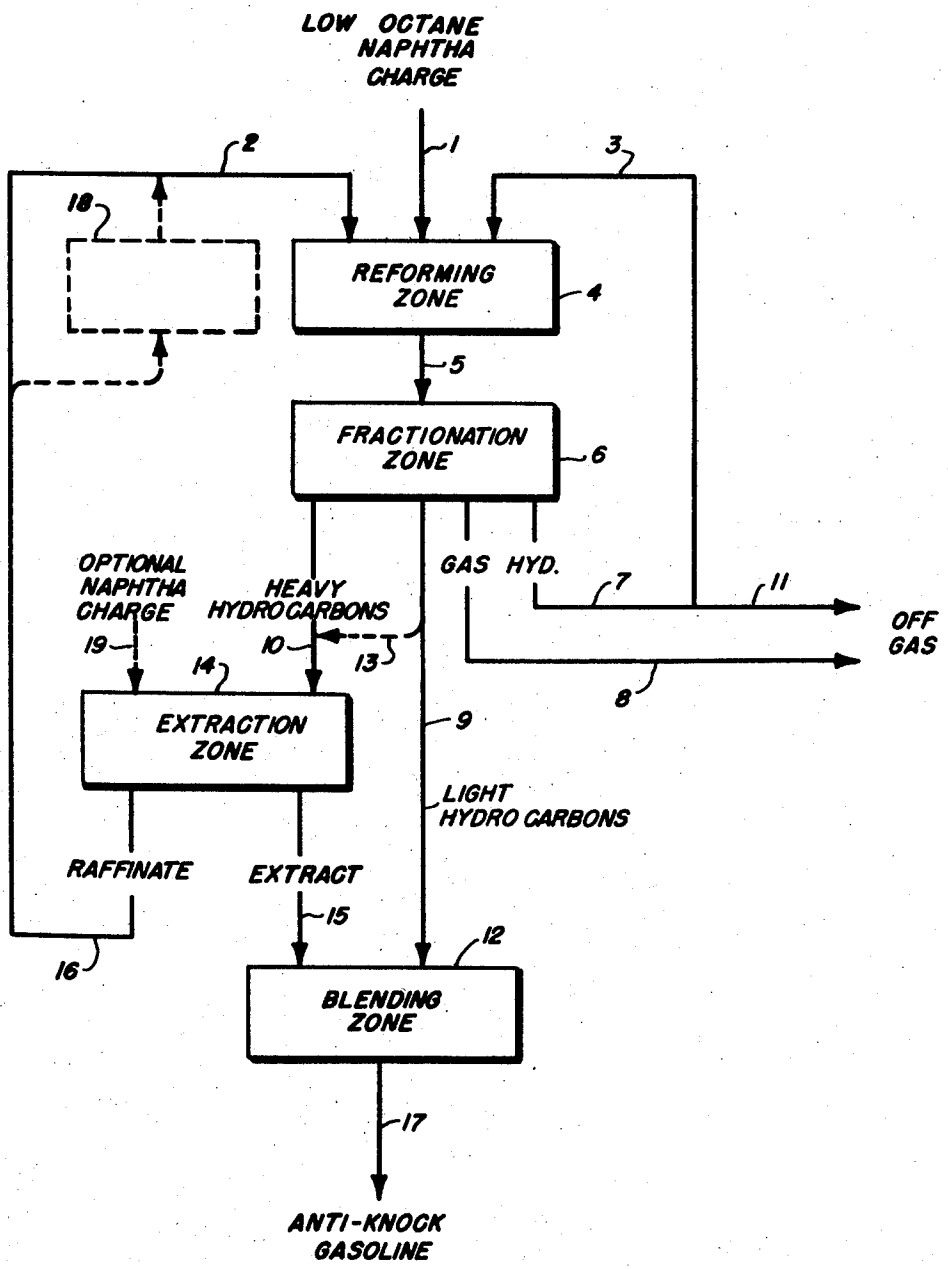
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MANUFACTURE OF ANTI-KNOCK GASOLINE

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MANUFACTURE OF ANTI-KNOCK GASOLINE

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1 Claim. (Cl. 208—96)

This invention relates to the catalytic reforming of naphtha fractions to produce gasoline constituents of high anti-knock quality. More particularly, it relates to a combination of catalytic reforming and separation processes whereby a greater yield of high quality product is obtained than can be achieved by catalytic reforming alone.

Progress in the automotive industry has resulted in the development of gasoline engines of higher and higher compression pressures, requiring gasoline fuels with correspondingly higher anti-knock properties or "octane rating." To meet this demand, the petroleum industry has developed various processes for producing gasoline of increased octane rating. One of the more efficient of such processes is catalytic reforming wherein low-octane naphtha is contacted in the vapor-phase with suitable catalyst at temperatures above 800° F., in the presence of substantial volumes of hydrogen. A common type of catalyst used for catalytic reforming is platinum supported on a carrier of alumina and/or silica. Several such platinum catalysts are marketed which will produce good yields of 85 to 90 "research" octane number (ASTM Method D908–53) reformate under operating conditions sufficiently mild that the catalyst can be used for extended periods of time without "regeneration" to remove carbon formed by undesirable cracking reactions.

More recent developments in the automotive industry have created a need for gasoline having a research octane number substantially above 90 (before the addition of tetra-ethyl lead or other anti-knock compound) and preferably above 96. To meet this requirement by catalytic reforming processes now in use, it is necessary to increase the severity of operating conditions to an extent that a substantial amount of hydro-cracking occurs with concomitant decrease in naphtha yield, increased equipment and operating cost to regenerate the catalyst (by burning off the carbon formed) and increased cost for a suitable catalyst capable of tolerating frequent regeneration without a prohibitive amount of deterioration.

In accordance with the present invention, by the use of certain separation processes in combination with catalytic reforming under mild conditions, a higher yield of usable components for a 96 to 98 (or higher) octane gasoline can be obtained, than can be produced by catalytic reforming alone under conditions severe enough to produce the same anti-knock quality.

Broadly, the invention comprises catalytically reforming a naphtha of low anti-knock quality, separating from the reformate a concentrate containing most of the aromatics therein, and returning the remaining predominately paraffinic portion of the reformate to the reforming step for further conversion. Concentration of the aromatics may be by any suitable process, such as for example, by use of silica gel; by extractive distillation in the presence of phenol, cresylic acids, sulfolanes or glycol-water mixtures; or by solvent extraction (e.g. with liquid sulfur dioxide). The low anti-knock naphtha fed to the process may be a virgin naphtha or it may be a fraction

produced from other refining processes such as hydrodesulfurization. In a particular form of the invention, the naphtha feed is first combined with reformate previously produced, and the mixture subjected to the separation step, thereby removing aromatics which may be contained in the feed prior to subjecting the remainder to reforming and, likewise, increasing the efficiency of the separation step by decreasing the percentage of aromatics in the total fraction subjected to the separation. In a specific form of the invention, low-boiling, predominately isoparaffinic hydrocarbons are removed by fractionation from the reformate prior to the separation step and are combined with the aromatic concentrate to produce a mixture of increased value in gasoline blending.

The invention may be more readily understood by reference to the drawing which is a diagrammatic flow diagram of the process. Naphtha in line 1, together with raffinate in line 2, and recycle hydrogen in line 3 is charged to catalytic reforming zone 4, wherein the mixture of hydrocarbons and hydrogen is passed in the vapor phase through a bed of reforming catalyst at temperatures in excess of 800° F. and at conditions of pressure, time and hydrogen concentration, to convert a substantial amount of the paraffinic charge to aromatic hydrocarbons with concomitant isomerization of other paraffinic constituents and production of hydrogen and certain low-boiling hydrocarbons. As is well known to the art, increased time and temperature and reduced pressures in catalytic reforming tend to increase cracking reactions with resulting formation of larger quantities of normally gaseous hydrocarbons and carbon. In accordance with the present invention, the conditions in zone 4 are maintained sufficiently moderate to permit treatment of at least 30 barrels of naphtha per pound of catalyst (and preferably more) without regeneration or replacement of catalyst. While such conditions vary with the naphtha treated and with the particular catalyst used, those conversant with catalytic reforming can readily select suitable conditions.

The effluent from the catalytic reforming zone 4, comprising hydrogen, normally gaseous hydrocarbons, and normally liquid aromatic and paraffinic hydrocarbons, is discharged through line 5 into fractionating zone 6 which includes suitable traps, stills, absorption equipment and the like to fractionate the effluent into (1) a hydrogen fraction containing upwards of about 70% hydrogen, shown as leaving zone 6 through line 7; (2) a gas fraction composed principally of the C_1 to C_3 hydrocarbons formed in zone 4, but which may also contain some hydrogen and any excess C_4 not usable in the finished gasoline, shown as leaving through line 8; (3) a light hydrocarbon fraction (line 9) composed mainly of hydrocarbons boiling below about 200° F.; and (4) heavy hydrocarbons, boiling above about 200° F., which leave through line 10.

Part of the hydrogen fraction in line 7 is recycled to the reforming zone 4 through line 3 to maintain required ratio of hydrogen therein in accordance with known principles. If desired, such hydrogen fraction may be treated to remove hydrogen sulfide or other unwanted impurities prior to entry into zone 4. The remainder of the hydrogen fraction in line 7 is passed through line 11 for any desired disposal. Likewise, the gas fraction in line 8 is disposed of as desired.

Due to the nature of catalytic reforming, the light hydrocarbons in line 9 contain high percentages of isoparaffins of very high anti-knock value. In a preferred form of the invention, these are passed directly to blending zone 12 to be included in the finished gasoline. However, if desired, any or all of the hydrocarbons in line 9 may be mixed with the heavy hydrocarbons in line 10

to be treated therewith, as illustrated in the drawing by dotted line 13.

The heavy hydrocarbons in line 10, together with any desired hydrocarbons from line 9, are charged to extraction zone 14. In extraction zone 14, the hydrocarbons are separated into an extract (composed predominately of aromatic hydrocarbons, shown as leaving through line 15) and raffinate (composed of predominately paraffinic hydrocarboons, shown as leaving through line 16). As indicated prior, any one of the various well-known methods for separating aromatic from paraffinic hydrocarbons may be used for the separation in extraction zone 14. Extraction with liquid sulfur dioxide has proven suitable, and will be used elsewhere herein for illustration.

The extract in line 15 is passed to blending zone 12 where it is blended with light hydrocarbons from line 9 to form anti-knock gasoline shown as leaving zone 12 through line 17. If desired, ingredients from other sources may be added in zone 12 for augmenting the quantity, correcting the volatility, or further improving the octane number.

The raffinate in line 16 is returned through line 2 to reforming zone 4 for further treatment. It is thus seen that the raffinate is treated to extinction, with the products of the process being a predominately aromatic gasoline and gas. Due to the repeated recycling of the raffinate, portions thereof recycled several times may prove somewhat more refractory to catalytic reforming than the original charge. In such cases it may be desirable to charge the raffinate first to an auxiliary reforming zone (indicated in the drawing as 18) prior to entering zone 4, thus giving the raffinate more reforming treatment than the naphtha charge. The conditions in the auxiliary zone 18 may be milder, the same as, or somewhat more severe than those in zone 4. The preliminary treatment of the raffinate, such as in zone 18, is the subject of and claimed in copending application of Ammer and Viland, filed March 27, 1956, Serial No. 574,295.

In certain cases, particularly when the naphtha charged to the process contains appreciable quantities of anti-knock constituents extractable by the method employed in zone 14, or when the aromatic content of the heavy hydrocarbons in line 10 is so high as to render difficult the operations in zone 14, it may be desirable to introduce part or all of the fresh naphtha charge to zone 14 (as shown by dotted line 19) instead of through line 1. With this modification of the invention, the aromatics in the naphtha charge will pass directly to the finished gasoline without being subjected to reforming conditions, and the paraffinic portions of the naphtha charge will reduce the percentage of aromatics in the total charge to zone 14 facilitating separation in some instances.

To further illustrate the invention, the following examples of operations under typical conditions are presented:

EXAMPLE 1

Six thousand four hundred barrels per day of naphtha obtained from the hydrodesulfurization of mixed refinery stocks together with 3,600 barrels per day of raffinate obtained from a later stage of the process are catalytically reformed over a typical platinum-on-alumina reforming catalyst under mild (non-regenerative) conditions. Hydrogen to maintain desired hydrogen to hydrocarbon ratio during the reforming is obtained by recycling hydrogen produced during the reforming reaction. The effluent from the reforming is cooled and passed to a high pressure gas separator from which a hydrogen stream of about 90% purity is withdrawn, part of which stream supplies the recycle hydrogen and the remainder (representing the major part of the hydrogen produced by the reforming reaction) is diverted to other uses.

The liquid hydrocarbons from the high pressure separator are stabilized at lower pressure to produce a gas stream composed of propane and lighter hydrocarbons, a butanes stream, and a debutanized "reformate" stream containing about 45% aromatic hydrocarbons. This reformate is extracted by countercurrent extraction with liquid sulfur dioxide at −25° F. to give 3,600 barrels per day of the recycle raffinate analyzing about 15% aromatics and an extract stream of 5,250 barrels per day of debutanized, highly aromatic blending stocks having a research octane number of 98, suitable for use as the major constituent of high anti-knock gasoline or for other blending purposes as desired (either with or without the addition of part or all of the butanes stream). Table 1 shows additional data relating to this example.

Table 1

Reformer operating conditions:	
Reactor temperature, ° F.	900–910
Reactor pressure, p.s.i.g.	500
Space velocity (ratio liquid volume of charge per hour to gross volume catalyst)	3.0
Hydrogen ratio, mol. H_2/mol. H.C.	5.5
Catalyst life, days	150
Reformer charge:	
Fresh naphtha, bbls./day	6,400
Recycle raffinate, bbls./day	3,600
Total, bbls./day	10,000
Reformer yields:	
Hydrogen fraction (net), M c.f./day	10,000
Dry gas fraction, M c.f./day	1,000
Butanes, bbls./day	600
Debutanized reformate, bbls./day	8,850
Extraction conditions:	
Volume SO_2 per volume reformate	1.25
Temperature, ° F.	−25
Extraction yields:	
Raffinate, bbls./day	3,600
Extract, bbls./day	5,250
Overall processing yields:	
Butanes, percent of fresh naptha charge	9.4
Extract, percent of fresh naphtha charge	82.0
Yield of blending components	91.4
Octane No. extract (ASTM D-908–53)	98+
Octane No. extract plus butanes	98+

The properties of the various stocks made in Example 1 are shown in Table 2.

Table 2

	Naphtha Charge	Hydrogen Fraction	Dry Gas	Reformate	Raffinate	Extract
Hydrogen, percent		90	15			
Methane, percent		10	4			
C_2 and C_3, percent		trace	80			
ASTM Distillation, ° F.:						
10%	220			230	225	240
50%	260			265	270	260
90%	335			340	350	335
Aromatic Content, Percent	13			45	15	65+

Table 3 shows typical results obtained when treating the same fresh naphtha charge by reforming alone (*a*) at the same operating conditions as shown in Table 1 and (*b*) at operating conditions sufficiently sever to yield about 98 octane number debutanized reformate.

Table 3

	Mild	Severe
Operating Conditions:		
Reactor Temperature, ° F.	900–910	950–960
Reactor Pressure, p.s.i.g.	500	225
Space Velocity, LHV	3.0	1.5
Hydrogen Recycle Ratio	5.5	10
Catalyst Life, days	150	50
Fresh Naphtha Charge, bbls./day	10,000	5,000
Yield Butanes, bbls./day	670	500
Yield Debutanized Reformate, bbls./day	8,230	3,880
Yield Debutanized Reformate, Percent	82.3	77.6
Octane No. Debutanized Reformate	86	97.8
Yield Hydrogen Fraction (net) M c.f./day	10,000	4,000
H_2 in Hydrogen Fraction, Percent	90	80

EXAMPLE 2

Ten thousand barrels per day of raffinate, obtained from a later stage of the process, are catalytically reformed over the same type of platinum catalyst and with similar operating conditions as in Example 1. The effluent from the reforming is fractionated in a manner similar to Example 1 to obtain a hydrogen stream, a dry gas stream of propane and lighter hydrocarbons, a butanes stream, and a debutanized reformate stream. The debutanized reformate stream is further fractionated to remove a 10% light cut composed chiefly of (predominately isoparaffinic) pentanes and hexanes, leaving a 90% heavy cut containing the aromatic hydrocarbons produced in the reforming reaction.

The heavy cut, which may have a volume of about 8,000 barrels per day and may analyze about 50% aromatics, is combined with 8,000 barrels per day of fresh naphtha charge to the process. The fresh naphtha selected for this example is a 200° to 400° F. boiling range straight-run naphtha distilled from California crude and analyzing about 15% aromatics. The mixture of heavy cut and fresh naphtha charge, now analyzing about 30 to 35% aromatics, is countercurrently extracted at —25° F. with liquid sulfur dioxide to give 10,000 barrels per day of recycle raffinate (constituting the charge to the reformer) and 6,000 barrels per day of blending stock having an aromatic content of about 70%. This blending stock may be blended as desired wtih gasoline components from other sources to enhance their anti-knock value. However, preferably, this blending stock is combined with the 10% light cut previously mentioned to obtain a maximum yield of high octane gasoline, to which is added sufficient of the butanes stream to meet seasonal volatility requirements.

Table 4 shows additional data relating to this example.

Table 4

Reformer operating conditions:	
Reactor temperature, ° F.	900
Reactor pressure, p.s.i.g.	500
Space velocity, LHV	3.0
Hydrogen ratio, H_2/H.C.	5.5
Catalyst life, days	150
Reformer charge: Recycle raffinate, bbl./day	10,000
Reformer yields:	
Hydrogen fraction (net) M. c.f./day	9,500
Dry gas fraction, M c.f./day	950
Butanes, bbl./day	600
Light reformate cut, bbl./day	850
Heavy reformate cut, bbl./day	8,000
Extraction conditions:	
Volume SO_2 per volume hydrocarbons	1.25
Temperature, ° F.	—25

Extraction charge:	
Fresh naphtha charge, bbl./day	8,000
Heavy reformate cut, bbl./day	8,000
Total	16,000
Extraction yields:	
Raffinate, bbl./day	10,000
Extract, bbl./day	6,000
Overall processing yields:	
Light reformate cut, percent fresh naphtha charge	10.6
Extract, percent of fresh naphtha charge	75.0
Butane-free components, percent	85.6
Butanes, percent of fresh naphtha charge	7.5
Total blending components	93.1
Octane No. extract	98+
Octane No. extract plus light cut	97
Octane No. extract plus light cut plus butanes	98

As illustrated in the foregoing examples, it is evident that greatly increased yields of high octane gasoline components may be made by the combination of aromatic concentration with catalytic reforming, over yields obtainable by catalytic reforming alone. The examples, however, are given to illustrate the processing steps and yields obtainable, and are not to be considered as limiting the invention in its broadest scope. As aforementioned, the invention, broadly, contemplates the use of any catalytic reforming method conducted in the presence of hydrogen wherein substantial quantities of aromatics are produced, and any method for concentrating the aromatics produced to obtain a predominately aromatic and a predominately paraffinic fraction.

I claim:

A process for producing highly aromatic anti-knock gasoline components, which comprises: passing a continuous stream of predominately paraffinic hydrocarbon naphtha vapors and hydrogen through a bed of reforming catalyst under conditions to convert a substantial portion of said naphtha to aromatic hydrocarbons and additional hydrogen without substantial deposition of carbon on said catalyst, fractionating the resulting products into a gas fraction, a light hydrocarbon fraction composed predominately of isoparaffinic hydrocarbons of from 4 to 6 carbon atoms and boiling below about 200° F. and a heavy hydrocarbon reformate fraction boiling above 200° F., separating said gas fraction and said light hydrocarbon fraction from said heavy hydrocarbon reformate fraction, combining said latter reformate fraction with fresh, predominately paraffinic naphtha of the type initially charged to the process, solvent extracting said reformate fraction-fresh naphtha mixture to produce a predominately aromatic gasoline extract and a predominately heavy paraffinic raffinte, recycling the raffinate to said catalyst bed as part of said hydrocarbon naphtha vapor feed, and blending at least part of said light hydrocarbon fraction with said aromatic gasoline extract.

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