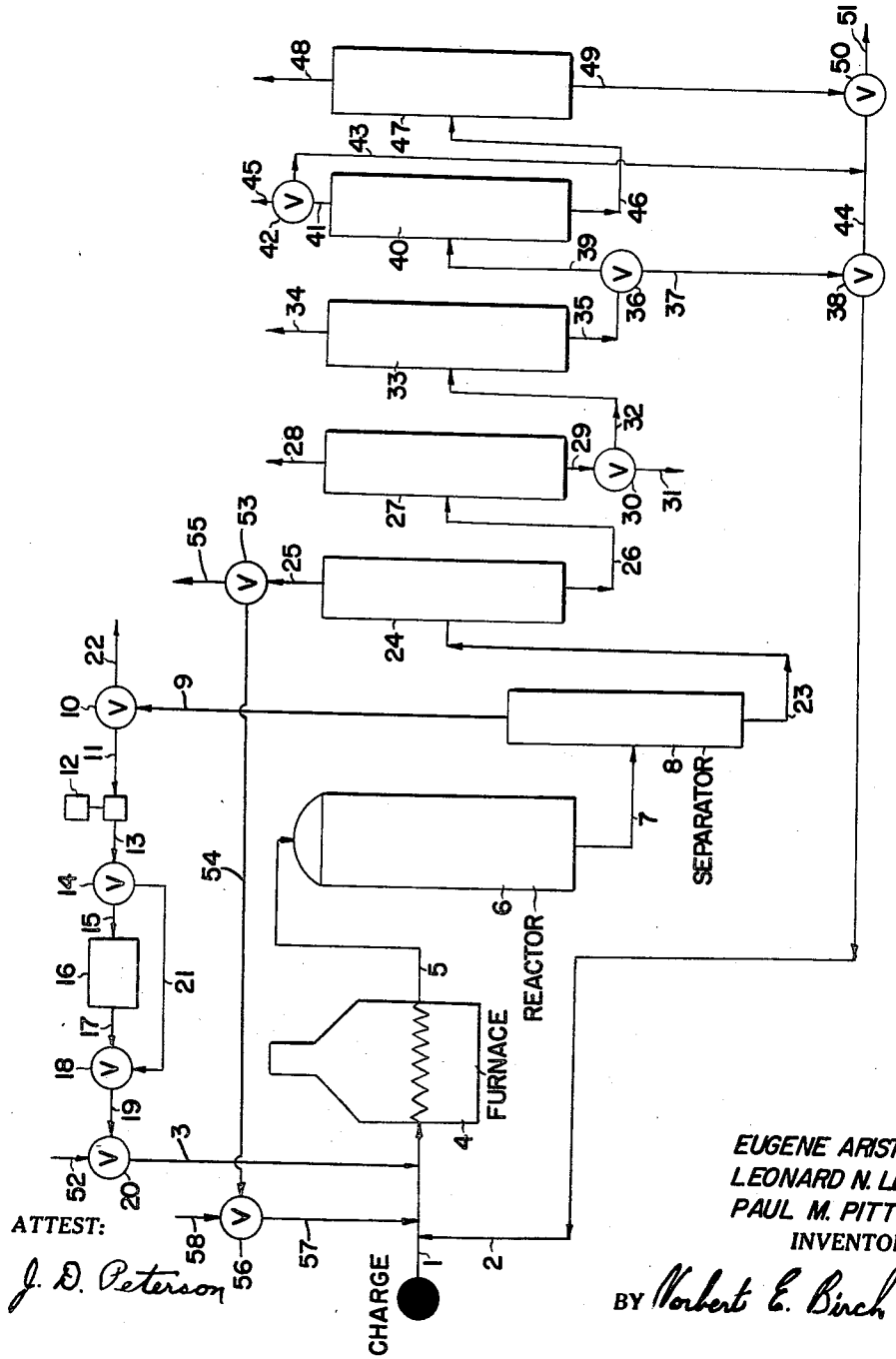
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HYDROCARBON CONVERSION PROCESS WITH SUBSTANTIAL PREVENTION OF COKE FORMATION DURING THE REACTION

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HYDROCARBON CONVERSION PROCESS WITH SUBSTANTIAL PREVENTION OF COKE FORMATION DURING THE REACTION

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6 Claims. (Cl. 208—133)

This invention relates to a method for increasing the cyclic hydrocarbon content of a normally liquid hydrocarbon distillate fraction. More particularly, this invention is concerned with reduction of coke formation during the production of benzene and naphthalene from alkylated aromatic-containing normally liquid hydrocarbon distillate fractions.

The process of treating hydrocarbon distillate fractions at high temperatures and under specific process conditions to increase the cyclic hydrocarbon content of such fractions by the dealkylation of alkylated aromatics to produce benzene and naphthalene at very high yields, or to increase the antiknock characteristics of such fractions is known.

The instant process is concerned with an improvement to the aforementioned process whereby the production of coke during the reaction is markedly decreased.

It is an object of this invention to increase the cyclic hydrocarbon content of normally liquid hydrocarbon distillate fractions with minimum production of carbonaceous materials and residues.

It is a further object of this invention to improve the antiknock characteristics of hydrocarbon distillate fractions boiling in the gasoline-kerosene range with minimum production of carbonaceous materials and residues.

It is a further object of this invention to produce benzene and naphthalene from alkylated aromatic hydrocarbon containing fractions with minimum production of carbonaceous materials and residues.

It is a further object of this invention to accomplish the desired conversions with minimum production of carbonaceous materials and residues by the use of hydrogen together with high temperatures and specific process conditions.

Additional objects will become apparent from the following description of the invention and the appended claims.

The present invention may be described briefly as a method for treating a normally liquid hydrocarbon distillate fraction to convert the paraffinic hydrocarbons into gaseous products and to remove the paraffinic radicals or components of the alkyl aromatics with minimum production of carbonaceous material. According to the present invention this may be accomplished by subjecting an alkyl aromatic-containing normally liquid hydrocarbon distillate fraction, together with one or more normally gaseous saturated hydrocarbons having from 2 to 4 carbon atoms in the molecule, to temperatures in the range from 950° F. to 1250° F. in a reaction zone devoid of catalytically active material. In addition to the elevated temperatures, the feed hydrocarbons together with the added normally gaseous saturated hydrocarbons are subjected to pressures in excess of 1000 pounds per square inch and ranging up to 10,000 pounds per square inch for times ranging between 30 seconds and 30 minutes and in the presence of hydrogen in amounts between 1.0 and 20.0 mols of hydrogen per mole of normally liquid hydrocarbon distillate charge, the moles of hydrocarbon charge being based on the average molecular weight of the hydrocarbon charge. The unconsumed hydrogen is separated from the reactor effluent and recycled to the reaction zone together with makeup hydrogen. The amount of hydrogen consumed by the reaction depends to a considerable degree upon the particular reaction conditions employed. In general, however, this amount will range between 1 and 2 mols of hydrogen per mole of hydrocarbon converted. At least a portion of the normally gaseous saturated hydrocarbons containing from 2 to 4 carbon atoms which are separated from the reactor effluent may be recycled to the reaction zone together with any makeup normally gaseous saturated hydrocarbons that may be required for the purpose of this invention.

The amount of normally gaseous saturated hydrocarbons introduced with the normally liquid hydrocarbon charge to the reaction may vary between 1 part by weight of normally gaseous saturated hydrocarbons to 9 parts by weight of normally liquid charge and 1 part by weight of normally gaseous saturated hydrocarbons to 1 part by weight of normally liquid charge.

The liquid product of the reaction after the removal of hydrogen is stabilized and the stabilized high antiknock product sent to the gasoline pool or to a purification system for benzene and naphthalene production. In the purification system the benzene and naphthalene produced by the conversion are separated from the products preferably by distillation and those products whose boiling range is between that of benzene and naphthalene and the products whose boiling range is above the naphthalene boiling range are preferably recycled to the reaction zone for further conversion to these pure aromatics.

Although the invention contemplates operation within the process limits set forth above, in many instances somewhat narrower ranges of process conditions are preferred for optimum conversion. It is preferred to operate in the temperature range between 1000° F. and 1200° F., at a pressure in excess of 1000 pounds per square inch up to 5000 pounds per square inch for times ranging between 2 and 30 minutes, in the presence of hydrogen ranging in amounts between 2.5 to 8.0 mols of hydrogen per mole of normally liquid hydrocarbon distillate charge. The preferred normally gaseous saturated hydrocarbon is propane and the amount of normally gaseous saturated hydrocarbon preferably ranges between 1 part by weight to 6 parts by weight of normally liquid charge and 1 part by weight to 2 parts by weight of normally liquid charge. In the case where octane improvement is the object, reaction times ranging between 3 and 16 minutes are the most preferable.

A variety of feed stocks may be employed for conversion in accordance with the instant invention. As has been pointed out, the invention is essentially a method for selectively removing paraffinic constituents or components and, accordingly, feed stocks may be employed which require that the entire selective removal of paraffins be accomplished by the process of this invention. Examples of such feed stocks are the virgin or straight run hydrocarbon fractions. Alternatively, feed stocks may be employed wherein the cyclic hydrocarbon content of the fraction has already been increased by prior refining process, such as catalytic cracking or catalytic reforming. Generally, prior art combination refining processes, such as catalytic cracking or catalytic reforming combined with solvent extraction for the concentration of the aromatic fraction, produce feed stocks particularly suitable for the production of benzene and naphthalene in accordance with the process of this invention.

As examples of the straight run feed stocks, a petroleum distillate fraction known as straight run naphtha boiling up to between 400° F. and 450° F. having octane numbers generally below 70 (CFR—F—1, clear) may be

treated advantageously by the present process to produce gasolines having octane numbers in excess of 100. Another feed stock whose cyclic hydrocarbon content may be advantageously increased or whose octane number may be materially raised is produced from catalytically cracking or catalytically reforming straight run petroleum distillates. These catalytic processes employ either single-functional or poly-functional catalysts well known to the industry. Catalytic cracking generally employs a single-functional catalyst, such as silica-alumina. Catalytic reforming generally employs a poly-functional catalyst, for example heavy metals such as cobalt, molybdenum, nickel, platinum, etc., either in metallic form or in the form of their oxides, and deposited on an active carrier such as alumina or silica-alumina. These poly-functional reforming catalysts produce reformates boiling in the gasoline-kerosene range which contain large quantities of aromatic hydrocarbons. These catalytic reformates, while generally high in octane number, may be further raised in octane number by treatment according to the instant process.

A petroleum distillate fraction known as straight run or virgin furnace oil, which fraction generally boils between about 300° F. and 650° F. may be employed particularly for the production of benzene and naphthalene. A similar boiling range fraction produced as the result of catalytically cracking a petroleum gas oil fraction likewise contains hydrocarbons suitable for conversion to benzene and naphthalene. In the case of the catalytically cracked furnace oil, the aromatic content may range from 40 percent to 70 percent by weight of the total fraction, and with both the virgin and catalytically cracked furnace oil the aromatic hydrocarbons may be concentrated by solvent extraction techniques well known to the industry which will produce fractions containing 90 percent to 95 percent or higher aromatic concentrations. These aromatics are largely alkylated aromatics and accordingly form particularly desirable feed stocks for the production of benzene and naphthalene.

When the process of the instant invention is employed for the production of benzene and naphthalene or either one separately, particularly desirable sources of alkylated aromatic hydrocarbons are the solvent extracts of either catalytic reformates or catalytically cracked products. Obviously, if but a single pure aromatic is desired, the feed stock may be treated by distillation to produce a fraction containing either mono-cyclic alkylated aromatic hydrocarbons which may be reduced to benzene or alkylated condensed di-cyclic hydrocarbons which may be converted to naphthalene. In the latter case, a charge stock boiling from about 400° F. to about 650° F. is particularly desirable.

For a further understanding of the invention, reference should be made to the accompanying drawing in which the single figure represents a flow diagram illustrating schematically certain important features of the invention.

Referring now to the drawing, numeral 1 designates the charge line through which any one of the feed stocks described is introduced into the system. This charge is mixed with recycle hydrocarbons contained in line 2, normally gaseous saturated hydrocarbons contained in line 57 and hydrogen in line 3 and is sent through furnace 4 where the mixture is heated to reaction temperature. From the furnace the heated charge is sent by line 5 to reactor 6. The reactor 6 has surfaces free of active catalytic material and contains no active catalytic material, although it may be desirable to fill part of the reaction space with non-catalytic beads or granules, such as ceramic materials, or with non-catalytic metallic shapes, such as cylinders, rods and the like.

The product from reactor 6 is removed by line 7 to separator 8, where the hydrogen, methane and small amounts of two-carbon and three-carbon hydrocarbons are separated and transferred by line 9 through valve 10 and thence either by line 11 for subsequent recycle as will be described, or if a purge stream is desired, into line 22. If the hydrogen is to be recycled, it is transferred by line 11 into compressor 12 and line 13 and thence either by line 15, hydrogen purification system 16, which may be a conventional absorber-stripper system or similar conventional purification means into line 17, valve 18, line 19, valve 20 and finally into line 3 for recycle, or if the hydrogen contains only very small amounts of methane, the hydrogen purification system may be by-passed by appropriate settings of valve 14 into line 21 and valve 18 into line 19. The bottoms from the separator 8 are transferred to fractionating tower 24 by means of line 23.

A product fraction containing ethane, propane and, if desired, some or most of the butanes is removed overhead by means of line 25, valve 53 and thence either by line 54 for subsequent recycle, as will be described, or, if a purge stream is desired, to line 55. If the saturated hydrocarbons are to be recycled they are transferred by line 54 to valve 56 and line 57 for combination with the charge in line 1. Any makeup or additional normally gaseous hydrocarbons may be added to the system through line 58 and valve 56 for combination with recycle normally gaseous hydrocarbons in line 57.

The bottoms from tower 24 are transferred by line 26 into tower 27 where they are fractionated to produce an overhead fraction containing any four-carbon hydrocarbons not previously removed together with five-carbon hydrocarbons. This overhead fraction is removed by line 28 and the bottoms fraction is removed by line 29. In those cases where the process is being employed to improve the antiknock characteristics of the feed, the liquid products removed from tower 27 are separated from the system by means of valve 30 and line 31. This antiknock fraction may be blended with any desired amount of the four-carbon and five-carbon fraction taken overhead to produce a gasoline having the desired vapor pressure characteristics. In those cases where the system is being operated not only to produce high antiknock gasoline but also pure aromatic hydrocarbons, or where the system is being used solely for the production of aromatic hydrocarbons, the bottoms fraction from tower 27 is transferred from line 29 to line 32 by appropriate setting of value 30 and from line 32 introduced into fractionating tower 33 where the benzene fraction is removed overhead via line 34 and the bottoms fraction removed via line 35.

If the boiling range of the feed is such that it contains no hydrocarbons boiling in the naphthalene or higher boiling range, the bottoms from line 35 are transferred by means of value 36 into line 37 and valve 38 for recycling into line 2. If, however, hydrocarbons are present boiling in the naphthalene boiling range and higher, the bottoms from tower 33 contained in line 35 are transferred into tower 40 by appropriate settings of valve 36 and the use of line 39.

In fractionating tower 40 material boiling above the benzene boiling range and below the naphthalene boiling range is removed overhead by means of line 41 to valve 42 which is normally adjusted so that the material will pass into line 43, line 44 through valve 38, into line 2 and thus be recycled to the charge. If desired, a portion or all of this fraction boiling between the benzene boiling range and the naphthalene boiling range may be removed from the system without recycle by adjusting valve 42 so that it will pass out through line 45.

The bottoms from the tower 40 which contain the naphthalene boiling range fraction and heavier materials are transferred by means of line 46 to fractionating tower 47. In fractionating tower 47 the naphthalene boiling range fraction is removed overhead by means of line 48, while the fraction boiling above the naphthalene boiling range is removed as bottoms from tower 47 by means of line 49. If it is desired to recycle this bottoms fraction, valve 50 is adjusted so that the bottoms will pass

into line 44 and thus be transferred via valve 38 and line 2 into the charge. If, however, it is desired to produce a fraction boiling above naphthalene as a product, valve 50 is adjusted so that the bottoms from tower 47 will pass into line 51.

Since there is hydrogen consumed by the reaction, it is necessary to add hydrogen to the system. This is advantageously done by means of line 52 to valve 20 where it will be combined with recycle hydrogen.

The following examples are presented to illustrate certain details and features of the invention.

A normally liquid hydrocarbon distillate fraction comprising 425° F. to 450° F. boiling range cut of catalytically cracked furnace oil with an analysis by the mass spectrometer as set forth in Table I under the heading "Charge Composition" was treated in a continuous system under the conditions also set forth in Table I under the heading "Run No. 1, Conditions." The product from this reaction was isolated and analyzed by the mass spectrometer, the analysis set forth under the heading "Run No. 1, Liquid Product Composition."

A second portion of the same charge material was run under similar conditions ("Run No. 2, Conditions") with the exception that one part by weight of propane to 4 parts by weight of the normally liquid hydrocarbon distillate charge was introduced into the reaction zone together with the charge. The results of the treatment of the charge distillate under these conditions are set forth under "Run No. 2, Liquid Product Composition."

Table I

		Run No. 1—Conditions	Run No. 2—Conditions
Temperature, ° F., Average		1,080	1,077
Pressure		3,000	3,000
H_2/Hydrocarbon (Mol Ratio)		5.9	6.8
H_2/Hydrocarbon (Cu. ft./bbl.)		4,600	5,290
Contact Time at Reaction Temp		2.2 Min.	2.3 Min.
	Charge Composition, Wt. Percent	Run No. 1—Liquid Product Composition, Wt. percent Based on Charge	Run No. 2—Liquid Product Composition, Wt. percent Based on Furnace Oil Charge
Paraffins	22.0	0.0	1.3
Cycloparaffins	17.0	0.0	0.6
Alkyl benzenes	15.0	25.2	24.9
Tetralins, indans, etc	17.0	4.3	4.5
Naphthalene	4.0	17.2	17.8
Methyl naphthalene	25.0	14.1	14.0
Dimethyl naphthalene	0.0	0.6	0.6
Coke (Weight percent based on furnace oil charged)		0.042	0.009

It will be seen from these data that large amounts of naphthalene are produced, both in the presence and in the absence of propane, and accordingly there are no deleterious effects of addition of a normally gaseous saturated hydrocarbon to the feed. Furthermore, these data show that if a normally gaseous saturated hydrocarbon is introduced into the reaction zone, together with the feed, a very marked reduction in coke formation is accomplished. The amount of coke produced was measured by noting the increase in weight of the reactor and its packing after each run. These results were checked by combustion analyses. Exceedingly close checks were obtained indicating a high degree of accuracy for these measurements.

A study of the amounts and types of light hydrocarbons produced in Run No. 2, as set forth in the analysis in Table II will show that no dehydrogenation reactions have occurred; that is, the normally gaseous saturated hydrocarbons have not functioned as hydrogen donors under the conditions of the reaction, but instead the entire amount of hydrogen consumed has been from the gaseous hydrogen added originally to the feed.

Table II

	Mol percent
CH_4	11.6
C_2H_6	6.2
C_2H_4	0.0
C_3H_8	6.9
C_3H_6	0.0
Iso C_4H_{10}	0.5
n C_4H_{10}	0.2
C_4H_8	0.0
H_2	74.6

The exact function of the normally gaseous hydrocarbons having from 2 to 4 carbon atoms in the molecule in inhibiting coke formation in thermal reactions, as has been described, is not understood. A theory of such mechanism is not required, however, in order to practice this invention the limits of which are set forth in the claims.

We claim:

1. In a process for increasing the cyclic hydrocarbon content of a normally liquid hydrocarbon distillate fraction wherein said fraction is subjected to thermal conversion in the presence of hydrogen at a temperature ranging between 950° F. and 1250° F. at a pressure in excess of 1000 pounds per square inch and ranging up to 10,000 pounds per square inch for a time in the range between 30 seconds and 30 minutes and the amount of hydrogen ranges between 1.0 and 20 moles of hydrogen per mole of hydrocarbon charge, the improvement which comprises introducing a normally gaseous saturated hydrocarbon containing from 2 to 4 carbon atoms in the molecule into the reaction zone together with the normally liquid hydrocarbon distillate fraction, said normally gaseous saturated hydrocarbon being in an amount sufficient to substantially decrease the production of coke during the reaction.

2. In a process for improving the antiknock characteristics of a hydrocarbon distillate fraction boiling in the gasoline-kerosene range, wherein said fraction is subjected to thermal conversion in the presence of hydrogen at a temperature ranging between 950° F. and 1250° F., at a pressure in excess of 1000 per square inch, and ranging up to 10,000 pounds per square inch, for a time in the range between 30 seconds and 30 minutes, and the amount of hydrogen ranges between 1.0 and 20 moles of hydrogen per mole of hydrocarbon charge, the improvement which comprises introducing a normally gaseous saturated hydrocarbon containing from 2 to 4 carbon atoms in the molecule into the reaction zone together with the hydrocarbon distillate fraction boiling in the gasoline-kerosene range, said normally gaseous saturated hydrocarbon being in an amount sufficient to substantially decrease the production of coke during the reaction.

3. In a process for improving the antiknock characteristics of a hydrocarbon distillate fraction boiling in the gasoline-kerosene range, wherein said fraction is subjected to thermal conversion in the presence of hydrogen at a temperature ranging between 950° F. and 1250° F., at a pressure in excess of 1000 pounds per square inch and ranging up to 10,000 pounds per square inch, for a time in the range between 3 minutes and 16 minutes, and the amount of hydrogen ranges between 1.0 and 20 moles of hydrogen per mole of hydrocarbon charge, the improvement which comprises introducing a normally gaseous saturated hydrocarbon containing from 2 to 4 carbon atoms in the molecule into the reaction zone together with the hydrocarbon distillate fraction boiling in the gasoline-kerosene range, the amount of normally gaseous saturated hydrocarbon ranging between 1 part by weight to 9 parts by weight of the hydrocarbon distillate fraction and 1 part by weight to 1 part by weight of the hydrocarbon distillate fraction.

4. In a process for the preparation of benzene and

naphthalene wherein an alkylated aromatic hydrocarbon-containing fraction boiling up to 650° F. is subjected to thermal conversion in the presence of hydrogen at a temperature ranging between 950° F. and 1250° F., at a pressure in excess of 1000 pounds per square inch and ranging up to 10,000 pounds per square inch, for a time in the range between 30 seconds and 30 minutes, the amount of hydrogen ranging between 1.0 and 20 mols of hydrogen per mole of hydrocarbon charge, the hydrogen, a benzene boiling range fraction and a naphthalene boiling range fraction removed from the products of the thermal conversion and the hydrogen together with the liquid products remaining from the benzene and naphthalene separation recycled to the thermal conversion step, the improvement which comprises introducing a normally gaseous saturated hydrocarbon containing from 2 to 4 carbon atoms in the molecule into the reaction zone together with the alkylated aromatic hydrocarbon containing fraction, the amount of normally gaseous saturated hydrocarbon ranging between 1 part by weight to 9 parts by weight of the alkylated aromatic hydrocarbon-containing fraction and 1 part by weight to 1 part by weight of the alkylated aromatic hydrocarbon containing fraction.

5. In a process for the preparation of benzene wherein an alkylated aromatic hydrocarbon-containing fraction boiling up to 650° F. is subjected to thermal conversion in the presence of hydrogen at a temperature ranging between 950° F. and 1250° F., at a pressure in excess of 1000 pounds per square inch and ranging up to 10,000 pounds per square inch. for a time in the range between 30 seconds and 30 minutes, the amount of hydrogen ranging between 1.0 and 20 mols of hydrogen per mole of hydrocarbon charge, the hydrogen and a benzene boiling range fraction separately removed from the products of thermal conversion and the hydrogen, together with the liquid products remaining from benzene separation are recycled to the thermal conversion step, the improvement which comprises introducing a normally gaseous saturated hydrocarbon containing from 2 to 4 carbon atoms in the molecule into the reaction zone together with the alkylated aromatic hydrocarbon-containing fraction, the amount of normally gaseous saturated hydrocarbon ranging between 1 part by weight to 9 parts by weight of the alkylated aromatic hydrocarbon-containing fraction and 1 part by weight to 1 part by weight of the alkylated aromatic hydrocarbon-containing fraction.

6. In a process for the preparation of naphthalene wherein an alkylated condensed ring aromatic hydrocarbon-containing fraction boiling between 400° F. and 650° F. is subjected to thermal conversion in the presence of hydrogen at a temperature ranging between 950° F. and 1250° F., at a pressure in excess of 1000 pounds per square inch and ranging up to 10,000 pounds per square inch, for at ime in the range between 30 seconds and 30 minutes, the amount of hydrogen ranging between 1.0 and 20 mols of hydrogen per mole of hydrocarbon charge, the hydrogen and naphthalene boiling range fraction separately removed from the products of thermal conversion and the hydrogen, together with the liquid products boiling higher than the naphthalene boiling range, are recycled to the thermal conversion step, the improvement which comprises introducing a normally gaseous saturated hydrocarbon containing from 2 to 4 carbon atoms in the molecule into the reaction zone together with the alkylated condensed ring aromatic hydrocarbon-containing fraction, the amount of normally gaseous saturated hydrocarbon ranging between 1 part by weight to 9 parts by weight of the alkylated condensed ring aromatic hydrocarbon-containing fraction and 1 part by weight to 1 part by weight of the alkylated condensed ring aromatic hydrocarbon-containing fraction.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 2,929,775 March 22, 1960

Eugene Aristoff et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

In the grant, lines 1 and 2, for "Eugene Aristoff, of Newton Square, and Leonard N. Leum and Paul M. Pitts, of Media, Pennsylvania," read -- Eugene Aristoff, of Newton Square, and Leonard N. Leum and Paul M. Pitts, of Media, Pennsylvania, assignors to The Atlantic Refining Company, of Philadelphia, Pennsylvania, a corporation of Pennsylvania, --; lines 11 and 12, for "Eugene Aristoff, Leonard N. Leum, and Paul M. Pitts, their heirs" read -- The Atlantic Refining Company, its successors --; in the heading to the printed specification, lines 5 and 6, for "Eugene Aristoff, Newton Square, and Leonard N. Leum and Paul M. Pitts, Media, Pa." read -- Eugene Aristoff, Newton Square, and Leonard N. Leum and Paul M. Pitts, Media, Pa., assignors to The Atlantic Refining Company, Philadelphia, Pa., a corporation of Pennsylvania --.

Signed and sealed this 23rd day of August 1960.

(SEAL)
Attest:

KARL H. AXLINE
Attesting Officer

ROBERT C. WATSON
Commissioner of Patents