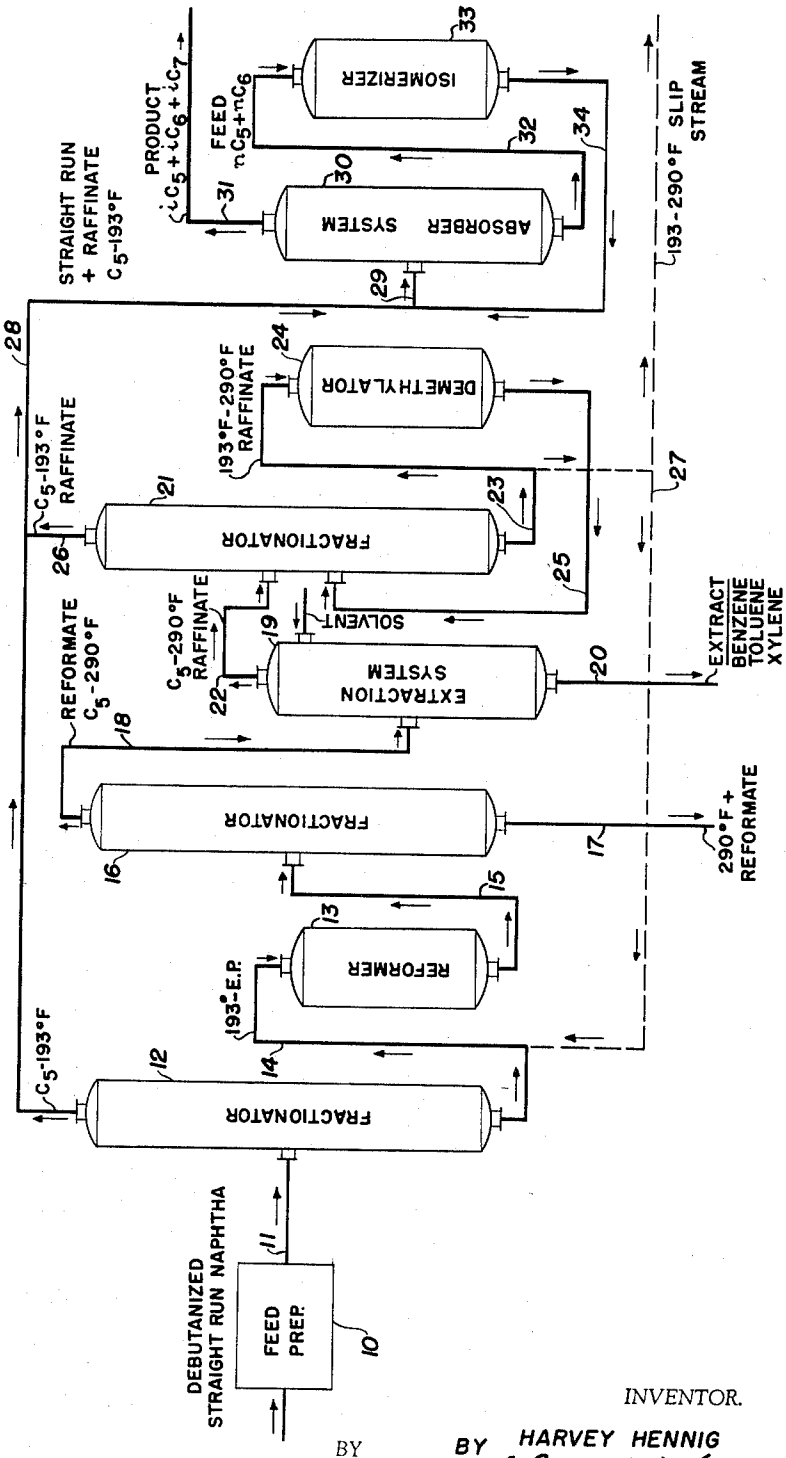
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PROCESS FOR IMPROVING THE OCTANE NUMBER OF NAPHTHAS

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PROCESS FOR IMPROVING THE OCTANE NUMBER OF NAPHTHAS

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This invention relates to the processing of full-boiling-range, straight-run gasolines to produce high-octane-number blending stocks. It is more specifically concerned with the integration of a plurality of unit petroleum refining processes to provide a combination operation for the upgrading of straight-run gasoline.

According to this invention, the unit processes of catalytic refining, catalytic demethylation and catalytic hydroisomerization are combined with adjunct fractionation processes, including solvent refining, adsorption and thermal fractional distillation, to provide an integrated scheme for the efficient upgrading of straight-run gasolines to produce high yields of a high-octane-number blending stock.

Motor fuels required for the efficient operation of modern high-output, high-speed, spark-ignited, internal combustion engines are high-octane-number formulations produced by blending a number of selected blending stocks. Quality as well as progressive competitors have necessitated that refiners of petroleum products evaluate the inter-relation of existing refining processes and make appropriate changes to meet the exigencies of the situation. In processing normally liquid hydrocarbons boiling in the gasoline range, reforming has played an important part. When straight-run gasolines are used as feed stocks, constituents such as the low-boiling saturated hydrocarbons are not efficiently processed for maximum improvement in octane number. It is more desirable in processing these straight-run gasolines to high octane levels to use several processes designed to be more selective to a specific reaction among the number of reactions occurring in conventional reforming.

It is, therefore, the primary object of this invention to provide a combination of processes centering around reforming for octane-number improvement of straight-run gasolines. It is another object of this invention to provide a combination of conventional refining processes integrated to produce high-octane-number blending stocks from straight-run gasoline. These and other objects will become more apparent from the following detailed description of this invention.

The single figure shows a simplified flow sheet of the process of this invention.

It is known that full-boiling-range, straight-run gasolines contain normal and branch-chain paraffins, naphthenes, and aromatics. Of these major types of constituents, the branch-chain paraffinic hydrocarbons and aromatics, in general, have relatively high octane numbers and are suitable for direct use in motor fuel. Naphthenes, even though they have intermediate octane numbers, can be converted to relatively high octane number aromatics by

reforming, thereby increasing the octane number of a refinery gasoline pool. The low-boiling, straight-chain paraffins (pentane, hexane and heptane) can be converted to branch-chain paraffins which have relatively high octane numbers. However, octane, nonane, and other heavy straight-chain paraffins are not satisfactory for these isomerization processes. Even the isomerization of n-heptane will be marginal in some instances. While it is possible to hydrocrack these heavier straight-chain paraffinic hydrocarbons in reforming operations, conditions must be so severe that large losses as gas and coke result. Accordingly, this approach is undesirable, even though commercially practiced. According to this invention, a process for the efficient conversion of full-boiling, straight-run gasolines to high-octane blending stocks at exceptionally high yield has been developed.

Referring to the simplified flow diagram in the single figure, obvious auxiliary equipment such as valves, pumps, heat exchangers, etc., have been omitted for simplicity. Also, major process steps are shown schematically. In the process of this invention, debutanized, straight-run gasoline having a true end-point within the range of 370° to 420° F., having been desulfurized in a conventional manner in feed preparation unit **10**, enters through line **11** and is distilled in fractionator **12** into light and heavy fractions. The heavy fraction has a true boiling range of 193° F. to 370–420° F., contains naphthenes, some aromatics and heavy paraffinic hydrocarbons, and flows to catalytic reformer **13** through line **14**. Reformer **13** is operated at conditions such that the naphthenes are substantially dehydrogenated, and thereby converted to aromatic hydrocarbons, and part of the heavy paraffins are hydrocracked. Conditions, however, are maintained at a mild conversion level so that the gas and coke make are minimized and high yields are obtained.

Effluent from catalytic reformer **13**, after being freed of hydrogen gas and debutanized by suitable means not shown, is conducted through line **15** to raffinate fractionator **16**. This tower divides the stream into heavy and light fractions, the heavy, predominantly aromatic fractions boiling above about 290° F. being withdrawn as product through line **17**. The light reformate, containing pentanes, benzene, toluene, xylenes, branch-chain and straight-chain paraffinic hydrocarbons boiling below about 290° F., and small amounts of naphthenes, is withdrawn from fractionator **16** through line **18** to solvent extraction system **19**. In this solvent extraction system, the aromatics are extracted from the light reformate and after separation from the solvent, they are withdrawn as product through line **20**. Raffinate from extraction system **19** is conducted to raffinate fractionator **21** through line **22**. In raffinate fractionator **21** a separation is made between the high-octane isoheptanes (e.g., dimethyl pentanes) and lighter components, and low-octane isoheptanes (e.g., methyl hexanes) and heavier components. The heavier fraction is withdrawn from the bottom of extraction tower **21** through line **23**, to demethylation reactor **24**. In this reactor terminal methyl groups are selectively removed from the heavy paraffin molecules and some ring-breaking and demethylation of the smaller amounts of heavier naphthenes present takes place. Upon being returned to raffinate fractionator **21** through line **25**, those components that have been demethylated sufficiently to form high-octane (lower boiling) dimethyl pentanes, isohexanes, or lighter materials,

are separated and taken overhead with the lighter components of the raffinate through line **26**. Those materials that are still heavier than desired are recycled through the demethylation reactor until they have become volatile enough to boil below about 193° F. If the naphthenes passing through the demethylation unit are of such a character that they do not readily thermally decompose to form paraffins, a small slip-stream, such as that indicated by broken line **27**, is provided for recycling these naphthenes to reformer **13**.

The overhead stream from raffinate fractionator **21** containing only paraffinic and naphthenic compounds boiling below 193° F. joins with the overhead from naphtha fractionator **12**, flowing through line **28**, to form stream **29** which passes to system **30** for separating branched-chain paraffinic hydrocarbons. In this system, normal paraffins are selectively removed from the stream, leaving only isomeric paraffins and light naphthenes to pass overhead through line **31**. These materials are removed as product. The straight-chain paraffinic hydrocarbons are passed through line **32** to catalytic isomerization reactor **33** where they are partially converted to branch-chain paraffins. The effluent from this reactor is returned to separation system **30** via line **34**, the branch-chain paraffinic hydrocarbons are removed as product, and the straight-chain paraffinic hydrocarbons are recycled to isomerization reactor **33**. Accordingly, the straight-chain paraffinic hydrocarbons are recycled to extinction. Product streams **17**, **20** and **31** may be combined to form a high-octane-number blending stock, or parts of the streams may be employed for selective blending of motor fuels.

In order to effectuate the objectives of this invention, each of the component unit processes must perform a specific function. In order to function compatibly in the interrelated process, each unit process must be operated within a specific range of operating conditions as set forth in the following detailed discussion of each phase of the combination process of this invention. The function of the catalytic reforming section is to achieve maximum aromatization of the heavy naphtha fraction with a minimum of hydrocracking of octane and lighter paraffin hydrocarbons. Because of the superior yield-conversion relationship that is obtained employing platinum or palladium catalysts, this reforming phase is carried out in the presence of a reforming catalyst comprising platinum or palladium supported on alumina, or on a siliceous cracking catalyst. Catalysts of this type are well known in the prior art and contain about 0.1 to 1.0% by weight of platinum or palladium on the selected support. Complete descriptions of such catalysts are contained in a number of U.S. patents, e.g., 2,478,916; 2,479,109; 2,550,531; 2,589,189; 2,705,329; and others. If desired, the catalysts can have a combined halogen (0.1–0.8% of fluorine or chlorine based on the support) incorporated therein.

These catalysts can be prepared in accordance with conventional techniques by impregnating the selected support, e.g., alumina, silica-alumina, silica-zirconia, silica-alumina-zirconia, etc., with an aqueous solution of chloroplatinic acid or chloropalladic acid, or with an aqueous solution of the ammonium salts of these acids. The impregnated support is dried at about 210°–250° F. and reduced in a hydrogen atmosphere at a temperature within the range of about 200°–250° F. (cf. Industrial and Engineering Chemistry, 45, 147, 1953). Operating conditions for carrying out the reforming steps are selected for producing optimum aromatization. Accordingly, the following conditions are employed:

Temperature	900–930° F.
Pressure	250–350 p.s.i.g.
Space velocity	1–2 liquid rate hourly space velocity.
Hydrogen rate	4500–7000 ft.³/barrel of feed stock.

The solvent extraction process for the recovery of aromatic hydrocarbons, including benzene, toluene and xylene, from the C_5-290° F. fraction obtained from the reformate is employed because conventional distillation cannot be used since aromatic and certain non-aromatic hydrocarbons tend to form azeotropes. The solvent used must have a high solubility for aromatics, combined with good selectivity. It must be stable at the operating temperature employed and preferably has a high boiling point to permit the distillation of the aromatic hydrocarbons therefrom. The latter characteristic greatly reduces utility requirements. Specific solvents include glycols, polyglycols and acyl derivatives, etc., such as diethylene glycol and triethylene glycol, phenol, nitrobenzene, furfural, Chlorex and others. In addition, mixed solvents, such as those having the foregoing characteristics discused by Kalichevsky, ACS Monograph #76, Reinhold, can also be employed. Preferably, diethylene and triethylene glycols are utilized. In accordance with conventional practice, it is preferred to employ sufficient amounts of water to permit adjusting the selectivity, solubility, and solvency of the solvent to the optimum for the individual case and at the same time provide a partial pressure of water vapor such that the aromatics can be recovered by stripping or distillation at moderate temperatures and pressures. Generally, 2.5 to 10 volumes of solvent per volume of water is used. In carrying out the extraction, a solvent/feed volume ratio of 10 to 30 to 1 is used employing extraction temperatures in the range of 110–300° F. The time of contacting should be sufficient for attainment of essentially equilibrium conditions, and if necessary, plural-stage extraction should be used. Selection of optimum conditions will depend upon the characteristics of the C_5-290° F. fraction being treated and can be readily determined experimentally (Vide U.S. Patent 2,803,685). The solvent extraction process is operated at a pressure sufficient to maintain the system in the liquid phase. Conventional extraction apparatus such as sieve-tray, packed, or other type of towers can be used.

To promote demethylation of the feed to demethylation reactor **24**, the reactor is preferably packed with a catalyst capable of relatively demethylating hydrocarbons, such as silica-alumina cracking catalyst impregnated with nickel molybdate, or with palladium and the catalyst is then subjected to a conditioning treatment. A silica-alumina cracking catalyst containing 75% by weight of silica and 25% by weight of alumina and impregnated with 10% by weight of nickel molybdate, then dried and pelleted into pellets having a diameter of about ⅛–⅜ inch, can be activated to a selective demethylation state as follows. The catalyst is oxidized with a mixture of oxygen and inert gas containing oxygen at a partial pressure of 30–500 mm. Hg, at a temperature of 800–875° F. for a period of time (about ½–2 hours) to assure that all constituents in the catalyst which are oxidizable at this temperature level are oxidized. The oxidizing gas should be substantially dry (less than 10 mm. Hg water partial pressure). The oxidized catalyst is then treated as follows.

(1) *Purge.*—Oxygen and combustion products are removed from the catalyst bed by purging with inert gas, or by evacuation to a low absolute pressure in the range of 10 mm. Hg.

(2) *Reduction.*—The reducible constituents of the composition then are reduced in a three-stage sequence wherein—

(*a*) The "oxidized" catalyst is contacted with a flowing stream of substantially dry, hydrogen-containing gas at a temperature of about 600–975° F. for a period sufficient to remove water, generated by the reduction reaction, from the catalyst bed;

(*b*) The catalyst is contacted further with dry hydrogen, either by continuing flow or shutting in the catalyst

for 15–30 hours while temperature is maintained at 900–973° F., and pressure at 0–600 p.s.i.g.; and

(*c*) The "reduced" catalyst then is contacted with flowing hydrogen containing about 20–30 mm. Hg water partial pressure, at a temperature of about 875° F. for a period of 15–30 hours.

A noble metal catalyst such as 75% silica-25% alumina cracking catalyst impregnated with about 0.1 to 1%, and preferably about 0.4 to 0.6% by weight of palladium, if properly conditioned may also be used in the demethylation step. Noble metal catalysts are conditioned as follows:

(1) *Purge.*—The catalyst bed is purged with an inert gas for a time sufficient to displace gaseous hydrocarbons and/or hydrogen therefrom.

(2) *Oxidation.*—The catalyst is contacted with an oxygen-containing inert gas, containing oxygen at a partial pressure of 10–500 mm. Hg and water vapor at a partial pressure of 0–90 mm. Hg, at a temperature of 825–975° F. for 1–20 hours. Temperature, water-vapor partial pressure, and length of treatment are critically interrelated in this step. At an oxidation temperature of 825° F., the water-vapor partial pressure must be in the range of 20–90 mm. Hg and the length of treatment must be about 20 hours. At an oxidation temperature of 975° F., the water-vapor partial pressure must be in the range of 0–15 mm. Hg, and the length of treatment must be limited to about 1 hour.

(3) *Purge.*—Oxygen, combustion products, and moisture then are removed from the catalyst bed by purging with inert gas, or by evacuation to a subatmospheric pressure in the range of 10 mm. Hg, absolute.

(4) *Reduction.*—The reducible constituents of the "oxidized" catalyst composition then are reduced to the greatest extent possible by passing a stream of dry, hydrogen-containing gas through the catalyst bed for 1–30 hours at a temperature of 850–950° F. and a pressure of 15–750 p.s.i.g. While dry gas is preferred, water-vapor partial pressures as high as 10 mm. Hg can be employed without serious deleterious effect.

Because the function of the catalytic demethylation step is to remove a terminal methyl group from the heptane and heavier paraffinic hydrocarbons to form paraffins lighter than heptane, as well as to decyclize naphthenic rings and demethylate the resulting paraffinic hydrocarbons, operating temperatures are selected which favor demethylation over indiscriminate hydrocracking. Accordingly, the operating conditions employed in the demethylation step are as follows:

Temperature, ° F.	620–680
Pressure, p.s.i.	300–750
Space velocity	1–3
H_2/hydrocarbon mol ratio	1–3/1

The separating system employed in processing the C_5–193° F. overhead fractions obtained from the naphtha fractionator, and the fractionator employed in separating the raffinate stream obtained in the solvent extraction process into its lower-boiling and higher-boiling constituents, has the function of separating normal paraffins from branch-chain paraffins and light naphthenes for subsequent isomerization. This separation can be achieved by precision fractionation or selective adsorption. If fractionation is used, conventional towers are employed to separate normal pentane and normal hexane from the branch-chain and naphthenic materials. If preferred, a superfractionation system can be used to separate the normal pentane and normal hexane constituents from the feed introduced into this fractionation system. In such an installation a plurality of bubble-tray towers employing bubble-trays is used. The number of trays, their diameter and spacing, as well as reflux ratios and other details, are selected in order to separate stream constituents with boiling point differentials of only about 6 to 25° F. The alternative adsorption processes also can effect the substantially quantitative separation of straight-chain paraffinic hydrocarbons from branch-chain paraffinic hydrocarbons and naphthenes. If this alternative is employed as the fractionation technique, it is preferred that so-called molecular-sieve adsorbents be employed in this service. These adsorbents are available from the Linde Air Products Company and are composed of crystalline sodium and calcium alumino-silicates that have been heated to remove their water of hydration. The resulting crystals are highly porous and the pores are of molecular dimensions, being only 15–20 billionths of an inch in diameter and of uniform size. A calcium alumino-silicate-type molecular sieve having a pore diameter of about 5 Angstroms will quantitatively separate the straight-chain paraffinic hydrocarbons from the branch-chain paraffins and naphthenes. In U.S. Patent 2,306,610 is described the fractionation of mixtures of hydrocarbons employing molecular sieves of the crystalline zeolite type. Other adsorbents employed for selectively adsorbing straight-chain paraffins from branch-chain paraffin hydrocarbons or cyclic hydrocarbons include activated coconut charcoal described in U.S. Patent 2,425,535, Saran charcoal prepared by the pyrolysis of polyvinylidene, and other similar adsorbents having small and uniform pore diameters sufficient to selectively separate straight-chain paraffinic hydrocarbons from admixture with cyclic and branch-chain compounds. To effectuate this separation, pore diameters of about 5 Angstroms are necessary.

The straight-chain paraffinic hydrocarbons which are recovered from the fractionation system **30** are subsequently converted to branch-chain paraffinic hydrocarbons in a catalytic isomerization step carried out under conditions which will effect the isomerization without concomitant demethylation and hydrocracking. Catalysts which will convert substantial amounts of the straight-chain paraffinic hydrocarbons to branch-chain hydrocarbons with excellent selectivity are the noble metal catalysts, such as platinum and palladium incorporated on refractory, mixed oxides, acidic-type carriers. About 0.1% to 1.0% by weight of the noble metal is included or incorporated in the mixed oxides support. These catalysts can be prepared as described above in connection with the noble metal catalysts as utilized in the reforming phase of the invention, preferably using 75–25 or 85–13 silica-alumina as the cracking catalyst support. High space velocities are preferred because they favor isomerization over hydrocracking, thereby achieving superior conversion-yield relationships. The following conditions are employed in the isomerization phase of this invention.

Temperature	650–800
Pressure	150–1000 p.s.i.g.
Space velocity	1–5 liquid rate hourly space velocity.
H_2/hydrocarbon mol ratio	1–3/1.

To illustrate the advantages which are obtained in employing the combination process of this invention for the production of high-octane-number blending stocks, the combination of a catalytic reforming process employing a platinum catalyst with a solvent extraction unit employing diethylene glycol, and an isomerization process to make a high-octane-number blending material are compared with the improved integrated process of this invention. The results of this comparative study are tabulated in Table I in which case I represents the data obtained employing catalytic reforming, solvent extraction and isomerization, and case II is exemplary of the data obtained employing this invention.

Table I

	Case I	Case II
Straight-Run gasoline, percent v. (100–380° F., ASTM:		
boiling range from Illinois Crude)	100	100
193° F. E.P. to isomerization	25	25
193–400° F. to reforming	75	75
Reforming: [1]		
Debutanized yield, percent v. of charge	80.5	85.0
F-1 octane, +3 cc. TEL	103.5	95.5
Heavy reformate (290–440° F. true boiling point), percent v. of charge		33.1
Percent v. of Total S.R.		20
Extraction: [2]		
Extract (benzene, toluene, Xyl.)—		
Percent v. of Reformate	66.9	24.6
Percent v. of Total S.R.	40.4	15.7
Raffinate (C_5–C_9 Paraffins) to isomerization, percent v. of Total S.R.	20	28
Recycle to reforming, v. percent Total S.R.	33	
Demethylation: [3]		
Fresh heavy raffinate reactor feed, v. percent Total S.R.		18
Recycle, to reactor, percent v. Total S.R.		12
Total C_5–193° F. liquid to isomerization		25.2
Isomerization: [4]		
Fresh feed, percent v. Total S.R.	25	50.2
Product, percent v. Total S.R.	24.4	49.0

Products, Vol. percent of total S.R. and blending octanes, F-1+3 cc. TEL:

	Vol. percent	O.N.	Vol. percent	O.N.
Isomerate	43.9	97.0	49.0	97.0
Extract	40.4	109.6		
Heavy Reformate+Extract			35.7	114.4
	84.3	103.0	84.7	104.2

[1] Reforming Conditions:

	Weight Hourly Space Velocity	Temperature Avg., ° F.	Pressure, p.s.i.g.	H_2 circ., M s.c.f./bbl. Feed
Case I	2.0	930	300	7,000
Case II	1.5	910	300	5,000

Recycle, Vol. percent of fresh feed is 44 in Case I.
The catalyst in both cases is Sinclair-Baker (platinum on activated alumina).

[2] Extraction:

	Solvent/oil ratio	Treating Temp., ° F.
Case I	6/1	250
Case II	8/1	300

(Solvent—Triethylene glycol with 8% by weight H_2O.)

[3] Demethylation (Case II, only):
Weight hourly space velocity: 1.0; Avg. Temp.: 630° F.
H_2/Hydrocarbon mole ratio: 2.0; Avg. Press.: 500 p.s.i.g.
Catalyst: (10% nickel molybdate on 75% Si—25% Al.).
Yield, Vol. percent of fresh feed: 84.5.

[4] Isomerization:
Weight hourly space velocity: 2; Avg. Temp. nC_5 reactor 760° F.
H_2/Hydrocarbon mole ratio: 3.0; Avg. Temp. nC_5 reactor 725° F.
Average reactor pressure: 500 p.s.i.g.
Catalyst: 0.6% Pd. on 87% Si—13% Al.

The intermediate fractionation adjuncts employed to separate the effluent from the catalytic reformer into selected feed stocks for subsequent processing, and the fractionator utilized to distill the raffinate from the solvent extraction step, as well as the effluent from the catalytic demethylation, are conventional fractional distillation towers, the size of which as well as the selection of the operating conditions can readily be determined by those skilled in the art to which this invention pertains.

What I claim as my invention is:

1. A process for preparing high-octane number fuel from low-octane number naphtha comprising desulfurizing and fractionating said low-octane naphtha into a higher-boiling fraction and a lower boiling fraction, containing normal pentane and hexane and having an end point of about 193° F., catalytically reforming said higher boiling fraction in the presence of hydrogen at temperatures of 900–930° F. and pressures of 250–350 lb./sq. in., separating from the reformed product a lower boiling fraction containing benzene, toluene and xylenes admixed with paraffin hydrocarbons, and a higher boiling fraction, withdrawing the higher boiling fraction from the system, solvent extracting the lower boiling reformed fraction to separate a raffinate of low aromatic content and an extract of high aromatic content, fractionating said raffinate into fractions, one of which contains predominantly C_6 and lighter hydrocarbons, and the other of which contains C_7 and heavier hydrocarbons, subjecting the fraction containing C_7 and heavier hydrocarbons to demethylation in the presence of hydrogen and a catalyst composed of silica-alumina cracking catalyst promoted with nickel molybdate, which is selective for the demethylation reaction at a temperature of 620–680° F. and pressure of 300–750 lb./sq. in., fractionating the demethylated product together with said raffinate, combining said first-mentioned lower boiling fraction with said raffinate fraction containing predominantly C_6 and lighter hydrocarbons, separating said combined fractions into predominantly isoparaffin and normal paraffin fractions and isomerizing said normal paraffin fractions in the presence of a selective noble metal isomerization catalyst at temperatures of 650–800° F. and pressures of 150–1000 lb./sq. in. in the presence of hydrogen to produce an isomerized product of high iso-paraffin content.

2. Process in accordance with claim 1 in which the isomerization catalyst is a silica-alumina cracking catalyst promoted with about 0.1 to 1% by weight of palladium.

3. Process in accordance with claim 1 in which at least portions of said high aromatic content extract, said isomerized product of high iso-paraffin content and said combined predominantly iso-paraffinic fraction are blended together to make high octane motor fuel.

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