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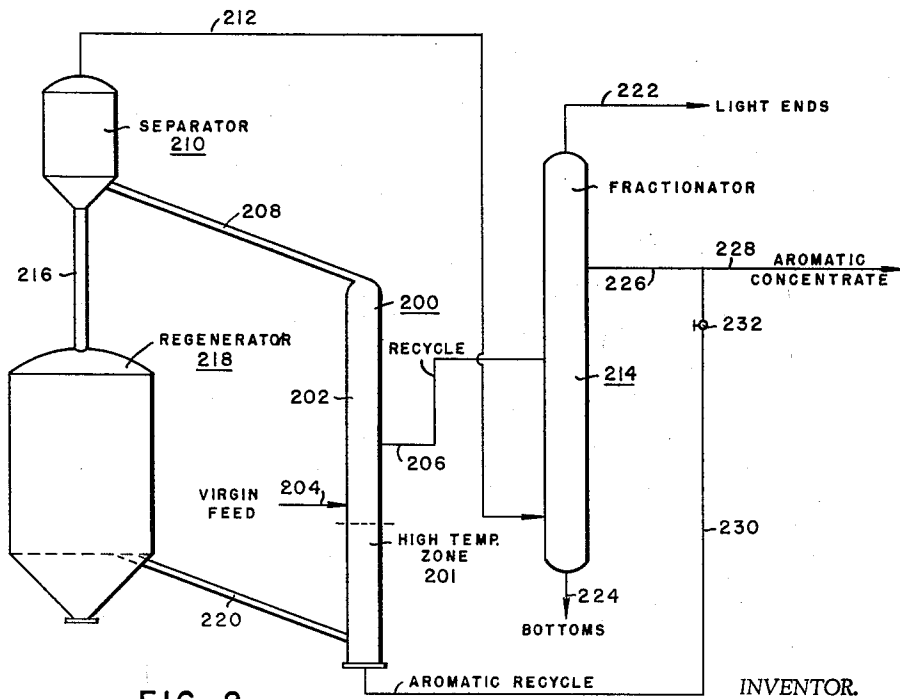
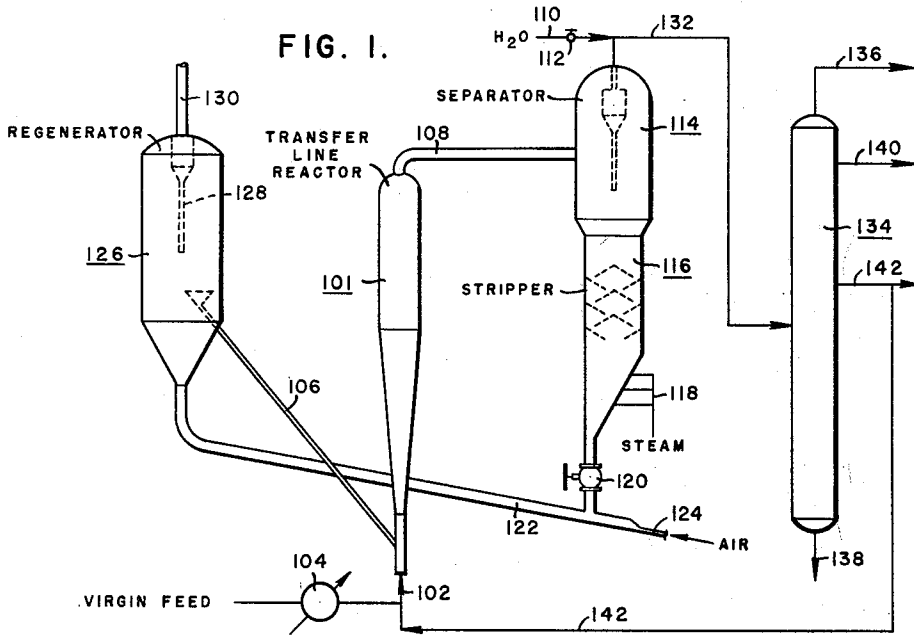
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TRANSFER LINE CATALYTIC CRACKING

Filed Oct. 27, 1961

2 Sheets-Sheet 1



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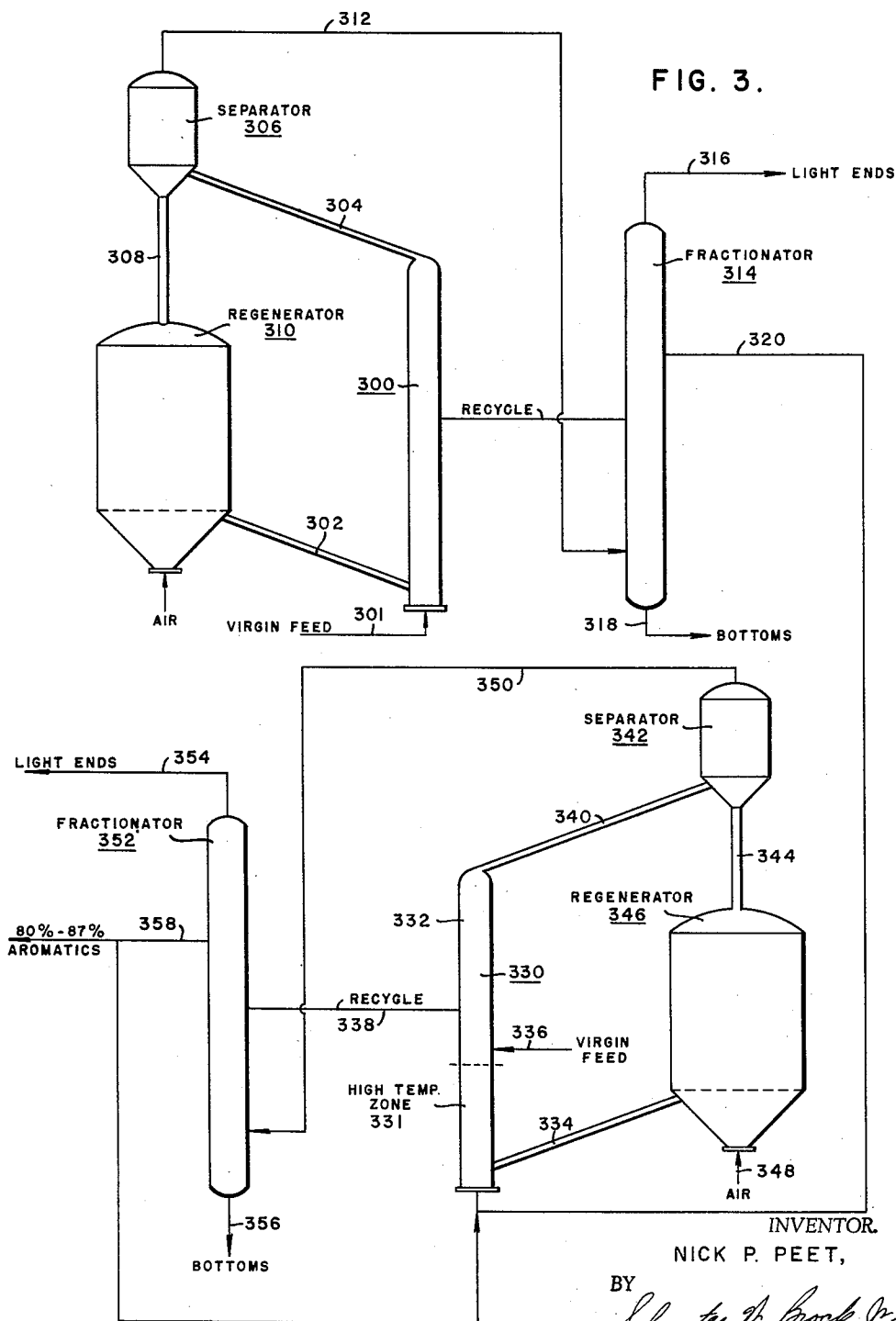
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TRANSFER LINE CATALYTIC CRACKING

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2 Sheets-Sheet 2

FIG. 3.



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## TRANSFER LINE CATALYTIC CRACKING

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 3 Claims. (Cl. 208-74)

The present invention relates to the high temperature-short contact time transfer line catalytic cracking of hydrocarbons. More particularly, the present invention relates to the selective cracking of nonaromatic hydrocarbons present in a hydrocarbon stream containing aromatics whereby coke formation and product degradation are minimized. In another aspect, the present invention relates to the production of a highly aromatic specialty oil boiling in the catalytic heating oil range by cracking a relatively low aromatic content virgin feed stock under mild conditions followed by severe high temperature-short contact time cracking of the heating oil product thereof.

In the catalytic cracking of hydrocarbon feed stocks, utilizing a silica-alumina catalyst or catalyst similar thereto, it has been discovered that a considerable amount of the hydrocarbon stream is degraded into coke which represents a net product loss and must be burned from the surface of the catalyst in order to continue the cracking operation. In accordance with the present invention, it has surprisingly been found that by carrying out the catalytic reaction in a transfer line reactor under high temperatures, within the range of 1000° F. to about 1200° C., and with hydrocarbon residence times not exceeding about 5 seconds, preferably from 0.5 second to about 3.0 seconds, and catalyst residence times not exceeding 20 seconds, preferably from 1.0 to about 10 seconds, an unexpected decrease in the coke formation is obtained together with a surprising selectivity of cracking of the nonaromatic constituents of the hydrocarbon stream to lighter hydrocarbons and coke. This results in a hydrocarbon product in the feed stock boiling range which is more highly aromatic than that feed stock. Concomitant with these results, an increased light gas yield is experienced (relative to conventional cracking) representing the portion of hydrocarbons which otherwise would have been cracked to coke. This increases the light olefin yield and reduces the coke yield per barrel of feed. The aromatic constituents of the charge stock are not decomposed into coke but are dealkylated to some extent. This represents also an added advantage in that the lighter aromatic hydrocarbons are commercially more attractive.

A further advantage accruing from the practice of the present invention is the fact that the catalyst time within the reaction zone is held to a minimum, which does two things: (1) it reduces polymerization of aromatics to coke and (2) maintains the general catalyst cracking activity at a higher level than otherwise would be attainable. In addition, the use of a catalyst which is low in metallic contaminants is desired in that this tends to reduce the specific cracking of aromatic rings and attendant coke formation. Cracking catalysts such as conventional 13% alumina catalyst or the high-temperature stable 40% alumina catalysts, etc., are suitable for use in the present invention.

These and other advantages of the practice of the present invention will be apparent by reference to the appended drawings, wherein:

FIG. 1 represents schematically the process of high temperature-short contact time transfer line cracking of a hydrocarbon stream;

FIG. 2 represents the practice of the present invention while utilizing a recycle stream in order to increase aromaticity of the heating oil product; and

FIG. 3 schematically represents the process of the separate cracking of a virgin gas oil followed by a high temperature cracking of the catalytic heating oil obtained therefrom.

Referring now to FIG. 1, there is shown a transfer line reactor 101 into which a hydrocarbon feed stock is introduced by way of line 102 and heater 104. Hot catalyst is introduced into the transfer line reactor by way of line 106. The admixed hot catalyst and hydrocarbon feed is passed through the reactor 101 to provide a hydrocarbon residence time within the period from about 0.5 to about 5.0 seconds, the residence time of the catalyst ranging from about 0.5 to about 20.0 seconds. The temperature within the reaction zone 101 is maintained within the range of about 1000° F. to about 1200° F. In order to accomplish these combinations of temperatures and residence times, the catalyst-to-oil ratio is maintained within the range of about 5:1 to about 35:1. The catalyst and hydrocarbon pass from the reactor through line 108 into a separator 114 wherein the vaporous material is separated from the solid catalyst which settles from the separator 114 into a stripper 116 wherein a gaseous stream of steam or flue gas or other suitable material is passed by way of means 118 in order to remove residual traces of hydrocarbon from the surface of the catalyst. The stripped catalyst settles by way of control valve 120 into line 122 where it is admixed with air introduced by line 124 and transported into a regenerator 126 wherein the carbon on the surface of the catalyst is burned and the catalyst regenerated. The flue gases from the regeneration combustion are passed by way of cyclone separator 128 and vent stack 130 for disposition as is desired, while the regenerated catalyst is passed by way of line 106 for admixture with the hydrocarbon feed as aforesaid. The temperature of the catalyst being recirculated by way of line 106 is between about 1100° F. and about 1250° F. The hydrocarbon from the separator 114 is passed by way of line 132. As the hydrocarbon stream is discharged from separator 114 by way of line 132, a waterquench stream is introduced by way of line 110 controlled by valve 112 in order to reduce the temperature of the hydrocarbon stream to about 950° F. In order to accomplish this, about 6 weight percent of water based on the feed is required. The quench stream may also be steam or oil, as long as the temperature is adequately reduced. The quenched stream is charged into a fractionator 134 wherein a light gas portion is taken off overhead by way of line 136, a heavy bottoms stream is withdrawn by way of line 138, and one or more side streams are recovered by way of lines 140 and 142. The product stream 142, for example, may comprise a catalytic heating oil boiling within the range of 400° F. to 650° F. A portion of this stream may be recycled via line 102 into the reaction zone 101 in order to increase the aromaticity of the heating oil. It should be stressed that by the operation of the present invention, the gaseous stream withdrawn by way of line 136 will be greater than the gaseous stream normally recovered from the catalytic cracking of hydrocarbons, and will increase the yield of valuable light olefins over that which is normally accomplished. The olefin yield in the range of from 2 to 5 carbon atoms is increased by almost 100% over that normally accomplished in the catalytic cracking of hydrocarbons. Feed stocks which are suitable for processing in the manner set forth in FIG. 1 are obtained in refinery operations as virgin streams boiling within the range of 400° F. to 950° F. and containing from about 19% to about 75% (by weight)

aromatic hydrocarbons and/or naphthenes. These streams may be obtained by fractionation and/or extraction of crude fractions.

Referring now to FIG. 2, a cracking scheme is schematically set forth wherein a high temperature-short contact zone is combined with a normal catalytic cracking zone in a transfer line reactor whereby a recycle stream from the fractionator may be accommodated in order to raise the aromaticity of the various streams. In FIG. 2 a transfer line reactor 200 is divided into a high temperature zone 201 and a normal temperature zone 202. A virgin feed boiling within the range of 400° F. to 950° F. and containing from 20% to 60% aromatics and/or naphthenes is introduced by way of line 204 into the normal temperature zone 202 and is passed therethrough in conjunction with the total effluent from the high temperature zone 201 and a recycle stream which may, if desired, be introduced by way of line 206 into the same zone 202. The hydrocarbon products as a total product stream and the catalyst are then passed by way of line 208 into separator 210 from whence the total product stream is passed by way of line 212 into a fractionator 214. The catalyst from separator 210 is passed by way of line 216 into a regenerator 218 from whence the regenerated catalyst is withdrawn by way of line 220 and introduced into the high temperature zone 201 of the reactor 200. The fractionator 214 is operated in order to recover a light ends product by way of overhead line 222 and a bottoms stream by way of line 224. An intermediate recycle stream may be recovered by way of line 206 as aforesaid, including material boiling, for example, within the range of about 650° F. to 850° F. A specialty oil fraction is withdrawn by way of line 226 and a first portion is passed by way of line 228 to storage or for further processing by way of hydrotreatment, etc., as desired. A second portion (from 2 to 5 times as great as said first portion) of the specialty oil fraction is recycled by way of line 230 controlled by valve 232 and is passed into the high temperature zone 201 of the reactor 200 in admixture with the catalyst recycled by way of line 220. Within the high temperature zone 201, the temperature is maintained within a range of about 1000° F. to 1200° F., preferably between about 1025° F. and 1075° F. with a hydrocarbon residence time of about 0.5 to about 5.0 seconds, with a preferred range of 0.5 to about 3.0 seconds. Catalyst residence time should not exceed 20 seconds and preferably is maintained within the range of about 1.0 second to about 10.0 seconds. The catalyst-to-oil ratio in the high temperature zone is within the range of about 5:1 to about 35:1. In the high temperature zone 201, catalytic heating oil is cracked preferentially in its nonaromatic content, thereby raising the percentage of aromatics present in the recycle stream. Upon passage into contact with the virgin feed injection by way of line 204, the temperature is immediately dropped, as in the case of a quench stream, to a temperature within the range of about 925° F. to about 975° F. Within the normal temperature zone 202, a hydrocarbon residence time of between 5 and 10 seconds is preferred. In the zone 202, the space velocity varies between 20 barrels of oil per pound of catalyst per hour to 40 barrels of oil per pound of catalyst per hour.

It is thus seen that by the recycle of a selected portion of the catalytic heating oil fraction boiling within the range of 400° F. to 650° F., the aromaticity of this fraction may be raised to obtain a product useful as a specialty oil. The amount of improvement in the aromatics content is dependent upon the ratio of the recycle stream. Where the feed stock contains, e.g., 20% to 60% aromatics and naphthenes and the amount of the recycle stream is within the range of about 2 to 5 times the stream withdrawn by way of line 228, an aromatics content of about 80% may be obtained. The corresponding heating

oil obtained by normal catalytic cracking contains between 40% and 60% aromatics. Similarly, aromatics content improvement is experienced in feed stocks having as little as 1% aromatics or as much as 85% aromatics. The improvement in product quality is apparent, and it should be stressed that no extraction step is utilized. Feed stocks suitable for the process of FIG. 1 are also suitable for use in the process above described.

Referring now to FIG. 3, there is shown a more particular application and preferred embodiment of the practice of the present invention. In the catalytic cracking of virgin gas oils, it has been found that the portion boiling within the range of 400° F. to 650° F. contains less aromatic hydrocarbons and naphthenes (aromatic precursors) than the gas oil streams boiling above 650° F. Therefore, in order to obtain a more aromatic fraction from the catalytic cracking of hydrocarbon, it has been the practice in the past to take a catalytic heating oil fraction boiling, for example, within the range of 400° F. to 650° F. and subject it to an extraction step, for example, with sulfur dioxide, in order to recover a highly aromatic fraction (about 80% aromatic hydrocarbon) useful as a specialty oil. By the practice of the invention as set forth in FIG. 3, a feed stock boiling within the range of about 400° F. to 950° F. and containing from 20% to 60% of aromatic hydrocarbons and naphthenes is separated into a first portion falling within the range of 400° F. to 650° F. and into a second portion boiling above 650° F. The first portion of virgin feed is charged into a first catalytic cracking reactor 300 which is shown as a transfer line reactor but which may be of any type, for example, a dense phase catalytic cracker, by way of line 301 and is admixed with catalyst which is charged into the reaction zone by way of line 302 and is cracked to obtain a first cracked hydrocarbon stream. The temperature within the reactor 300 depends upon the type of reactor chosen, but will normally range between 900° F. and 975° F. If a transfer line reactor is used, the hydrocarbon residence time is maintained within about 5 to about 10 seconds and the catalyst residence time is within the range of about 20 seconds to about 2 minutes. The hydrocarbon and catalyst are discharged from the reactor 300 by way of line 304 and passed into a separator 306 from whence the separated catalyst is passed by way of line 308 into a regenerator 310. It should be understood that the sketch shown in FIG. 3 is entirely schematic and does not represent the actual relation of equipment. The regenerated catalyst from regenerator 310 is passed by way of line 302 aforesaid for introduction into the reactor. The hydrocarbon from the separator 306 is passed by way of line 312 into a fractionator 314 wherein the hydrocarbon stream is separated to recover a light ends and motor gasoline fraction overhead by way of line 316 and a bottom stream 318. A first 400° F. to 650° F. catalytic heating oil fraction is withdrawn as a side stream by way of line 320 and is passed into a second transfer line reactor 330 which is divided into two zones, a high temperature zone 331 and a normal temperature zone 332. The catalytic heating oil fraction from the first reactor 300 is charged into high temperature zone 331 by way of line 320 and is admixed with hot regenerated catalyst introduced by way of line 334. The admixture of catalyst and catalytic heating oil from the first reactor is passed through the high temperature zone at a temperature of about 1000° F. to 1200° F., preferably between 1025° F. and 1075° F. The residence time in the high temperature zone for the hydrocarbon is between 0.5 and 5.0 seconds while the residence time of the catalyst is less than 20 seconds, preferably between 1.0 and 10.0 seconds. The temperature is dropped at the exit end of the high temperature zone by introducing the 650° F.+ virgin gas oil feed stock into the reactor by way of line 336. This feed stock may advantageously comprise the 650° F.+ boiling range fraction of the initially separated gas oil feed. A recycle stream by way of line 338 may also be introduced at about this point. The tem-

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perature within the normal temperature zone 332 of the second reactor 330 is maintained at a temperature within the range of about 900° F. to about 975° F., preferably between 925° F. and 950° F. The hydrocarbon residence time may vary from between 5 to 10 seconds in the normal temperature zone while the catalyst residence time may be greater than 20 seconds. The catalyst-to-oil ratio in the high temperature zone 331 will be about 10 to 35 pounds of catalyst per pound of hydrocarbon while in the normal temperature zone 332, the catalyst-to-oil ratio will vary between 5 and 10 pounds of catalyst per pound of hydrocarbon.

In the high temperature zone 331, the non-aromatic portion of the heating oil charge stock is preferentially catalytically cracked, thereby raising the percentage of aromatics present in this hydrocarbon stream. As the total effluent from the high temperature zone is passed through the normal temperature section 332, a slight amount of further cracking will be attained but the aromatic fraction will remain substantially undisturbed. The mixed products from the high temperature zone and the normal temperature zone constitute a second cracked hydrocarbon stream and are discharged along with the catalyst through line 340 and passed to a separator 342 whence the catalyst is passed by way of line 344 into a regenerator 346 where the carbon laid down upon the surface of the catalyst is burned off by means of air introduced by way of line 348. It is to be understood that in the normal practice of catalytic cracking, the catalyst is carried by way of an air stream into the regenerator.

The second cracked hydrocarbon stream is carried by way of line 350 to a fractionator 352 from whence a light ends and motor gasoline fraction is recovered overhead by way of line 354 and is passed to a subsequent fractionation unit for separation and recovery. The bottoms fraction is also recovered by way of line 356. A recycle gas oil boiling within the range of 650° F. to 850° F. may be returned by line 338 as a side stream as aforesaid for passage through the cracking zone 332. A 400° F. to 650° F. catalytic heating oil is recovered as a side stream by way of line 358 for further treatment as, for example, hydrodealkylation to recover a light aromatic product or for direct use as a specialty oil. The catalytic heating oil recovered by the practice of the present invention will contain about 80% aromatics, as compared to about 70% aromatics obtainable by the normal catalytic cracking of the unseparated feed stock. No extraction step is required in attaining the 80% aromatic product.

As exemplary of the advantages of the practice of the present invention, the following examples are given.

#### EXAMPLE I

A gas oil feed stock boiling within the range of about 400° F. to about 950° F. is charged to a dense phase catalytic cracker and is contacted with hot catalyst at a temperature of about 950° F. with a hydrocarbon residence time of about 6 seconds and a catalyst residence time of about 75 seconds. The catalyst-to-oil ratio is about 8.0. The products of the cracking reaction are separated and the hydrocarbon product is fractionated. A cold dry gas recovery of about 10.7% by weight is experienced ( $H_2$  through  $C_3$ ). About 13.5% butanes and butylenes are recovered, with 26+% of  $C_5$  through 430° F. naphtha being recovered. During the reaction, 7.7% coke is formed, and the 430° F.+ fraction amounts to 47.5% with an API gravity of 21.9°.

#### EXAMPLE II

The same feed stock is charged to a high temperature-short contact time transfer line catalytic cracker in accordance with the scheme shown in FIG. 1. The reactor temperature is held at about 1050° F. with a hydrocarbon residence time of 2 seconds and a catalyst residence time of 4 seconds. The catalyst-to-oil ratio is held at 12:1. A 56% volume percent conversion is attained as compared to 51% in Example I, with the total dry gas being recov-

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ered at 22.6%. Butane and butylenes amount to about 10.7% with the  $C_5$  to 430° F. naphtha amounting to about 23.7%. The 430° F.+ fraction amounts to about 42.7%, having an API gravity of 8.1. The coke formation is only 2.2%. The results of these comparative runs are shown below in Table I.

Table I

	Conventional Catalytic Cracking	High Temperature-Short Time Catalytic Cracking
Reactor Temperature, ° F. ....	950	1050
Hydrocarbon Residence Time, Secs. ....	6	2
Catalyst Residence Time, Secs. ....	75	4
Catalyst, Oil Ratio .....	8	12
Conversion, Vol. Percent .....	51	56
Total Dry Gas ( $H_2-C_3$ ), Wt. Percent .....	10.7	22.6
Ethane, Wt. Percent .....	1.4	3.1
Ethylene, Wt. Percent .....	0.9	6.4
Propane, Wt. Percent .....	3.3	0.7
Propylene, Wt. Percent .....	3.0	7.3
Butanes, Vol. Percent .....	9.3	0.3
Butylenes, Vol. Percent .....	4.2	10.4
$C_5-430^\circ F.$ Naphtha, Vol. Percent .....	26.1	23.7
430° F.+ , Vol. Percent .....	47.5	42.7
Coke, Wt. Percent .....	7.7	2.2
430° F.+ Gravity, ° API .....	21.9	8.1

#### EXAMPLE III

The feed stock of Example I is separated into two fractions, one boiling from 400° F. to 650° F. and another containing 650° F.+ boiling material. The 400° F. to 650° F. fraction is charged to a conventional dense phase catalytic cracker under conditions as follows: The reactor temperature is about 950° F. with the hydrocarbon residence time of about 6 seconds and catalyst residence time of about 75 seconds. The catalyst-to-oil ratio is maintained at about 8:1. The product is separated in a fractionator and a 400° F. to 650° F. catalytic heating oil is obtained having an aromaticity of about 40%. This catalytic heating oil is charged into a transfer line reactor having two zones, a high temperature zone maintained at about 1025° F. to 1075° F. and a normal temperature zone maintained between about 925° F. and 975° F. The catalyst-to-oil ratio in the high temperature zone is maintained at about 12:1. The 650° F.+ fraction of feed stock is charged into the normal temperature zone of the reactor wherein the temperature is maintained at about 925° F. to 975° F. The hydrocarbon residence time in the normal temperature zone is about 6 seconds with a catalyst residence time of about 30 seconds. The mixed product stream is separated from the catalyst and passed to a fractionator from whence a recovered stream of about 400° F. to 650° F. catalytic heating oil is withdrawn. This catalytic heating oil stream is found to contain about 80% aromatic hydrocarbon.

#### EXAMPLE IV

A virgin gas oil feed boiling within the range of about 400° F. to about 950° F. is charged into a transfer line reactor maintained at about 1025° F. to 1050° F. The hydrocarbon residence time is maintained at about 2 seconds with the catalyst residence time about 4 seconds. The product is withdrawn and the catalyst separated from the hydrocarbon. The hydrocarbon is fractionated and a 400° F. to 650° F. side stream is withdrawn as a catalytic heating oil fraction. A recycle stream is withdrawn from this fraction amounting to about 75% of the side stream and is returned to the catalytic cracker and is charged into a high temperature zone maintained at about 1050° F. The recycle stream is passed through the high temperature zone in about 2 seconds. The catalyst-to-oil ratio in the reactor is about 12:1. The aromatic content of the catalytic heating oil obtained after the catalytic unit is lined out is about 80%.

It is to be understood that suitable charge stocks for use in the practice of the present invention in each of its modes comprise a hydrocarbon stream boiling within

the range of 350° F. to 700° F., or a selected fraction boiling within those limits. The hydrocarbon stream will contain a certain percentage of aromatic hydrocarbons. By the practice of the present invention, the percentage of aromatics in the final product streams will be increased along with a decrease in coke formation and an increase in light olefin formation.

In the claims, the term "aromatic hydrocarbons" is intended to include the naphthenic hydrocarbons which are the precursors of the true aromatic compounds, while the term "aromaticity" refers only to the true aromatic compounds contained in the hydrocarbon stream.

Applicant having disclosed in detail the nature of the present invention and a preferred mode of carrying out said invention having been set forth, what is desired to be protected by Letters Patent is to be limited not by the specific examples given, but rather by the appended claims.

I claim:

1. A method of obtaining a highly aromatic specialty oil boiling within the catalytic heating oil range from a virgin gas oil containing from about 20% to about 60% aromatic hydrocarbons and naphthenes and boiling within the range of 400° F. to 950° F.  
 in a system comprising a first reaction zone and a second reaction zone,  
 said second reaction zone having a normal temperature zone and a high temperature zone,  
 which comprises separating said virgin gas oil into a first portion boiling within the range of 400° F. to 650° F. and a second portion boiling about 650° F.,  
 contacting said first portion in said first reaction zone with a cracking catalyst under catalytic cracking conditions including a temperature within the range of 900° F. to 975° F., to obtain a first cracked hydrocarbon stream,  
 recovering from said first cracked hydrocarbon stream an first oil fraction boiling within the range of 400° F. to 650° F.,  
 contacting said oil fraction in said high temperature zone of said second reaction zone with a cracking catalyst under catalytic cracking conditions including a temperature within the range of 1000° F. to 1200° F., a hydrocarbon residence time of 0.5 second to 5.0 seconds, and a catalyst residence time within the range of 1.0 second to 20 seconds,  
 passing the total effluent of said high temperature cracking zone into said normal temperature zone of said second reaction zone,  
 contacting said total effluent with said second portion of said virgin gas oil under cracking conditions including a temperature within the range of 925° F. to 950° F., to obtain a second cracked hydrocarbon stream,

recovering from said second cracked hydrocarbon stream a specialty oil fraction of increased aromaticity and charging a portion of said specialty oil fraction into said high temperature zone of said second reaction zone along with said oil fraction boiling within the range of 400° F. to 650° F. which was recovered from said first cracked hydrocarbon stream.

2. A method in accordance with claim 1 wherein the cracking catalyst in said second reaction contains 40% alumina.

3. A method of producing a highly aromatic specialty oil from a virgin hydrocarbon stream containing from 20% to 60% aromatics and boiling within the range of 400° F. to 950° F. which comprises

in a catalytic cracking reaction zone having a high temperature zone and a normal temperature zone contacting said virgin feed in said normal temperature zone with the total effluent from said high temperature zone including the cracking catalyst,  
 at a temperature of 925° F. to 975° F.,  
 a hydrocarbon residence time of 5 to 10 seconds,  
 and a space velocity of 20 to 40 barrels of oil per pound of catalyst per hour,

to obtain a cracked total product stream,  
 separating the total product stream from the cracking catalyst,  
 regenerating said catalyst to obtain a freshly regenerated catalyst,

fractionating said total product stream to obtain a specialty oil fraction boiling within the range of 400° F. to 650° F.,  
 withdrawing a first portion of said specialty oil fraction as a specialty oil product stream,

withdrawing a second portion of said specialty oil fraction which is from 2 to 5 times by volume as great as said first portion,  
 passing said second portion into said high temperature zone in contact with said freshly regenerated catalyst,  
 at a temperature of 1000° F. to 1200° F.,  
 a hydrocarbon residence time of 0.5 to 5 seconds,  
 and a catalyst residence time of 1 to 20 seconds,  
 and a catalyst-to-oil ratio of 5:1 to 35:1,  
 and passing the total effluent from said high temperature zone into said normal temperature zone in contact with said virgin feed,  
 whereby said specialty oil product stream is produced having an aromaticity of about 80%.

#### References Cited in the file of this patent

#### UNITED STATES PATENTS

2,396,109	Martin	Mar. 5, 1946
2,844,523	Veltman	July 22, 1958
2,908,630	Friedman	Oct. 13, 1959
3,041,273	Smith et al.	June 26, 1962