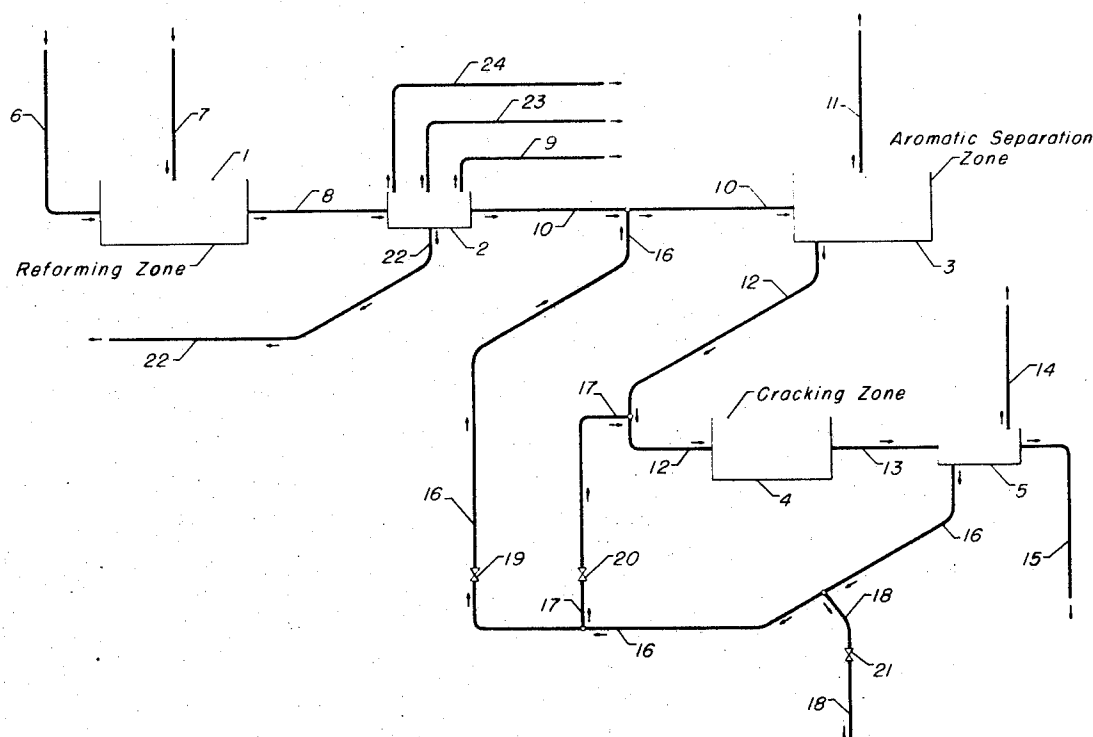
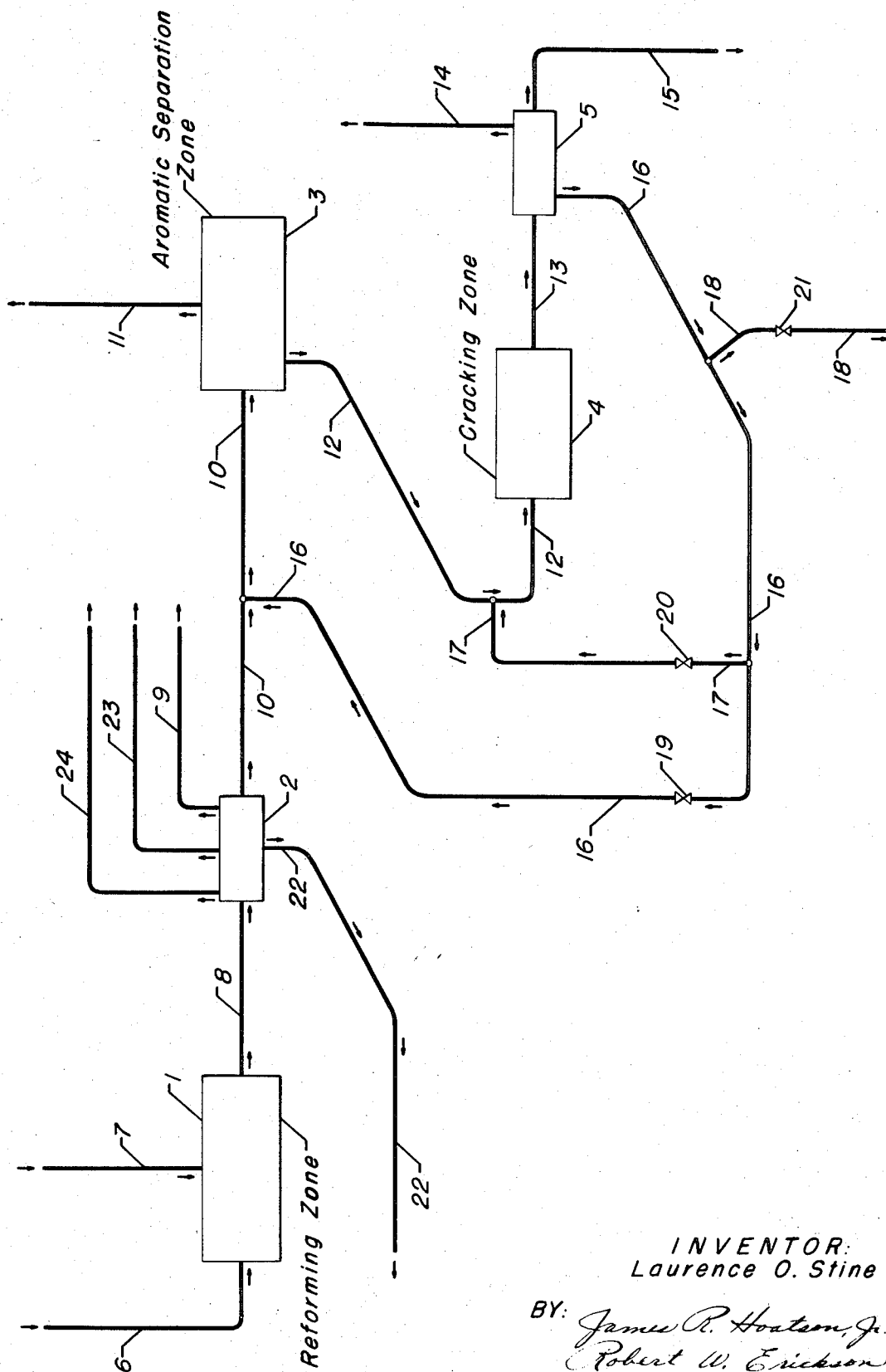


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11 Claims, 1 Drawing Figure





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HIGH OCTANE GASOLINE PRODUCTION

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a continuation-in-part application of my copending application Ser. No. 885,859 filed on Dec. 17, 1969, all the teachings of said copending application being incorporated into this application by specific reference thereto.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The field of art to which this invention pertains is catalytic conversion of hydrocarbons. More specifically, this invention pertains to a combination of integrated refinery processes including low severity reforming, aromatic concentration and cracking of hydrocarbons to provide a resulting high octane gasoline pool, requiring, in most cases, no lead addition for present-day gasoline octane requirements for internal combustion engines.

2. Description of the Prior Art

Typical of the problems encountered in refinery processes when producing high octane motor fuels is the loss of liquid yield when producing high octane gasoline via reforming operations. In reforming operations the primary octane improving reactions are naphthene dehydrogenation, naphthene dehydroisomerization and paraffin dehydrocyclization. The naphthene dehydrogenation reaction is quite rapid and is the primary octane improving reaction in catalytic reforming. When five membered alkyl naphthenes are present in a naphtha feed it is necessary to isomerize the alkyl cyclopentanes into six membered ring naphthenes followed by the dehydrogenation to aromatics. Aromatization of paraffins is achieved by the dehydrocyclization of paraffins having at least six carbon atoms per molecule. Dehydrocyclization is limited in the once-through reforming operations because as the aromatic concentrations increase through the reforming zone the rate of additional dehydrocyclization of paraffins is greatly reduced. This leaves unreacted paraffins present in the reformat effluent which greatly reduces the octane rating of the reformat. In the reforming zone, the paraffins which at low reforming severity would pass through unreacted, are cracked at high reforming severity, to yield partly gasoline material but largely light hydrocarbons. Because of the hydrogen present during the cracking step the light hydrocarbons are saturated forming primarily normal and non-normal paraffins generally in the C₁ to C₄ carbon number range.

The unreacted saturates which pass through the reforming zone typically are of low octane rating and in some cases require further processing to upgrade the gasoline pool. Further processing in order to improve the octane rating of the saturates leaving the reforming zone can be eliminated by in effect "overwhelming" the low octane components of the reformat by increasing the reformer severity of operations to produce an increased quantity of aromatic components. This type of operation has a twofold effect in increasing a reformat octane rating; first, additional high octane aromatic components are produced; and, secondly, the lower octane components are partially eliminated by being converted into aromatic components or into light products outside the gasoline boiling range.

The improvement in octane accompanied by the increased severity of the reforming zone, therefore, results in lower liquid yields of gasoline partly due to the "shrinkage" of the molecular size of the paraffins and naphthenes when they are converted to aromatic type hydrocarbons and partly due to production of the aforesaid light products. It has been found that instead of "overwhelming" the lower octane components of reformat gasoline with high octane aromatic components, that the cracking of the low octane reformat components (paraffins and naphthenes) into lower molecular weight olefins and paraffins allows subsequent processing to convert these materials into improved high octane components which improve the overall refinery gasoline pool octane while substantially eliminating the volumetric yield loss which accompanies high severity reforming conditions.

I have found that in the operations described above that it is necessary to crack the saturate components of the reformat stream in a saturate cracking zone which is operated at conditions which generally require recycling of a portion of the cracking zone effluent to the cracking zone to crack materials which have not been converted to valuable light hydrocarbons C₃ olefins, C₄ olefins and i-C₄ paraffins) or to gasoline components (aromatics produced in the cracking zone).

While recycle operations have been disclosed for the saturate cracking zone, there has been no disclosure or teaching of removing aromatic components from the material recycled to the saturate cracking zone. The aromatic components are generally quite refractory and require high cracking temperatures and long catalyst oil contact times to be cracked to lower molecular weight components. In instances in which unreacted paraffins or cycloparaffins and olefins are in admixture with aromatics which are being recycled to the cracking zone, conversion of some of the non-aromatic material to aromatics would lead to a build up of aromatics in the recycle system. A difficult problem arises where there is a build-up of aromatics which boil in the same general temperature range as the non-aromatics. Drag streams containing the aromatic component could be withdrawn at a rate sufficient to prevent aromatic build-up but unreacted saturates which could be reacted if recycled are lost resulting in poor yields.

I have found that if a portion or all of the recycle stream is passed into an aromatic separation zone that the aromatics can be separated and the non-aromatics which generally comprise saturates can be passed to the cracking zone to be cracked to valuable high octane precursors. Some of the recycle material can be directly passed to the saturate cracking zone with enough of the recycle material being diverted to an aromatic separation zone to prevent an aromatic build-up in the recycle loop.

SUMMARY

It is an object of this invention to provide an integrated refinery process wherein the gasoline produced from said process is of high octane quality and in most instances does not require addition of lead to increase its octane rating to meet the requirements of most present day or future internal combustion engines.

It is another object of this invention to operate an integrated refinery process wherein a reforming zone is operated at relatively low severity conditions to effect the production of aromatic hydrocarbons while reducing hydrocracking and dehydrocyclization reactions in said reforming zone, separating aromatic and non-aromatics from the reformat and, thereafter passing the non-aromatic portion of the reformat through a saturation cracking zone wherein olefinic and paraffinic light hydrocarbons and a heavy cracked product are produced.

Because throughout this specification numerous terms will be used to characterize various hydrocarbon charge stocks and fractions thereof, various conversion products, and various characteristics of the aforesaid stocks, fractions and products, such terms will first be defined in order to facilitate an understanding of the subsequent description of the invention.

The term light hydrocarbons generally refers to those hydrocarbons which have from one to four carbon atoms per molecule. The light hydrocarbons having one and two carbon atoms per molecule are generally referred to as dry gases and are generally used as refinery fuel gases while the C_3 and C_4 portions of the light hydrocarbons are valuable; the C_3 and C_4 olefins can be used in the process of this invention for alkylate or polymer or isopropyl alcohol production; the C_3 and normal C_4 paraffin portions of the light hydrocarbons are generally referred to as liquid petroleum gases and can be used as such.

Light naphtha streams generally refer to hydrocarbon streams containing hydrocarbons in the C_5 and C_6 carbon range. The light naphthas generally are recovered directly, as virgin light naphthas, from a crude distillation unit. The end boiling point of most light naphthas is generally from about 175° F. to about 200° F. The heavy naphthas are generally referred to as those hydrocarbons streams having boiling points from about 180° F. to about 400° F. which includes those hydrocarbons having carbon numbers of about 7 or greater and which boil below about 400° F. The general term naphtha can include various proportions of both heavy and light naphtha.

As with most definitions of hydrocarbons based on boiling points, there is a certain amount of overlap of the boiling range of the individual hydrocarbons of adjacent carbon numbers when referring to hydrocarbon boiling ranges in this specification. The hydrocarbon stream identified by a boiling range shall be assumed to have about 5 percent of its volume boiling below the lower temperature and about 95 percent of its volume boiling below the upper temperature of its given boiling range.

In order to fully understand the process of this invention, a brief explanation of the various reaction zones which are used as part of the process of this invention are described in greater detail below.

REFORMING ZONE

In the reforming zone a suitable hydrocarbon feed stock is contacted with a reforming catalyst to effect conversion of the reformer feed stock to a higher octane reformat product. Hydrocarbon feed stocks which can be used in the reforming zone include hydrocarbon fractions containing cycloparaffins or

naphthenes and paraffins. The preferred stocks are those consisting essentially of naphthenes and paraffins although in some cases aromatics or olefins or both aromatics and olefins may be present. Preferred reformer feeds include straight-run gasoline, natural gasolines, and the like. It is frequently advantageous to charge thermally or catalytically cracked gasolines or higher boiling fractions thereof to the reforming zone. The reformer charge stock may be a full boiling range gasoline charge stock having an initial boiling point of from about 50° F. to about 100° F. and an end boiling point within the range of from about 325° F. to about 425° F., or may be a selected fraction thereof.

The catalysts which can be used in the reforming zone include refractory inorganic oxide carriers containing one or more reactive metallic component thereon. Inorganic refractory oxides which can be used as carriers for reforming catalysts include alumina, the crystalline aluminosilicates such as the faujasites or mordenite, or combinations of alumina and the crystalline aluminosilicates. Metallic components which are generally recognized in the art as being favorable catalytic components for reforming operations generally include the Group VIII and IV metals. Rhenium, tin and lead have also been shown to have catalytic properties when used with platinum. Reforming catalysts may also contain combined halogen as one of the catalytic components. The halogens which can be used include fluorine, chlorine, bromine, iodine or mixtures thereof.

Effective reforming operating conditions include temperatures within the range of about 800° F. to about 1,100° F. and preferably between about 850° F. and about 1,050° F., liquid hourly space velocities in the range of from about 0.5 to about 15.0 and preferably in the range of from about 1 to about 5 are normally used. The quantity of hydrogen-rich recycle gas which is charged along with the hydrocarbon feed stock to the reforming zone, generally is present in amounts of from about one-half to about 20 moles of hydrogen per mole of hydrocarbon feed, and preferably from about 4 to about 12 moles of hydrogen per mole of hydrocarbon feed. The reforming zone may be effected in any suitable process system familiar to those skilled in the art such as fluidized type processes, moving bed-type process, etc. Particularly suitable processes comprise the well-known fixed bed system in which the catalyst is disposed in the reaction zone, and the hydrocarbons to be converted are passed therethrough in either upward or downward flow. The reforming zone reactor effluent, or reformat, is generally passed through a separation zone where it can be fractionated to remove lighter weight components from heavier weight liquid components of the reformat and where the recycle gas, which is reused in the reforming zone can be easily separated. Since normal reforming operations produce excess amounts of gaseous hydrogen, a certain amount of the recycled gas is generally removed from the reforming system to maintain a given operating pressure. Reforming zone pressures generally used in normal reforming operations are generally within the range of from about 10 to about 1,500 pounds per square inch.

The reforming zone used in this combination process is operated at low severity. To those familiar to the reforming art, the term relatively high severity

generally indicates high temperature or low space velocity or both high temperature and low space velocity operating conditions. The direct results of high severity operations are generally noticed in the reformat octane being increased substantially. While the reforming zone used in this operation does not necessarily upgrade the octane of the reformer feed to that of the pool gasoline, the reforming zone feed stock is substantially improved in octane rating.

Low severity reforming operations as used in the specification and attached claims shall generally define a reforming process in which a large percentage of the naphthenes in the reformer feed are dehydrogenated to high octane aromatic compounds with the qualification that the dehydrocyclization of feed paraffins to aromatics is substantially reduced. A more detailed definition of the term low severity reforming operations can include conversion of feed naphthenes to aromatics within the range of from about 80 moles of aromatics produced per 100 moles of naphthenes charged to the reforming zone to about 100 moles of aromatics produced per 100 moles of naphthenes charged to the reforming zone and less than about 40 moles of aromatics produced per 100 moles of alkanes charged to the reforming zone. In determining the degree of conversion of naphthenes to aromatics (dehydrogenation) and alkanes to aromatics (dehydrocyclization), it is generally assumed that a relatively small amount of naphthenes are cracked or converted to hydrocarbons other than aromatics and that a major portion of the alkanes which disappear through the reforming zone are converted to aromatic hydrocarbons with some naphthenes and higher molecular weight alkanes being converted to low value light gas alkanes. The individual naphthenes and alkanes are also assumed to be aromatic precursors having substantially the same number of carbon atoms per molecule as the aromatic hydrocarbons they form.

AROMATIC SEPARATION ZONE

One or more aromatic separation zones may be used to concentrate aromatics from the reformat and recycle streams. In some instances it is preferred to allow separate aromatic separation zones to concentrate aromatics from the recycle and reformat streams because of the different character of the compositions of these two streams. The aromatic separation zones can be selected from two general classes of separation zones. The first class is the adsorptive-separation processes in which aromatics are concentrated by using a selected solid adsorbent which can either selectively adsorb aromatics or non-aromatics or separate them by their physical size or shape difference. The other type separation process generally include the extraction process and typically are solvent extraction operations in which a solvent is used which allows aromatics or non-aromatics to be selectively solubilized by the solvent materials.

The adsorptive-separation processes generally employ said adsorbents which effect aromatic concentration in swing bed operations or in continuous moving bed or fixed bed flow patterns. Typical of the adsorbents which may be used are the molecular sieves such as the type X or Y zeolites or the crystalline aluminosilicates having pore openings greater than about 5 ang-

stroms. Operating conditions for these type separations include pressures of from atmospheric to about 700 psig and temperatures of from about ambient to about 500° F. After adsorption of the selectively retained component of the feed steam has taken place that component can be desorbed from the adsorbent by any number of methods including flushing the adsorbent with a desorbent material which displaces the adsorbed material or a high temperature operation with or without reduction in operating pressure to effect desorption. Also gas purge desorption can be used coupled with an increased adsorbent temperature and reduced pressure if desired. Desorbent materials can include gases such as nitrogen, hydrogen, steam or hydrocarbons such as aromatics, straight and branched chain paraffins and olefins. If the desorbent is desired to be reused it is necessary that it be easily separated from the adsorbed and unadsorbed portions of the feed steam.

The extraction processes which can be used to separate the recycle and reformat aromatics from non-aromatics generally include the solvent extraction process. Solvents which find use in these type separation processes include organic compounds generally selected from the group of those oxygen containing compounds which include aliphatic and cyclic alcohols, cyclic momeric sulfolanes, the glycols and glycol ethers, as well as the glycol esters and glycol ester ethers. The mono- and polyalkylene glycols in which the alkylene group contains from two to three carbon atoms, such as ethylene glycol, diethylene glycol, triethylene glycol and tetraethylene glycol, propylene glycol, dipropylene glycol, and tripropylene glycol, as well as the methyl, ethyl, propyl, and butyl ethers, of the glycol hydroxyl groups and the acetic acid esters thereof. A preferred cyclic monomeric sulfolane is tetrathiodiithiophene-1, 1-dioxide. Various phenols, such as phenol and resorcinol and their alkyl ethers, such as para-cresol and thymol, are effective solvents for aromatic hydrocarbons. Aliphatic nitriles and cyano-substituted ethers and amines of appropriate boiling point, such as acetonitrile, the di-alpha, di-beta, and di-gamma, propion-nitriles and the diethers and polyalkylene polyamines constitute another group of useful solvents when combined with water in certain proportions to provide solvent compositions having the desired selectivity. The polyalkylene glycols also constitute especially good solvents when mixed with various quantities of water.

SATURATE CRACKING ZONE

The function of the saturate cracking zone is to crack the non-aromatic hydrocarbons fed to it by either thermal or catalytic means or both. The feed stock to the saturate cracking zone is generally the saturated portion of the reformat along with recycle material. Depending on the quantity of recycle material recycled, and the concentration of aromatics in the recycle material, various proportions of the recycle material pass through an aromatic separation zone or directly to the saturate cracking zone. The saturate cracking zone must be able to selectively crack the zone's feed stock saturates to lower molecular weight hydrocarbons in a manner so as to minimize the production of dry gases such as methane, ethane, ethylene or acetylene, while

maximizing the production of C_3 and C_4 un-saturates and isobutane and cracked gasoline material. The saturate cracking zone produces cracked gasoline and valuable light hydrocarbons from most of the aromatic precursors which are not converted to aromatics in the reforming zone because the reforming zone is operated at low severity conditions to gain an overall advantage in liquid yield of a high octane gasoline pool.

The materials produced in the saturate cracking zone generally comprise a heavy cracked material relatively rich high octane cracked gasoline plus C_3 through C_5 light hydrocarbons comprising propane, propylene, normal and iso-butane, normal and iso-butene, and pentanes and pentenes. The products are excellent feed stocks for other processes which form valuable gasoline components such as amines, esters, ethers, ketones, branched chain paraffins or alcohols. The olefinic portion of the aforesaid light hydrocarbons are suited for conversion to the below mentioned gasoline components with the paraffinic portion of the saturate cracking zone effluent which contains a relatively large amount of branched chain molecules best suited for production of alkylate gasoline.

A general but not all inclusive listing of individual valuable gasoline components which can be produced from the saturate cracking zone light hydrocarbons includes methyl alcohol, ethyl alcohol, isopropyl alcohol, isobutyl alcohol, tertiary butyl alcohol, isoamyl alcohol, tertiary amyl alcohol, hexanol, isopropylamine, n-butylamine, diethylamine, triethylamine, methyl acetate, ethyl acetate, isopropyl acetate, isobutyl acetate, propylene oxide, n-propyl ether, isopropyl ether, m-butyl ether, isoamyl ether, acetane, methyl ethyl ketone, methyl n-propyl ketone, diethyl ketone, C_3 alkylate, C_4 alkylate gasoline and polymerized gasoline.

In order to catalytically crack the saturates fed to the saturate cracking zone, high activity catalysts and high temperature operating conditions are required. It is preferred to use reaction temperatures within the range of from about 850° F. to about 1,250° F. and preferably temperatures within the range of from about 850° F. to about 1,150° F. Probably the most important operating parameter for the selective production of olefinic light hydrocarbons (propylene and butene) is the contact time between the paraffinic cracking zone feed and the catalyst contained therein. In fixed bed type cracking incorporating once-through operations, the weight ratio of olefins over saturates is almost directly related to the space velocity being used in the reaction zone. Increasing the space velocity of the saturated feed passing through the reaction zone increases the amount of olefinic hydrocarbons produced.

In fluidized catalytic cracking operations, space velocity is generally measured in terms of weight hourly spaced velocity (WHSV) which is defined as the weight per hour of charge oil passed into this reaction zone over the weight of the catalyst inventory in the reaction zone. The WHSV based on raw charge oil is most frequently used. Weight hourly space velocities greater than about 1-2 min.⁻¹ are preferred when effecting saturate cracking in the saturate cracking zone.

In instances where the conversion of saturate cracking zone feed is relatively low, a portion or all of the heavy cracked material or unreacted feed or both is

eventually recycled back to the cracking zone to effect a further conversion to more valuable components.

The catalytic cracking zone requires a catalyst that specifically can produce the valuable saturated and un-saturated light hydrocarbons which contribute to the process efficiency after further conversion to gasoline components. Additionally, the saturate cracking zone catalyst effects the production of a cracked gasoline product which contributes to the overall high octane gasoline pool. The catalyst used in this zone can be selected from a number of known materials including amorphous silica-alumina and zeolitic type aluminosilicates, both of which may contain composited thereon various catalytic components selected from the Periodic Table metals of combined or elemental character.

Cracking catalysts which may be used in the saturate cracking zone including certain types of silica-alumina, silica-magnesia, silica-zirconia and more preferably crystalline aluminosilicates characterized as having relatively high cracking activities.

The preferred crystalline aluminosilicate cracking catalysts can be mixed with less active amorphous type cracking catalysts or can be present in substantially pure form depending on the severities which are required of the process. The crystalline aluminosilicate may be naturally occurring or synthetically prepared. In the latter case the crystalline aluminosilicate may be selected from the group of synthetically prepared zeolites A, Y, L, D, R, S, T, Z, E, F, U, Q, B, X ZK-4, ZK-5, etc. The naturally-occurring materials include faujasite, mordenite, montmorillonite, etc.

Whether the catalyst comprises a crystalline aluminosilicate, or amorphous material, selected metals may be composited thereon by ion-exchange or impregnation methods. The metals composited on the catalyst may include the rare earth metals, alkali metals, alkaline earth metals, Group VIII metals, etc., and various combinations thereof. Hydrogen may also be present within the catalyst to effect increased catalyst activity.

In instances where the saturate cracking zone is a thermal type cracking zone, there is no need for a catalyst and the feed stock passed into the saturate cracking zone then generally produces a larger amount of lighter hydrocarbons than a catalytic cracking zone would yield. Thermal cracking conditions can vary from pressures ranging from about atmospheric to about 500 psig. and a temperature of from about 900° F. to about 1,500° F.

DESCRIPTION OF THE DRAWING

The attached drawing indicates a simplified diagram of one method of operating the flow of the combination process of this invention. Deleted from the drawing are the necessary heat-exchangers, preheaters, coolers, pumps, valves, and other equipment necessary to carry out the process of this invention in a refinery but not necessarily included for the interpretation of the invention as stated in the appended claims. An alternate flow pattern contemplated by the combination of this invention is to use two separate aromatic separation zones on the reformate and recycle streams.

The drawing shows three basic zones in which different operations take place. Reforming zone 1 which

is connected to aromatic separation zone 3 which in turn allows passage of a portion of its effluent into cracking zone 4. A portion or all of the effluent from the cracking zone is recycled via line 16 to the cracking zone 4. A portion of the recycle material can be diverted by line 17 directly to the cracking zone or a portion of the recycle material passes into aromatic separation zone 3 via line 16 and eventually to cracking zone 4.

Reforming zone 1 has a feed stream inlet line 6 through which passes a suitable naphtha charge stock. Recycle hydrogen passes into the reforming zone via line 7. Within the reforming zone is a suitable catalyst with this zone operated at the conditions previously described to effect the low severity operations in which a noticeable portion of the feed stock goes through the reforming zone in an unreacted state. The effluent from the reforming zone passes out of that zone via line 8 and into a separation zone 2. Basically separation zone 2 performs a minor operation of removing unwanted light gases such as hydrogen, methane and ethane via line 9 which can be vented or used as recycle gas for the reforming zone, light gases including some methane and ethane but primarily propane, butane, propylene and butene are removed via line 24 and may find use in other refinery operations such as alkylation to gasoline. The C_5/C_6 of the reformate is removed via line 23 and can be used as a component of the total gasoline product. The reformate which passes out of separation zone 2 via line 10 is substantially a C_5 or C_6 and heavier material depending upon the materials which are removed from the liquid reformate via line 23. The reformate passing through line 10 also contacts recycle material passing via line 16 with the mixture of recycle material and reformate material passing via line 10 into aromatic separation zone 3. As can be seen, the cracking zone recycle flow route which includes line 16 and line 20 with valves 19 and 17 located thereon respectively can be manipulated in a manner so that the ratio of recycle material passing directly into the cracking zone (via line 17) without passing into the aromatic separation zone compared to the quantity of material passing via line 19 to the aromatic separation zone can be varied in any predetermined manner in order to effect stable operations and to help eliminate aromatic build-up in the recycle loop when aromatic production occurs in the cracking zone.

The aromatic separation zone 3 can be any type of separation means including aforementioned liquid extraction type operations or the solid adsorptive-separation processes to effectively separate aromatics from non-aromatic hydrocarbons. In the process of this invention the aromatic material which is separated from most of the non-aromatic materials passes out of the aromatic separation zone via line 11 and can be collected for use in the gasoline pool. The non-aromatic materials which generally contain a large quantity of saturates pass out of aromatic separation zone via line 12 and into the cracking zone 4. In instances in which a portion of the recycle material from the cracking zone is desired to be passed directly into the cracking zone without passing into the aromatic separation zone the material passing through line 12 is mixed with recycle material passing via line 17 into line 12 for further cracking to valuable components including light hydrocarbons and cracked gasoline.

The cracking zone effluent passes out of zone 4 via line 13 and into separation zone 5. The cracking zone effluent material is then separated into light gas components which generally comprise C_4 and light hydrocarbons, materials boiling from the C_5 hydrocarbon range to the beginning of the gasoline range (100° – 10° F.), materials in the gasoline range (100° – 430° F.) and higher boiling materials.

The light hydrocarbon materials comprising hydrogen and up to C_4 pass out of the process via line 14 and can be used for other operations which include alkylation, hydration, polymerization or any other process in which these components can be converted to a relatively high octane component and used as an additional octane booster when present in the overall gasoline pool as a component thereof. The material passing out of line 15 can be the material belonging from the C_5 up to 110° F. boiling range material.

The material passing out of separation zone 5 via line 16 is generally a cracked gasoline boiling within the range of from about 100° to 430° F. There may also be heavier materials present along with the gasoline where the cracking conditions are more severe and in instances in which conversion of the feedstock to either cracked gasoline or olefins is not complete a portion of the paraffinic material from the feed stock is present. The primary purpose of recycling material back to the cracking zone is for additional production of cracked gasoline or unsaturates from the feed paraffins and where aromatic production accompanies the production of unsaturates it is a necessity that the recycle material pass into an aromatic separation zone in order to prevent a build up of relatively refractory aromatics in the recycle loop. A large build up of aromatics in the recycle loop reduces the capacity of the cracking zone at a given volumetric feed rate.

In most instances a portion of the material passing through line 16 and may be withdrawn from the process at a rate determined by the opening of valve 21 in line 18 and collected as a component of the gasoline pool. The remaining material eventually is passed into the cracking zone. It is one necessary limitation in the process of this invention that at least a portion of the recycle material be passed into an aromatic separation zone to separate a portion of the aromatics which are recovered via line 11. This limitation supposes the net production of aromatic materials in the cracking zone.

Line 22 which is located on separation zone 2 can be used to remove a portion of the reformate material from the process where it is desired that this material be used as a gasoline pool component. This material will be relatively low in octane because of the low severity operations in the reforming zone and additionally because this material will contain relatively high quantity of naphthenes and paraffins which in this state do not contribute to high octane materials or components.

The saturate cracking zone 4 can effect the cracking of non-aromatic materials from the aromatic separation zone by a fixed bed cracking or by fluidized type cracking operations. The operations and operating conditions for either type operations shown and previously described in extent necessary for a proper teaching of this portion of a combination process of this invention.

EXAMPLE I

In this example, a combination low severity reforming zone and a saturate cracking zone combination, as shown in the attached drawing was employed.

The feed stock used in this example and other examples was a Unifined naphtha which is generally described in Table I.

TABLE I

Unifined Naphtha Properties

API 55.0	Clear Research Octane 40.0
Sp.Gr. 0.7587	Clear Motor Octane 35.0
RVP 1.2	Aromatics 13.5 vol. %
Distillation	
10 vol. % 238° F.	
50 vol. % 278	
90 vol. % 331	

The reforming zone contained a typical platinum metal on an alumina base and was operated at conditions to produce a C₅+ platformate of about 85.0 Research Clear Octane Number (RON). The effluent from the low severity reforming zone was separated into a hydrogen rich stream, a C₁-C₄ light hydrocarbon stream, a C₅/C₆ gasoline stream and a C₇+ gasoline stream, the C₇+ reformate stream was passed into a solvent extraction zone which separated the C₇+ reform-

recycle operations would definitely help because of the increased production of C₃ olefins and C₄ olefins and isoparaffins which could eventually be converted to high octane alkylate gasoline components. The saturate cracking zone used a type Y zeolite commercial cracking catalyst.

TABLE II

Material Balance of Process Flow

Stream Description (refer to DRAWING)	BPD	LBS/HR
REFORMING SECTION		
Line 6, Reforming Zone Hydrocarbon Feed	25,899.7	286,710
Line 9, Hydrogen-Rich Separator Gas		14,593
Line 24, C ₃ -C ₄ Light Hydrocarbons		4,043
Line 23, C ₅ -C ₆ Gasoline	2,827.3	28,648
Line 10, C ₇ + Gasoline	20,384.4	239,390
Total Gasoline from Reformer	23,211.7	268,038
EXTRACTION SECTION		
Line 12, Saturate Rich Stream	8,512.8	89,053
Line 11, Aromatic Rich Stream	11,876.6	150,337
CRACKING SECTION ¹		
Line 14, C ₁ -C ₄ Light Hydrocarbons	6,855.3	65,665
Line 18, Cracked Gasoline	1,937.8	21,696
Coke Make		1,692
Total Gasoline Produced	16,641.7	180,677

1. No C₅/C₆ gasoline was removed from separation zone 5 as a pure stream.

TABLE III.—STREAM ANALYSIS

Line No.	6	9	24	23	10	12	11	14	18
Stream properties:									
API at 60° F.	55			72.0	44.3		31.6		52.6
Sp. gr. at 60° F.	0.7587			0.6953	0.8049		0.8676		0.7686
RVP	1.2			10.0	0.8		0.8		6.7
Distillation, ° F.:									
10 vol. percent	238			116	250		280		137
50 vol. percent	278			134	290		307		227
90 vol. percent	331			169	355		355		387
Clear octane No.:									
Research	40.0			77.0	86.1		115.0		95.0
Motor	35.0						95.0		84.0
Aromatics, vol. percent	13.5						100		20
Component, wt. percent:									
H ₂		41.2						0.8	
C ₁		11.8						4.8	
C ₂		15.7	7.2					8.6	
C ₃ olefins								23.6	
C ₃ paraffins		17.6	28.6					11.0	
C ₄ olefins								34.9	
i C ₄ paraffins		5.9	21.4					11.4	
n C ₄ paraffins		7.8	42.8					4.9	
Reformate gasoline					100.0				
C ₅ /C ₆ gasoline					100.0				
Cracked gasoline									100.0
Aromatic rich stream							100.0		
Saturate rich stream:									
Saturates						95.0	95.7		
Aromatics						5.0	4.3		

¹ Volume percent.

mate into an aromatic rich stream and a saturate rich stream with the saturate stream being passed into the saturate cracking zone for conversion to cracked gasoline and lower molecular weight light hydrocarbons. None of the cracked materials from the cracking zone were recycled to either the aromatic separation zone or the cracking zone (valves 20 and 21 were closed). This example is included to show the advantages obtained when employing the combination low severity aromatic separation and saturate cracking only. While there was no recycle operations involving passage of cracked gasoline into the aromatic separation zone with the saturate portion of the cracked gasoline eventually passed into the cracking zone, the

EXAMPLE II

In this example, a higher severity reforming zone was employed without subsequent cracking of the reformate saturate materials. The catalyst used was the same as the reforming catalyst used in Example I. The severity was such that the C₅-434° F. E.P. gasoline produced in the reforming zone was maintained at 92.0 RON. The higher octane reformate produced by these operations was much higher in aromatic content than the C₅+ reformate having an 85.0 RON of Example I. In fact, the 92.0 Octane reformate contained 69 vol.% aromatics while the 85.0 Octane reformate contained only about 45 vol.% aromatics. The higher octane reformate consequently was also lower in saturate con-

tent because of the higher quantity of saturates converted to aromatics via dehydrogenation of cycloparaffins and dehydrocyclization and/or cracking of paraffins.

The reforming zone effluent was separated into a hydrogen-rich gas stream, a C₁-C₄ light hydrocarbon stream and a C₅-434° F. E.P. gasoline material. Analysis of the products and material balance are shown in Table IV.

TABLE IV

Product Analysis and Material Balance of 92.0
Research Clear Reforming Zone Operation

Stream:	BPD	LBS/HR
Feed Stock to Reformer	25,889.7	286,710
Hydrogen Rich Separator Gas	—	16,285
C ₁ -C ₄ Light Hydrocarbons	—	18,981
C ₅ + Reformate Gasoline	21,828.0	251,445
Properties of C ₅ + Reformate Gasoline:		
API at 60°F.	47.7	
Sp.Gr. at 60°F.	.7896	
RVP	2.9	
Distillation, °F.		
10 vol. %	188	
50 vol. %	257	
90 vol. %	340	
End Point	434	
Clear Octane No.,		
Research	92.0	
Motor	82.5	
Aromatics, vol. %	69.0	

Hydrogen Rich Gas and C₁-C₄ Light Hydrocarbon
Stream Analysis:

Component, wt. %	H ₂ Rich Gas	C ₁ -C ₄ Hydrocarbons
H ₂	26.7	—
C ₁	25.0	3.0
C ₂	21.4	13.6
C ₃	17.9	34.9
i-C ₄	5.4	22.7
n-C ₄	3.6	25.8

A comparison of the overall results from the two above Examples indicates that improved gasoline production occurs when low severity reforming operations are employed in conjunction with aromatic separation and saturate cracking operation.

The reforming zone of Example II which was operated at 92.0 RON severity level yielded 21,828 barrels per day (BPD) of C₅ to 434° F. E.P. gasoline on a feed stock of about 25,900 BPD feed rate as seen from Table IV. Other valuable gasoline components recovered from the light hydrocarbons produced by the Example II reforming zone was about 523.5 BPD of isobutane which is an excellent feed material for an alkylation zone which can produce C₃ or C₄ alkylate gasoline having RON ratings of 92.0 and 98.0 respectively, and about 619 BPD of n-butane which adds volume for volume to the gasoline pool at 94 RON and is required to boost the RVP of the pool gasoline.

In comparison, about 16,642 BPD of gasoline was produced directly from the combination reforming-extraction-saturate cracking process as shown in Example I, Table II. The gasoline pool comprised cracked gasoline from the saturate cracking zone, C₅/C₆ gasoline derived directly from the reforming zone and an aromatic concentrate which was also obtained from the reforming zone after the C₇+ gasoline therefrom was solvent extracted to remove its aromatic hydrocarbons prior to the cracking operation. The C₅/C₆ gasoline was found to possess a RON of 71.0, the cracked gasoline possessed a RON of 95.0 and the aromatic rich gasoline from the solvent extraction zone

was 115.0 RON quality. Together the C₅+ gasoline pool from the combination process of this invention totaled 16,642 BPD and had an overall pool RON of 101.6 which is substantially higher than the pool octane of 92.0 obtained from the high severity reforming zone by itself. The cracked gasoline of Example I as shown in Table III, Line no. 18, contained about 20 vol. % aromatics. This stream could be upgraded by recycling a portion of it to an aromatic separation zone to concentrate the aromatic portion of the cracked material and allow the non-aromatic portion to be passed into the saturate cracking zone to allow production of high octane precursor C₃ and C₄ hydrocarbons.

In order, however, to fully appreciate the advantages which accompany the above combination, it is necessary to look to the quantity of the high octane precursors represented by the C₃ and C₄ olefins and the i-C₄ paraffins which are produced in large quantities from the saturate cracking zone by the catalytic cracking of paraffins and naphthenes which are allowed to pass through the reforming zone without molecular structural change via reformation and saturate cracking of the non-aromatics which are recycled to the cracking zone from the recycle stream when it is used. These high octane precursors can be readily alkylated in a suitable alkylation zone to yield alkylate gasoline components possessing RON's of 92.0 and higher depending on whether a C₃ or a C₄ alkylate gasoline is produced. The C₃ olefins, C₄ olefins and C₄ iso-paraffins can also be further reacted by polymerization, hydrolysis or other octane improving processes, yield a gasoline component which improves the overall gasoline pool in octane number and in some instances provides additional volumetric yields of gasoline based on the fresh feed.

The quantity of high octane precursor light hydrocarbons produced by the combination process as indicated in Tables II and III amounted to about 8,359 lb./hr. of isobutane, of which 865 lb./hr. was derived from the reforming zone 15,495 lb./hr. of propylene and 23,001 lb./hr. of butene which was derived from the saturate cracking zone. In order to take advantage of the high octane potential of the light hydrocarbons, they were passed into an alkylation zone to produce C₃ and C₄ alkylate gasoline. Because of the large amounts of propylene and butylene produced, it was required that a certain amount of outside isobutane be used to fully react all of the C₃ and C₄ olefins. A total of about 47,000 lb./hr. or 5,721 BPD of isobutane was consumed in producing the alkylate gasoline; of the 5,721 BPD of isobutane consumed, 4643.6 BPD was required from outside sources. The total gasoline pool composition including alkylate gasolines from the light hydrocarbons produced in the saturate cracking zone is illustrated in Table V below:

TABLE V

GASOLINE POOL	
C ₅ /C ₆ gasoline from 85 RON reforming zone	2827.3 BPD
Aromatic extract from extraction zone	11876.6 BPD
Cracked gasoline from saturate cracking zone	1937.8 BPD
C ₃ alkylate gasoline	3475.6 BPD
C ₄ alkylate gasoline	4742.4 BPD
TOTAL	24859.7 BPD

The overall octane rating of the gasoline pool of Table V was 102.1 RON. The outside isobutane required to

15

alkylate the butene and propylene, because it was additional feedstock, did allow the low severity reforming zone and saturate cracking zone to produce a larger absolute quantity of pool gasoline from the same amount of feed material passed into the reforming zone.

The liquid yield of C₅+ gasoline produced, including the C₃ and C₄ alkylate gasoline based on the reforming zone feed plus the outside isobutane required, was found to be 24,859.7 BPD of C₅+ gasoline/(25,899.7 BPD of reforming zone feed + 4643.6 BPD of outside isobutane) = 81.4 liquid volume percent or 81.4 barrels of 102.1 RON gasoline produced per 100 total barrels of feed to the combination process.

The high severity reforming zone gasoline yield was calculated taking account of the isobutane produced by that reformer as being converted to a C₄ alkylate gasoline. The 92.0 RON reforming zone produced only isobutane light hydrocarbons which were potentially alkylatable and consequently to take advantage of this high octane precursor outside butene was used in such quantity to convert all of the isobutane from this reforming zone to C₄ alkylate gasoline. The outside butylene was chosen to allow production of the high octane C₄ alkylate. Table VI shows the total gasoline pool produced by the high severity reforming zone.

TABLE VI

GASOLINE POOL	
C ₅ + reformat	21,828 BPD
C ₄ alkylate gasoline	964 BPD
TOTAL	22,792 BPD
Reforming zone feed	25,900 BPD
Outside butene required to alkylate i-C ₄	535 BPD
TOTAL	26,435 BPD

The overall pool gasoline octane rating of the above gasoline which included the C₄ alkylate produced from the isobutane was 92.3 RON. The increase in octane was due to the addition of the 98 RON C₄ alkylate gasoline component to the pool gasoline. The liquid volume yield of gasoline based on the reforming zone feed + the outside butene needed to alkylate the isobutane was 22,792 BPD of C₅+ gasoline/(25,900 BPD of reforming zone feed + 535 BPD of outside butene) = 86.2% or 86.2 barrels of 92.3 RON gasoline per 100 barrels of total feed used.

While the yield on total feed (reformer feed + outside butene or isobutane) for the 92.0 RON reformer was 86.2 liquid volume (L.V.) percent as compared to the yield of 81.4 L.V. % for the low severity reformer-saturate cracking zone combination, the combination process of this invention produced a substantially higher gasoline octane pool than the 92.0 reforming zone (102.1 versus 92.3).

EXAMPLE III

In this example, a reforming catalyst similar to the catalyst used in the previous examples was employed. The reforming zone was operated at conventional conditions to effect production of a C₅+ reformat having a 102.0 RON from a reformer feed stock identical to the feed stock used previously. The charge rate of material to the reforming zone was identical to the charge rate used in Examples I and II. The isobutane recovered from the C₁-C₄ light hydrocarbon was alkylated with outside butene to produce C₄ alkylate gasoline. Table VII below indicates the results of this experiment.

16

TABLE VII

C ₅ + reformat	18,740 BPD
C ₄ alkylate gasoline	2,266 BPD
TOTAL	21,006 BPD
Reforming zone feed	25,899.7 BPD
Outside butene required to alkylate i-C ₄	1,312.0 BPD
TOTAL	27,211.7 BPD

The overall RON of the above gasoline pool which comprised both C₅+ reformat and C₄ alkylate gasoline was about 101.6. The overall yield on the basis of the total fresh feed including reformat feed + butene required to alkylate the isobutane recovered from the reforming zone in the C₁-C₄ light hydrocarbon stream was about 77.3 L.V. % versus 81.4 for the combination of low severity reforming, aromatics separation and saturate cracking. It can be seen that in attempting to produce the higher octane reformat gasolines that reforming alone inherently creates volumetric losses greater than those of the combination disclosed.

EXAMPLE IV

In this example a saturate cracking zone was operated using a saturate rich feed which resembled the composition of a feed stock that would be expected from the aromatic separation zone after a large portion of the aromatics had been removed from a low severity reforming effluent stream. The feed stock inspection is shown in Table VIII below:

TABLE VIII

Saturate Cracking Zone Feedstock

Distillation:	
10 vol. %	210° F.
50 vol. %	270° F.
90 vol. %	320° F.
Mass Spectrometric Analysis:	
Paraffins	65 vol. %
Cycloparaffins	22 vol. %
Aromatics	13 vol. %

The cracking zone was made up of an elongated reactor in which 20-40 mesh particle size pellets comprising an amorphous silica-alumina cracking catalyst was placed. The reaction zone was maintained at about 1,050° F. and at about atmospheric pressure. The ratio of the volumetric feed rate over the catalyst volume in the reaction zone (LHSV) was maintained at about 0.5. The operations were continued to a catalyst life of 2 volumes of fresh feed passed over the catalyst per volume of catalyst in the reaction zone.

Analysis of the products of reaction were collected and analyzed. The product distribution of the effluent material is shown in Table IX below:

TABLE IX

Cracking Zone Feed Yields

Hydrogen	1.0 wt. %
C ₁	4.3 wt. %
C ₂	2.4 wt. %
C ₂ olefins	2.3 wt. %
C ₃ paraffins	5.3 wt. %
C ₃ olefins	8.0 wt. %
n-C ₄ paraffins	1.9 wt. %
i-C ₄ paraffins	5.6 wt. %
C ₄ olefins	6.1 wt. %
n-C ₅ paraffins	0.8 wt. %
i-C ₅ paraffins	3.4 wt. %
C ₅ olefins	2.4 wt. %
C ₆ and heavier	50.9 wt. %
Aromatics, total	20.0 wt. %
Aromatics, net	7.2 wt. %
Coke	5.6 wt. %

From the above product distribution it can be seen that on a once through operation that there is a net production of aromatics of about 7.2 wt.% based on the fresh feed. In instances in which a portion of the product material from the saturate cracking zone is to be recycled to the cracking zone to further effect the production of C₃ and C₄ olefins, the aromatics produced from the cracking reaction zone will pass through that zone without being reacted because of their generally highly refractory properties.

Depending on the ratio of cracked product withdrawn from the process over the cracked product recycled to the reaction zone, there is a possibility of an aromatic build up in the recycle stream. The process of my invention contemplates this problem and requires that a portion of the recycle material from the saturate cracking zone be passed into the aromatic separation zone in order to remove a portion or substantially all of the aromatics present in the recycle stream passed into the aromatic separation zone.

In referring to the attached drawing, the process of this invention can be operated in a specific manner by varying the ratio of recycle material passed to the aromatic separation zone via line 16 over the recycle material passed directly to the cracking zone 4 via line 17 from about (all recycle material going through the aromatic separation zone 3) down to a minimum ratio necessary to prevent a large aromatic build up in the recycle loop.

The above examples are intended to illustrate certain specific embodiments of the claimed invention and are not to be considered as undue limitations on the scope of the claimed matter.

EMBODIMENTS

A broad embodiment of the process of my invention resides in a process in which a naphtha material is passed into a low severity reforming zone at conditions to effect the production of aromatics with a portion of the saturates passing into the reforming zone leaving that zone unreacted; passing a portion of the reforming zone effluent to an aromatic separation zone wherein aromatic and non-aromatic materials are concentrated into separate streams; passing a portion of the non-aromatics concentrated in the aromatic separation zone to a saturate cracking zone to effect the production of light hydrocarbons and a heavy cracked material; recycling a portion of the heavy cracked material to an aromatic separation zone to effect the separation of aromatics and non-aromatics in the recycle material; and passing the non-aromatics along with the non-aromatics from the reforming zone to the saturate cracking zone.

I claim as my invention:

1. A process for the production of high octane gasoline from a naphtha feed which comprises the steps of:

- i. converting at least a portion of a naphtha fraction boiling within the range of from about 50° F. to about 425° F. in a reforming zone at relatively low severity reforming conditions to produce a gasoline reformat containing aromatic and saturated hydrocarbons;
- ii. separating at least a portion of said gasoline reformat into an aromatic portion and a non-aromatic portion containing saturates;
- iii. recovering said aromatic portion of said reformat;

iv. passing at least a portion of said non-aromatic portion of said reformat into a saturate cracking zone and cracking said non-aromatic portion at conditions to effect the production of saturated and unsaturated light hydrocarbons of from about two to about five carbon atoms per molecule and a heavy cracked product boiling within the range of from about 100° to 430° F. and containing aromatics;

v. recovering said saturate and unsaturated light hydrocarbons;

vi. separating at least an aliquot portion of said heavy cracked product into an aromatic portion and a non-aromatic portion; and

vii. recycling at least a portion of said non-aromatic portion to the saturate cracking zone.

2. The process of claim 1 further characterized in that said reformat is separated by passage into an aromatic separation zone which effects said separation of non-aromatic and aromatic hydrocarbons by solvent extraction means.

3. The process of claim 1 further characterized in that said reformat is separated by passage into an aromatic separation zone which effects said separation of non-aromatic and aromatic hydrocarbons by adsorptive-separation means.

4. The process of claim 1 further characterized in that at least a portion of said saturate and unsaturated light hydrocarbons are converted into a gasoline component.

5. The process of claim 1 further characterized in that said saturate cracking zone effects the catalytic cracking of said non-aromatics.

6. The process of claim 1 further characterized in that said saturate cracking zone effects the thermal cracking of said non-aromatics.

7. The process of claim 1 further characterized in that said gasoline reformat and said heavy cracked product are separated into aromatic and non-aromatic portions by passage into a single aromatic separation zone.

8. The process of claim 7 further characterized in that said aromatic separation zone is a solvent extraction zone.

9. The process of claim 7 further characterized in that said aromatic separation zone is an adsorptive separation zone.

10. A process for the production of high octane gasoline from a naphtha feed which comprises the steps of:

- i. converting at least a portion of a naphtha fraction boiling within the range of from about 50° F. to about 425° F. in a reforming zone at relatively low severity reforming conditions to produce a gasoline reformat containing aromatic and saturated hydrocarbons;
- ii. passing at least a portion of said gasoline reformat together with a first cracked recycle stream to an aromatic separation zone wherein there is effected a concentration of said reformat and cracked streams into an aromatic stream and a non-aromatic stream;
- iii. recovering said aromatic stream;
- iv. passing at least a portion of said non-aromatic stream along with a second cracked recycle stream into a saturate cracking zone to effect the production of saturated and unsaturated light hydrocarbons of from about two to about five carbon atoms and a heavy cracked product boiling within the

19

- range of from about 100° to 430° F. and containing aromatics;
- v. recovering said saturated and unsaturated light hydrocarbons;
 - vi. recycling an aliquot portion of said heavy cracked product to said aromatic separation zone as said first cracked recycle stream; and
 - vii. recycling an aliquot portion of said cracked

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product directly to said saturate cracking zone as said second cracked recycle stream.

11. The process of claim 10 further characterized in that said non-aromatic stream contains paraffins and cycloparaffins having from about three to about ten carbon atoms per molecule.

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