, have been believed to be substantially equivalent to those of the present invention with respect to these properties.

Fluid catalytic cracking has been repeatedly referred to in the above description and this is the preferred method of employing the present invention because certain of the advantages afforded by the invention are peculiar to this type of catalytic cracking. For example, the advantage of disposing of heavy catalytic cycle oils without increasing the carbon load on the catalytic cracking system is by far the greatest for fluid catalytic cracking. However, tars suitable for the manufacture of high quality furnace black may also be produced by thermally cracking in accordance with the invention heavy product oils from other catalytic operations, such as fixed bed, moving bed or suspensoid catalytic cracking operations or other heavy oils having similar characteristics.

The foregoing description and exemplary operations have served to illustrate specific embodiments of the invention but are not intended to be limiting in scope.

What is claimed is:

1. A process of producing aromatic tar suitable for the manufacture of carbon black, which comprises catalytically cracking a virgin gas oil to form cracked products including motor fuels, oils of intermediate boiling range and a catalytic cycle oil of relatively high boiling range, subjecting at least a portion of said cycle oil to thermal cracking at a temperature of 935°-950° F. and a pressure of about 300-600 p. s. i. g., separating vaporous from liquid cracking products in a separating zone at an elevated pressure substantially lower than said first-named pressure, separately withdrawing from said separating zone vapors at a temperature of 800-820° F. and liquid at a temperature of 790°-810° F., flashing and steam stripping said withdrawn liquid at about atmospheric pressure in a flashing zone, separately withdrawing

from said flashing zone vapors at a temperature of about 730° F. and liquid at a temperature of about 570° F., and recovering said aromatic tar in the form of said last-named withdrawn liquid.

2. The process of claim 1 in which at least a portion of said thermal cracking takes place in an externally heated narrowly confined extended path at an oil residence time corresponding to an oil throughput of about 6-16 volumes of cold oil per volume of cracking space at cracking temperature per hour.

3. The process of claim 2 in which a portion of said thermal cracking takes place in said path, said thermal cracking being completed in an expanded soaking zone at a total oil residence time corresponding to an oil throughput of about 0.5-1.2 volumes of cold oil per total volume of said path and soaking zone at cracking temperature per hour.

4. The process of claim 1 in which said catalytic cracking is carried out in the presence of a dense turbulent mass of subdivided cracking catalyst fluidized by an upwardly flowing gasiform medium.

5. The process of claim 4 in which said cycle oil is a clarified cycle oil having a gravity of about 17°-20° API.

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