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[54] **PROCESS FOR THE SIMULTANEOUS PRODUCTION OF AN AROMATIC CONCENTRATE AND ISOBUTANE**

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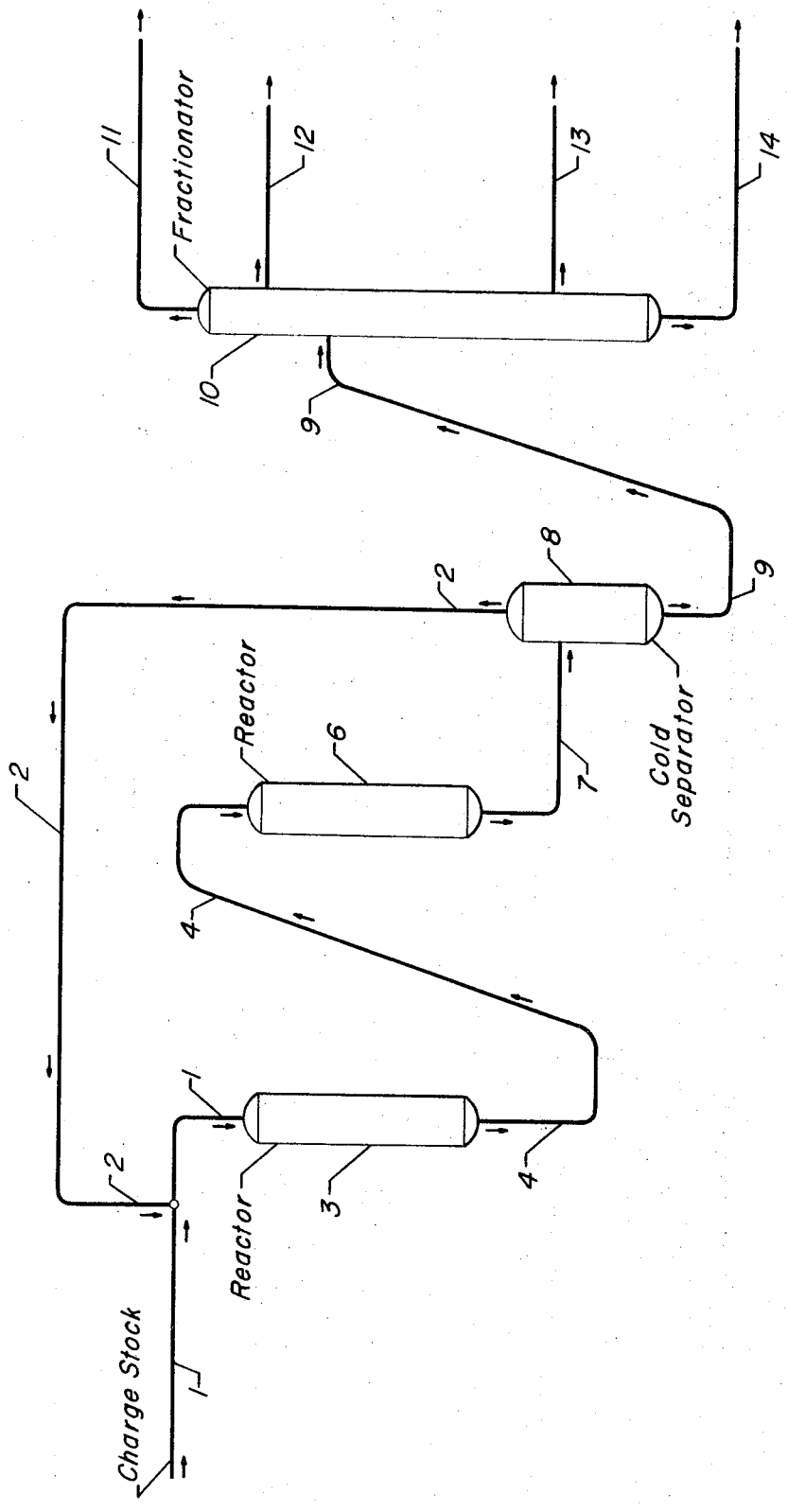
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[57] **ABSTRACT**

A naphtha boiling range hydrocarbon charge stock is converted into an aromatic concentrate and isobutane via a process combining a catalytic reforming zone and a hydrocracking zone. The catalytic reforming is effected at reforming conditions selected to convert paraffinic hydrocarbons containing more than five carbon atoms per molecule into aromatic hydrocarbons. The reforming zone effluent is then subjected to a particular hydrocracking process which results in exceedingly high yields of isobutane.

10 Claims, 1 Drawing Figure


Charge Stock
1
2
Reactor
3
4
Reactor
6
7
Cold Separator
8
9
10
Fractionator
11
12
13
14

PROCESS FOR THE SIMULTANEOUS PRODUCTION OF AN AROMATIC CONCENTRATE AND ISOBUTANE

The present invention involves a two-stage process for the conversion of naphtha or gasoline boiling range hydrocarbons to produce an aromatic concentrate and large quantities of isobutane.

Aromatic hydrocarbons, principally benzene, toluene, ethylbenzene and the various xylene isomers are required in large quantities to satisfy an ever-increasing demand for various petrochemicals which are synthesized therefrom. For example, benzene may be hydrogenated to produce cyclohexane for use in the manufacture of nylon; toluene is often used as a solvent and as a starting material for various medicines, dyes and perfumes; ethylbenzene is employed in large quantities in a dehydrogenation process to produce styrene. Additionally, aromatic hydrocarbons are utilized as gasoline blending components in view of their exceedingly high research octane value. For example, benzene has a clear, unleaded research octane value of 99, while toluene and all other aromatics have a blending value in excess of 100.

Isobutane is used in chemical sythesis, as a refrigerant and as an aerosol propellant. In chemical synthesis, isobutane is converted to isobutenes for use in the production of butyl rubber, the manufacture of copolymer resins with butadiene and acrylonitrile.

In accordance with one embodiment of the present invention, the two-stage process, for producing an aromatic concentrate and isobutane, is integrated into an overall refinery scheme for the product of a high-octane, unleaded gasoline pool, and the aromatic concentrate may be directly introduced into the unleaded gasoline pool.

Relatively recent investigations into the causes and cures of environmental pollution have shown that more than half of the violence committed with respect to the atmosphere stems from vehicular exhaust consisting primarily of unburned hydrocarbons and carbon monoxide. As a result of these investigations, a great deal of research has gone into the development of catalytic converters which, when installed within an automotive exhaust system, are capable of converting more than 90.0 percent of the noxious components into innocuous material. While developing these catalytic converters, it was learned that the efficiency of conversion, and particularly the stability of the selected catalytic composites was severely impaired when the exhaust fumes resulted from the combustion of lead-containing fuel. When compared to operations during the combustion of clear, unleaded gasolines, both the conversion of noxious components and catalyst stability decreased as much as 50.0 percent when the motor fuel contained lead and other metal additives. Therefore, it has been recognized throughout the petroleum industry, as well as in the major gasolineconsuming countries, that suitable gasoline must be produced without requiring the addition of lead to increase the octane rating. Also being recognized is the fact that unburned hydrocarbons and carbon monoxide are not the only extremely dangerous pollutants being discharged via vehicular exhaust. Japan has recently experienced an increase in the incidence of lead poisoning, and has thus enacted legislation to reduce the quantity of lead permitted in motor fuel gasolines intended for consumption in that country.

One natural consequence of the removal of lead from motor fuel gasoline, in addition to many others, resides in the fact that petroleum refinery operations will necessarily undergo modification in order to produce voluminous quantities of high-octane, unleaded motor fuels in an economically attractive fashion. One well known and well documented refining process. capable of significantly improving the octane-rating of gasoline boiling range fractions, is the catalytic reforming process. In such a process, the primary octane-improving reactions are naphthene dehydrogenation, naphthene dehydroisomerization, paraffin dehydrocyclization and paraffin hydrocracking. Naphthene dehydrogenation is extremely rapid, and constitutes the principle octane-improving reaction. Paraffin aromatization is achieved through dehydrocyclization of a straightchain paraffin; this reaction is rate limited in catalytic reforming operations. Unreacted, relatively low-octane paraffins, therefore, are present in the catalytically reformed product effluent and effectively reduce the octane rating thereof. When operating at a relatively high severity, the paraffinic hydrocarbons within the reforming zone are subjected to hydrogenative cracking. While this partially increases the octane rating of the gasoline boiling range product, substantial quantities of low molecular weight, normally gaseous material are produced. In view of the fact that hydrogen is present within the reaction zone, the light gaseous material is substantially completely saturated and comprises, methane, ethane and propane.

On the other hand, at a relatively low catalytic reforming operating severity, paraffin cracking is decreased with the result that an increased quantity of low octane rating saturates appears in the normally liquid product effluent. In order to upgrade the overall quality of the gasoline pool, either the addition of lead becomes necessary, or the low octane saturates must be subjected to further processing higher octane components. As previously stated, subsequent processing of the saturates for octane-rating improvement can be eliminated by increasing the operating severity within the catalytic reforming reaction zone. The high severity operation produces a two-fold effect while increasing the octane rating; first, additional high octane aromatic components are produced, and secondly, the low octane rating components are at least partially eliminated either by conversion to aromatic components, or light normally gaseous hydrocarbons. The results, therefore, include lower liquid yields or gasoline both to "shrinkage" in molecular size when paraffins and naphthenes are converted to aromatics, and the production of the aforesaid light, normally gaseous components. These problems are further compounded when the desired end result is the production of a high-octane, unleaded gasoline pool. In accordance with an overall refinery operation, into which the present invention is integrated, a lowseverity catalytic reforming unit is combined with at least a particular hydrocracking unit and an alkylation unit. As hereinafter indicated, the end result is the production of a high-octane, unleaded gasoline pool, in volumetric yields greater than would be attainable by direct, high-severity catalytic reforming.

The hydrocarbonaceous charge stocks, contemplated for conversion in accordance with the present invention, constitute naphtha boiling range hydrocarbon fractions and/or distillates. "Gasoline boiling range hydrocarbons" generally connotes those hydrocarbons

having an initial boiling point of at least about 100°F., and an end boiling point less than about 450°F., and the term is inclusive of intermediate boiling range fractions often referred to in the art as "light naphtha" and "heavy naphtha". Light naphtha generally refers to a hydrocarbon mixture having an end boiling point in the range of about 280°F. to about 340°F. A heavy naphtha is considered a hydrocarbon mixture having an initial boiling point of about 280°F. and end boiling point of about 400°F. to about 450°F., and principally includes those hydrocarbons having seven or more carbon atoms per molecule. It is not intended, however, to limit the present invention by a specific charge stock having a particular boiling range. Suffice to say that suitable charge stocks will generally have an initial boiling point above about 100°F. and an end boiling point below about 450°F. The precise boiling range of any given naphtha charge stock will be dependent upon the economic and processing considerations prevalent in the particular locale where the charge stock is available.

Prior art catalysts have demonstrated the ability to hydrocrack paraffins while preserving the cyclic hydrocarbons present in the feedstock. However, the cyclics are completely converted to the corresponding naphthenes. This characteristic of the catalysts has prevented the simultaneous production of aromatic hydrocarbons and isobutane by means of hydrocracking a naphtha boiling range feedstock rich in aromatics. If a feedstock is first hydrocracked and then reformed, valuable aromatic precursors are destroyed in the hydrocracking step which prevents the maximization of aromatic production. I have discovered a hydrocracking catalyst comprising a mordenite carrier material, a palladium component and a nickel component which promotes paraffin hydrocracking while preserving aromatics which are present in the feedstock.

A principal object of the present invention is the simultaneous production of aromatic hydrocarbons and an isobutane concentrate. A corollary objective resides in the production of a high-octane, unleaded motor fuel gasoline pool.

Another object of my invention is to provide an integrated refinery operation for producing high liquid yields of a high-octane, unleaded gasoline pool.

Therefore, in a broad embodiment, the present invention involves a process for the simultaneous production of an aromatic concentrate and isobutane, from a naphtha boiling point charge stock, which process comprises the steps of: (a) reacting said charge stock, in a low-severity catalytic reforming zone, at reforming conditions selected to convert paraffinic hydrocarbon containing more than five carbon atoms per molecule into aromatic hydrocarbons; (b) further reacting at least a portion of the resulting reformed product effluent with hydrogen, in a hydrocracking reaction zone, at hydrocracking conditions and in contact with a hydrocracking catalyst comprising a mordenite carrier material, a palladium component and a nickel component; and, (c) recovering said aromatic concentrate and isobutane from the resulting hydrocracking reaction zone effluent.

Other embodiments of my invention involve the use of various operating conditions and processing techniques. In one such other embodiment, at least a portion of the isobutane concentrate is reacted in a dehydrogenation reaction zone, at dehydrogenating conditions selected to produce butenes, and reacting said butenes in said alkylation reaction zone as said olefinic hydrocarbons.

As hereinbefore set forth, the present invention primarily involves a catalytic reforming reaction zone, and a particular saturate cracking zone. Additionally, in other embodiments, an integrated refinery scheme, incorporating the process of the present invention, utilizes a solvent extraction zone, an isomerization reaction zone and an alkylation reaction zone. In a specific embodiment, the overall process includes a dehydrogenation reaction zone to produce the olefinic hydrocarbons utilized within the alkylation reaction zone. In order that a clear understanding of the integrated refinery process is obtained, a brief description of the various individual reaction and separation zones, utilized in one or more embodiments, is believed to be warranted. In describing each individual zone, one or more references to United States Patents will be made in order that more detail will be readily available. Such references are not intended to be exhaustive or limiting, but simply exemplary and illustrative.

As hereinafter indicated in greater details, an essential feature of the present invention resides in the use of a particular hydrocracking reaction zone and catalyst which produces a hydrocracked product effluent having unique characteristics. Not only is the hydrocracked effluent rich in isobutane and pentane/hexane isomers, but the aromatics originally charged to the hydrocracking zone have been substantially retained without hydrogenation to the corresponding naphthene. The overall net result is the virtually complete elimination of low octane rating naphthenes and paraffins from the ultimate product.

As hereinbefore stated, the present process utilizes a catalytic reforming reaction zone. By comparison with current standards, the reforming zone can be considered a low-severity operation.

The naphtha boiling range charge stock to the catalytic reforming zone may be derived from a multitude of sources. For example, one such source constitutes those naphtha distillates which are derived from a full boiling range petroleum crude oil, another source is a naphtha fraction obtained from the catalytic cracking of gas oils, while another source constitutes the gasoline boiling range effluent from a hydrocracking reaction zone processing heavierthan gasoline charge stock. Since the greater proportion of such naphtha fraction are contaminated through the inclusion of sulfurous and nitrogenous compounds, it is contemplated that the catalytic reforming reaction zone may have integrated therein a hydrorefining zone, complete details of which are well known and thoroughly described in the prior art.

Catalytic composites, for utilization in the reforming reaction zone, include a refractory inorganic oxide carrier material containing a catalytically active metallic component which is generally selected from the noble metals of Group VIII. Recent developments in the area of catalytic reforming have indicated that catalyst activity and stability are significantly enhanced through the addition of various modifiers, especially tin, rhenium, nickel and/or germanium.

Suitable porous carrier materials include refractory inorganic oxides such as alumina, silica, zirconia, and crystalline aluminosilicates scuh as the faujasites, mordenite, and combinations of refractory inorganic oxides

with the various crystalline aluminosilicates. Generally favored metallic components, for utilization in the reforming reaction zone, include ruthenium, rhodium, palladium, osmium, iridium, platinum, rhenium, germanium, nickel and tin, as well as mixtures thereof. These metallic components are employed in concentrations ranging from about 0.01 percent to about 5.0 percent by weight, and preferably from about 0.01 percent to about 2.0 percent by weight. Since one of the functions of the reforming reaction zone is the dehydrocyclization of paraffins to form aromatics, the catalyst disposed therein may also contain combined halogen selected from the group of fluorine, chlorine, bromine, iodine and mixtures thereof.

Illustrations of catalytic reforming process schemes are found in U.S. Pat. Nos., 2,905,620 (Class 208–65), 3,000,812 (208–138) and 3,296,118 (Class 208–100). Effective reforming operating conditions include catalyst temperatures within the range of about 800°F. to about 1100°F., preferably having an upper limit of about 1050°F. The liquid hourly space velocity, defined as volumes of hydrocarbon charge per hour volume of catalyst disposed within the reforming reaction zone, is generally in the range of about 1.0 to about 5.0, although space velocities from about 0.05 to about 15.0 may be employed. The quantity of hydrogen-rich gas in admixture with the hydrocarbon feed stock to the reforming reaction zone is generally from about 1.0 to about 20.0 mols of hydrogen per mol of hydrocarbon. The reforming reaction zone effluent is generally introduced into a high-pressure separation zone at a temperature of about 60°F. to about 140°F., to separate lighter gaseous components from heavier, normally liquid components. Since normal reforming operations produce large quantities of hydrogen, a certain amount of the recycled gaseous stream is removed from the reforming system by way of pressure control. It is within the scope of the present invention that such excess hydrogen be employed in the hydrogen-consuming hydrocracking reaction zone as make-up hydrogen, as well as in the hydroisomerization reaction zone. Pressures in the range of about 100 to about 1500 psig. are suitable for effecting catalytic reforming reactions.

With respect to the catalytic reforming reaction zone, utilized in the present combination process, the reactions effected therein are conducted at a relatively low operating severity. To those familiar with the catalytic reforming art, the term "relatively high severity" indicates high temperature or low space velocity, or both a high temperature and low space velocity. The most noticeable direct result of a high severity operation is found in the octane rating of the normally liquid product effluent. Generally speaking, high operating severity levels are required for products having higher octane ratings. While the reforming zone utilized in the present process does not necessarily upgrade the octane rating of the charge stock to the level ultimately attained with respect to the unleaded gasoline pool, the charge stock is substantially improved in octane rating. As utilized herein, the term "low-severity reforming" alludes to a reforming process in which substantial quantities of naphthenic hydrocarbons are dehydrogenated to high octane aromatic hydrocarbons, while the cracking of paraffinic hydrocarbons is inhibited. Some dehydrocyclization of paraffinic hydrocarbons, to produce additional aromatics, is also effected in the catalytic reforming reaction zone. However, the greater proportion of paraffins originally present in the fresh feed charge stock remain intact and are subsequently processed in the hydrocracking reaction zone for the purpose of producing large quantities of isobutane. Thus, the low severity reforming operation, as effected in the reaction zone, may be defined by stating that about 90.0 to about 100.0 mols of aromatics are produced for every 100.0 mols of 6-membered ring naphthenes in the charge stock, while less than about 40.0 mols aromatics are produced for every 100.0 mols of paraffinic hydrocarbons. In determining the degree of conversion of naphthenes to aromatics (dehydrogenation and alkanes to aromatics (dehydrocyclization), it is assumed that a relatively small amount of naphthenes are cracked or otherwise converted to hydrocarbons other than aromatics, and that the major portions of paraffins which disappear are converted to aromatic hydrocarbons while some additional naphthenes are formed.

The product from the hydrocracking reaction zone is rich in aromatic hydrocarbons as well as isobutane. The saturated hydrocarbons which are also present in the hydrocracking effluent are separated from the aromatic hydrocarbons by any suitable separation technique known in the art, e.g., fractionation.

In a preferred embodiment, the charge to the hydrocracking reaction zone will be the heptane-plus fraction remaining in the catalytically reformed product effluent following removal of the pentane/hexane fraction therefrom. Although the hydrocracking feed stock may contain the pentane/hexane paraffins, a preferred technique, as hereinafter set forth, involves separate recovery of a pentane/hexane fraction for utilization as the charge to a hydroisomerization reaction zone wherein the same is converted into pentane and hexane isomers of significantly increased octane rating. The hydrocracking reaction zone of the present process is unlike present-day hydrocracking processes both in function and result. The charge to the hydrocracking zone constitutes paraffinic hydrocarbons boiling within the naphtha boiling range, and the product effluent contains only moderate amounts of methane and ethane. Propane recovered from the hydrocracking zone effluent can be utilized for subsequent alkylation of isopropyl alcohol production; another valuable use of propane is as a component of liquefied petroleum gas. Through the utilization of a particular catalytic composite and operating conditions, the hydrocracking of the paraffinic raffinate produces relatively large quantities of butanes, which butane concentrate is rich in isobutane, while preserving aromatic compounds. In view of the unique character of the product effluent, being rich in isobutane, the hydrocracking reaction zone is referred to herein as "I-cracking." Thus, with respect to increasing the yield of normally liquid hydrocarbons in the unleaded gasoline pool, the butane concentrate can be subjected to alkylation with a suitable olefinic hydrocarbon. Furthermore, with respect to the pentane/hexane fraction in the hydrocracked product effluent, the same is rich in pentane and hexane isomers; these can be separately recovered and sent directly to the unleaded gasoline pool.

The hydrocracking reaction conditions, under which the process is effected, will vary according to the physical and chemical characteristics of the charge stocks. In the past, hydrocracking reactions have generally been effected and pressures in the range from about

1,500 to about 5,000 psig., a liquid hourly space velocity of about 0.25 to about 5.0, hydrogen circulation rates of about 5,000 to about 50,000 standard cubic feed per barrel and maximum catalyst temperatures in the range of about 700°F. to about950°F. As discussed in the prior art, heavier charge stocks require a relatively high severity of operation including high pressures, high catalyst bed temperatures, a relatively low liquid hourly space velocity and high hydrogen concentrations. Lower severity operation may be employed with comparatively lighter feed stocks such as kerosenes and light gas oils. In the practice of the present invention, regardless of the characteristics of the naphtha charge stock, the hydrocracking process is effected at a lower severity of operation than those commonly in use. In accordance with the present invention the hydrocracking reaction zone has disposed therein a catalytic composite comprising a mordenite carrier material, a palladium component and a nickel component. The conversion conditions include a liquid hourly space velocity of 0.5 to about 10, a hydrogen circulation rate of about 3,000to about 20,000 standard cubic feet per barrel, a pressure from about 150 to about 2,000 psig., and preferably up to about 1,000 psig., and of greater significance, a maximum catalyst bed temperature from about 650°F. to about 850°F. In many instances, the operating pressure will consistently be in the range from about 200 to about 500 psig.

First considering the porous material serving as the carrier for the active metallic components, it is preferred that it be adsorptive and possess a high surface area of about **25** to about **500** square meters per gram. Heretofore, suitable carrier materials have been selected from the group of amorphous refractory inorganic oxides including alumina, titania, zirconia, silica, and and mixtures thereof. When of the amorphous type, the preferred prior art carrier material, for use in a hydrocracking catalytic composite, appears to be a composite of alumina and silica, with the latter being present in an amount of about 10.0 percent to about 90.0% by weight. Recent developments in the area of catalysis have further shown that various crystalline aluminosilicates can be utilized to advantage in some hydrocracking situations. Crystalline aluminosilicates are of an ordered crystalline structure comprising cages or cavities interconnected by smaller pores and channels of a definite size range characteristic of each crystalline aluminosilicate variety. The dimensions of the pores and channels are such as to accept molecules of certain dimensions while rejecting those of larger dimensions.

The crystalline aluminosilicates, hereinafter referred to as zeolites, are generally described as a three-dimensional network of fundamental structural units consisting of siliconcentered SiO_4, and aluminum-centered AlO_4 tetrahedra interconnected by a mutual sharing of apical oxygen atoms.

The SiO_4 and AlO_4 tetrahedra are arranged in a definite geometric pattern often visualized either in terms of chains, layers or polyhedra, all formed by the linking of the tetrahedra. The various zeolites may be classified according to the geometric pattern of their framework with its attendant pore size and by the SiO_2/Al_2O_3 mol ratio of their composition.

The essential carrier material for the present invention comprises a zeolite having the mordenite crystal structure and containing alumina fixed in combination therewith. Mordenite is a particular zeolite, highly siliceous in nature and generally characterized by a silica/alumina mol ratio of from about 6 to about 12 as manufactured or found in its natural state. The mordenite crystal structure comprises four and five membered rings of silica and alumina tetrahedra so arranged that the resulting crystal lattice comprises pores and channels running parallel along the crystal axis to give a tubular configuration. This structure is unique among the zeolites since the channels and tubes do not intersect and access to the cages or cavities is in only one direction. For this reason, the mordenite structure is frequently referred to as two-dimensional. This is in contrast to other well known zeolites, for example faujasite and zeolite A, in which the cages can be entered from three directions.

The zeolite having a mordenite crystal structure and containing alumina fixed in combination therewith is prepared by heating an amorphous silica-alumina composite in admixture with an aqueous alkali metal solution and forming a zeolite with a mordenite crystal structure. The resulting mordenite is then heated in an alumina sol, thereafter separating excess sol, treating the zeolite-sol product at conditions effecting gelation of the sol, aging the resulting composition in an alkaline media and thereafter washing, drying and calcining.

For purposes of the present invention, the catalyst may be formed in any desired shape such as spheres, pellets, pills, cakes, extrudates, powders, granules, etc. However, a particularly preferred form of the catalyst is the sphere; and spheres may be continuously manufactured by the well-known oil drop method which comprises forming an alumina hydrosol, preferably by reacting aluminum metal with hydrochloric acid, combining the hydrosol with a suitable gelling agent such as hexamethylenetetramine to form a dropping solution, uniformly distributing finely divided mordenite particles throughout the dropping solution, and dropping the resultant mixture into an oil bath maintained at elevated temperatures. Alternatively, the particles may be commingled with the sol to form a mixture thereof and the gelling agent thereafter added to the mixture to form the dropping solution. In either case, the droplets of the mixture remain in the oil bath until they set and form substantially spherical hydrogel particles. The spheres are then continuously subjected to specific aging treatments in oil and an ammoniacal solution to further improve their physical characteristics. The resulting aged and gelled particles are then washed and dried at a relatively low temperature of about 300°F. to about 400°F. and subjected to a calcination procedure at a temperature of about 850°F. to about 1300°F. for a period of about 1 to about 20 hours. This treatment effects conversion of the alumina hydrogel to the corresponding crystalline gamma alumina. See U.S. Pat. No. 2,620,314 for additional details regarding this oil drop method. Further details of the preparation of a suitable carrier material can also be found in U.S. Pat. No. 3,677,973.

The hydrocracking catalytic composite of the present invention comprises mordenite containing alumina fixed in combination therewith, as hereinabove described, a palladium component and a nickel component. The mordenite may be present in quantities ranging from about 60 percent to about 90 percent by weight of the carrier material. The palladium and nickel components may exist within the final composite

as a compound such as an oxide, sulfide and halide, or in an elemental state. In a preferred embodiment, the palladium and nickel components exist in the catalytic composite as a sulfide. In order to perserve the metals in the sulfided state during the processing operation, the charge stock may contain from about 5 to about 5000 ppm. by weight of sulfur. Generally, the amount of the palladium component is small compared to the quantities of the other components combined therewith. When calculated on an elemental basis, the palladium component generally comprises from about 0.01 to about 2 percent by weight of the final composite. With respect to the nickel component, and calculated on the basis of the elemental metal it will be present within the catalytic composites in an amount from about 0.01 percent to about 10 percent by weight.

The metallic components may be incorporated within the catalytic composite in any suitable manner including co-precipitation or co-gellation with the carrier material, ion-exchange or impregnation. The latter constitutes the preferred method of preparation, utilizing water-soluble compound of the various metallic components. Thus a palladium component may be added to the carrier material by commingling the latter with an aqueous solution of chloropalladic acid, palladic chloride or other water-soluble compound of palladium. Similarly, the nickel component may be added to the carrier material by commingling the latter with an aqueous solution of nickel nitrate hexahydrate, nickel chloride, or other water-soluble compound of nickel. Following impregnation, the carrier material is dried and subjected to a calcination, or oxidation, technique generally followed by reduction with hydrogen at an elevated temperature. Prior to its use, the catalytic composite may be subjected to a substantially water-free reduction technique. This is designed to insure a more uniform and finely divided dispersion of the metallic components throughout the carrier material. Substantially pure and dry hydrogen is employed as the reducing agent at a temperature of about 800°F. to about 1200°F., and for a time sufficient to reduce the metallic components.

The resulting reduced catalyst is preferably subjected to a presulfiding operation designed to incorporate in the catalytic composite from about 0.05 to about 2.0 wt. percent sulfur calculated on an elemental basis. Preferably, this presulfiding treatment takes place in the presence of hydrogen and a suitable sulfur-containing compound such as hydrogen sulfide, lower molecular weight mercaptans, organic sulfides, etc. Typically, this procedure comprises treating the reduced catalyst with a sulfiding gas such as a mixture of hydrogen and hydrogen sulfide having about 10 moles of hydrogen per mol of hydrogen sulfide at conditions sufficient to effect the desired incorporation of the sulfur component, generally including a temperature ranging from about 50°F. to about 1100°F. or more.

In view of the fact that the reactions being effected are exothermic in nature, an increasing temperature gradient is experienced as the hydrogen and paraffinic raffinate traverse the catalyst bed. In accordance with the present process, the maximum catalyst bed temperature, virtually the same as that measured at the outlet of the reaction zone, is maintained in the range of about 650°F. to about850°F. In order to assure that the catalyst bed temperature does not exceed the maximum allowable, the use of conventional quench streams, either normally liquid, or normally gaseous, and introduced at one or more intermediate loci of the catalyst bed, is contemplated.

As hereinbefore set forth, the product effluent from the hydrocracking reaction zone comprises butanes, the greater proportion of which constitutes isobutane. For this reason, the hydrocracking reaction zone is herein referred to as "I-cracking", the "I" alluding to isomer production.

Since the preferred use of the present invention concept is the integration thereof into an overall refinery scheme with the production of a high octane, unleaded motor fuel gasoline pool, the isobutane-rich effluent from the I-cracking zone may be utilized as fresh feed to an alkylation reaction zone. The alkylation is effected by intimately commingling the isobutane feed, an olefinic hydrocarbon and a particular catalyst as hereinafter described. It is understood that the source of the olefinic hydrocarbon, for utilization in the alkylation reaction zone, is not essential to the process encompassed by the present invention. Thus, "outside" olefinic material may be brought into the described process from any suitable source including a fluid catalytic cracking unit, or a thermal cracking unit. However, as stated in another specific embodiment of the present invention, at least a portion of the isobutane concentrate may be subjected to dehydrogenation in a dehydrogenation reaction zone to produce the alkylatable olefinic hydrocarbons. Similarly, the propane/butane concentrate obtained by the separation of the catalytically reformed product effluent may also be dehydrogenated and introduced into the alkylation reaction zone, as a portion of the olefinic hydrocarbons.

The alkylation reaction zone may be any acidic catalyst reaction system such as a hydrogen fluoride-catalyzed system, or one which utilizes sulfuric acid. Hydrogen fluoride alkylation is particularly preferred, and may be conducted substantially as set forth in U.S. Pat. No. 3,249,650 (Class 260–63.48). Briefly, the alkylation conditions, when effected in the presence of hydrogen fluoride catalysts, arae such that the catalyst to hydrocarbon volume ratio within the alkylation reaction zone is in the range of about 0.5 to about 2.5. Ordinarily, anhydrous hydrogen fluoride will be charged to the alkylation system as fresh catalyst; however, it is possible to utilize hydrogen fluoride containing as much as about 10.0 percent by weight of water. Excessive dilution with water is generally to be avoided since it tends to reduce the alkylating activity of the catalyst and further introduces a wide variety of corrosion problems into the process. In order to reduce the tendency of the olefinic portion of the charge stock to undergo polymerization prior to alkylation, the molar proportion of isoparaffins to olefinic hydrocarbons within the alkylation reaction zone is desirably maintained at a value greater than 1.0, and preferably from about 3.0 to about 15.0. Alkylation reaction conditions also include a temperature from 0° to about 200°F., and preferably from about 30°F. to about 125°F. The pressure maintained within the alkylation system is ordinarily at a level sufficient to maintain the hydrocarbons and hydrogen fluoride catalyst in substantially liquid phase; that is, from about atmospheric to about 40 atmospheres. The contact time within the alkylation reaction zone is conveniently expressed in terms of space-time, being defined as volume of catalyst within the contact zone divided by the volume rate per minute

of hydrocarbon reactants charged to the zone. Usually, the space-time factor will be less than thirty minutes and more preferably less than about fifteen minutes.

The alkylation reaction zone effluent is separated to provide an acid phase and a hydrocarbon phase, the latter being separated to recover the normally liquid alkylate product and unreacted isobutane. The alkylate product, in combination with the aromatic concentrate forms part of the unleaded gasoline pool, along with the isopentane and isohexanes from the I-cracking zone. Unreacted isobutane and olefinic hydrocarbons, if any, may be recycled to the alkylation reaction zone, or a portion thereof may be diverted to the dehydrogenation reaction zone for the purpose of producing additional olefinic hydrocarbons for utilization in the alkylation reaction zone.

As previously indicated, a significant quantity of pentanes and hexanes are produced in the catalytic reforming reaction zone. Additionally, those instances where the fresh feed charge stock to the process is a full boiling range naphtha distillate, the same may contain a pentane/hexane concentrate. In view of the fact that normal pentane has a clear research octane rating of 62 and normal hexane a clear research rating of 25, these components are not desirable in a gasoline pool which is intended to be free from lead additives.

Therefore, in still another embodiment of the present invention, the pentane/hexane stream is introduced into an isomerization reaction zone for the purpose of producing an effluent rich in pentane and heptane isomers. For example, isopentane has a research clear octane rating of 93, while 2,2-dimethylbutane has a rating of 92 and 2,3-dimethylbutane a rating of 104; the average clear research octane rating of the monomethylpentenes is 74. Since the selectivity of conversion in the isomerization reaction zone is virtually **100%**, the unleaded gasoline pool can be significantly increased in its clear research octane rating through the production of pentane/hexane isomers without incurring a detrimental volumetric yield loss.

As indicated in U.S. Pat. No. 3,131,235 (Class 260–638.3), the isomerization process is effected in a fixed-bed system utilizing a catalytic composite of a refractory inorganic oxide carrier material, a Group VIII noble metal component and combined halogen preferably selected from fluorine, chlorine and mixtures thereof. The refractory inorganic oxide carrier material may be selected from the group including alumina, silica, titania, zirconia, mixtures of two or more, and various naturally-occurring refractory inorganic oxides. Of these, a synthetically-prepared gamma alumina is preferred. The Group VIII noble metal is generally present in an amount of about 0.01 percent to about 2.0 percent by weight, and may be one or more metals selected from the group of ruthenium, rhodium, osmium, iridium, and especially platinum, or palladium. The amount of combined halogen will be varied from about 0.01% to about 8.0 percent by weight. Both fluorine and chlorine may be used to supply the combined halogen, although the use only of fluorine, in an amount of about 2.5% to about 5.0 percent by weight, is preferred.

Isomerization reactions are preferably effected in a hydrogen atmosphere utilizing sufficient hydrogen so that the hydrogen to hydrocarbon mol ratio to the reaction zone will be within the range of about 0.25 to about 10.0 Operating conditions will additionally include temperatures ranging from about 200°F. to about 800°F., although lower temperatures within the more limited range of about 300°F. to about 525°F. will generally be utilized. The pressure, under which the reaction zone is maintained, will range from about 50 to about 1500 psig. The reaction products are separated from the hydrogen, which is recycled and subsequently subjected to fractionation and separation to recover the desired reaction product. Recovered starting material is also recycled so that the overall process yield is relatively high. The liquid hourly space velocity will be maintained in the range of about 0.25 to about 10.0, and preferably within the range of about 0.5 to about 5.0. Another suitable isomerization process is found in U.S. Pat. No. 2,924,628 (Class 260–666).

As previously set forth, at least a portion of the isobutane-rich effluent from the I-cracking reaction zone may be subjected to dehydrogenation to produce the olefins required in the alkylation reaction zone. In still another embodiment, at least a portion of the propane/butane concentrate recovered from the catalytic reforming reaction zones may also be subjected to dehydrogenation. The advisability of the utilization of either, or both techniques will be primarily dependent upon the availability of outside olefins; for example, from a catalytic or thermal cracking unit. When dehydrogenation is deemed desirable, it may be effected essentially as set forth in U.S. Pat. No. 3,293,219 (Class 260–683.3). Briefly, the dehydrogenation reactions are generally effected at conditions including a temperature in the range of from 400°C. to about 700°C., a pressure of from about atmospheric to about **100** psig., a liquid hourly space velocity within the range of 1.0 to about 40.0 and in the presence of hydrogen in an amount to result in a mol ratio of from 1:1 to about 10:1, based upon the paraffin charge.

The dehydrogenation catalyst is a composite of an inorganic oxide carrier material, an alkali metal component, a Group VIII metal component, and a catalytic attenuator from the group consisting of arsenic, antimony and bismuth. A particularly preferred catalyst comprises lithiated alumina containing about **0.05%** to about **5.0%** by weight of a Group VIII noble metal, especially platinum. The catalytic attenuator is employed in amounts based upon the concentration of a Group VIII noble metal component. For example, arsenic is present in an atomic ratio of arsenic to platinum in the range of about 0.20 to about 0.45. Although lithium is the preferred alkalinous metal component, the catalyst may contain calcium, magnesium, strontium, cesium, rubidium, potassium, sodium, mixtures thereof. Still another preferred catalyst contains, in addition to the noble metal component, a component from the group of tin, germanium and rhenium.

The dehydrogenation reaction conditions, as well as the catalytic composite, are selected to result in a relatively low conversion per pass, accompanied, however, by a relatively high selectivity to the desired olefinic hydrocarbons. Thus, while the conversion per pass might range from about 10.0 percent to about 35.0 percent, the selectivity of conversion will range from about 93.0 percent to about 97.0 percent, or higher. In view of the fact that the alkylation reactions are effected with a molar excess of paraffins over olefinic hydrocarbons, the high selectivity and relatively low conversion, in the dehydrogenation reaction zone, are advantageous.

The inventive concept, emcompassed by the present process, and a preferred embodiment, are illustrated in the accompanying drawing. The illustration is presented by way of a block-type flow diagram, in which each block represents one particular step, or stage of the process. Miscellaneous appurtenances, not believed necessary for a clear understanding of the present combination process, have been eliminated from the drawing. The use of such details as pumps, compressors, instrumentation and controls, heat-recovery circuits, miscellaneous valving, start-up lines and similar hardware is well within the purview of one skilled in the art. Similarly, with respect to the flow of materials throughout the system, only those principal streams required to illustrate the interconnection and interaction of the various conversion zones are presented; thus, internal recycle lines, and vent gas streams have also been eliminated.

With reference now to the drawing, the basic inventive concept is depicted by reforming zone 3 and I-cracking zone 6. Fractionator **10** serves to provide the various indicated streams. The drawing will be described in conjunction with a commercially scaled unit designed to process 25,000 Bbl./day of a heptane-plus, straightrun naphtha which has been subjected to hydrorefining for desulfurization and olefin saturation. Pertinent properties of the naphtha fraction include a gravity of 56.4 °API, an initial boiling point of about 194°F., a 50.0 percent volumetric distillation temperature of about 255°F. and an end boiling point of about 362°F.; a hydrocarbon-type analysis indicates that the charge stock contains approximately 44.4 percent by volume paraffins, 48.8 percent by volume naphthenes and **6.8%** by volume aromatics.

The fresh feed is introduced via line **1** into reforming zone **3** which constitutes a low-severity reforming system intended for the production of a maximum quantity of a normally liquid product effluent having a clear research octane rating of about or 90. Operating conditions are selected to maximize the dehydrogenation of naphthenes to aromatics while simultaneously minimizing the hydrocracking or paraffins. Therefore, the charge is catalytically reformed at conditions including a pressure of about **150** psig., a liquid hourly space velocity of 3.0, a hydrogen/hydrocarbon molal ratio of 6.0:1 and an average catalyst bed temperature of about 900°F. The catalytic composite is an alumina carrier material containing 0.60 percent by weight of platinum, 0.35 percent by weight of germanium and 0.95 percent by weight of combined chloride, all of which are computed on the basis of the elements.

The product stream is separated to provide an internal hydrogen-rich recycle gas stream and a heptane-plus concentrate. Although the entire normally liquid portion of the product effluent may be introduced via line 4 into I-cracking zone 6, it is preferred to introduce the hexane-minus portion into separation system 10, which technique is not illustrated, limiting the material in line **4** to heptane-plus hydrocarbons. Component yields and product distribution respecting the effluent from the catalytic reforming zone **3** are presented in the following Table I:

TABLE I

Reforming Zone Product Distribution

Component	Wt.%	Vol.%
Hydrogen	2.64	—
Methane	0.65	—
Ethane	0.80	—
Propane	1.10	1.59
Isobutane	0.47	0.63
N-butane	0.37	0.48
Isopentane	1.82	2.19
N-pentane	0.65	0.78
Hexane-plus	91.49	85.75

Catalytic reforming is a hydrogen-producing process, and the 2.64 percent by weight of hydrogen, or about 1,310 scf./Bbl., may be utilized to advantage in the I-cracking zone, or in the prior hydrorefining zone, wherein hydrogen-consuming reactions are effected. As previously stated, it is preferred to limit the feed to I-cracking zone **6** to the heptane-plus portion of the product effluent. Therefore, of the hexane-plus portion, the hexanes, in an amount of about 1,438 Bbl./day are withdrawn directly and introduced into separation system **10,** along with about 743 Bbl./day of pentanes.

The remaining portion, in an amount of about 20,000 Bbl./day, is introduced into the I-cracking zone **6** at conversion conditions including a hydrogen/hydrocarbon molal ratio of 6:1, a pressure of about 750 psig., a liquid hourly spaced velocity of 1.0 and a catalyst bed temperature ranging from 700°F. to 750°F., representing an increasing temperature gradient of 50°F. The catalyst is a composite of mordenite, 5.0 percent by weight of nickel and 1.0 percent by weight of palladium. A component yield and product distribution are presented in the following Table II:

TABLE II

I-Cracking Yields and Product Distribution

Component	Vol.%	Bbl./day
Hydrogen	(1007) (Scf./Bbl.)	—
Methane	82.5 (Scf./Bbl.)	—
Ethane	16.5 (Scf./Bbl.)	—
Propane	23.1	1823
Isobutane	72.2	5700
N-butane	9.5	750
Isopentane	10.5	810
N-pentane	1.8	142
Isohexane	7.0	553
N-hexane	1.4	111
Heptane-plus	—	15,754

The distinct advantages of these particular hydrocracking reactions are readily ascertained from the foregoing Table II. A total of 6,450 Bbl./day of butanes are produced, of which about 88.4% by volume are isobutanes. With respect to all the butanes, pentanes and hexanes, of the 8,066 Bbl./day, 87.6 percent by volume are of the isoformation. Of the isohexanes produced, 55 Bbl./day constitutes 2,2-dimethylbutane, 63 Bbl./day is 2,3-dimethylbutane, 285 Bbl./day is 2-methylpentane and there are 15 Bbl./day of 3-methylpentane.

The effluent from I-cracking zone **6** passes via line **7** into separation zone 8; where a hydrogen rich gaseous stream comprising small quantities of methane and ethane is recovered and recycled via line **2** to the inlet of reforming zone **3.** The liquid stream recovered from

separation zone **8** is removed via line **9** to fractionator **10** where methane and ethane are recovered via line **11**; propane and butane via line **12**; and pentane and hexane via line **13**. The heptane-plus material, in an amount of about 13,016 Bbl./day, is recovered via line **14**.

The following TAble III summarizes the foregoing which is illustrative of the present inventive concept.

TABLE III

Overall Volumetric Yields and Product Distribution

Component	Vol.%*	Bbl./day
Propane	9.21	2,253
Isobutane	24.02	5,870
N-butane	3.60	880
Isopentane	5.74	1,402
N-pentane	1.44	353
2,2-dimethyl butane	0.23	55
2,3-dimethyl butane	0.27	63
2-methyl pentane	1.17	285
3-methyl pentane	0.62	151
N-hexane	0.45	111
Aromatic Gasoline	53.25	13,016
TOTALS	100.00	24,439

*Percent of Total Product Slate

As indicated in the foregoing Table III, 75.54 percent of the fresh feed in line **1** was converted into the desired aromatic hydrocarbons and isobutane concentrate. The aromatic hydrocarbon stream is generally considered to have a clear research octane rating of 115.0 and, when blended with the total pentanes and hexanes, will produce an unleaded gasoline pool of the character shown in Table IV. It is understood that the make-up of the gasoline pool will change to the extent that butanes are employed to produce the desired vapor pressure.

TABLE IV

Clear Gasoline Pool, Case I

Component	Bbl./day	Vol.%	Research Octane
Isopentane	1,402	9.08	93
N-pentane	353	2.29	62
2,2-DiMeBu	55	0.36	92
2,3-DiMeBu	63	0.41	104
2-Mepe	285	1.85	74
3-MePe	151	0.98	74
N-hexane	111	0.71	25
Aromatics	13,016	84.32	115
TOTALS:	15,436	100.00	109.9

The 2,253 Bbl./day of propane can be subjected to dehydrogenation to produce propylene which is then converted via hydrolysis into isopropyl alcohol having a clear research octane rating approximating 110 to 120. This technique will serve to increase both the yield and octane rating of the unleaded gasoline pool. On the other hand, the propylene might be utilized in an alkylation reaction zone for the production of a C_3-alkylate stream which has a clear research octane rating of about 92.0.

A preferred embodiment, utilizing the essence of the present invention as above set forth, involves the use of both an alkylation reaction zone and an isomerization zone. In this integrated refinery scheme, the aromatic concentrate from fractionator **10** is introduced directly, into an unleaded gasoline pool, the propane is a by-product stream, isopentane and isohexane are directly introduced into the gasoline pool and the 464 Bbl./day of n-pentane/h-hexane concentrate is introduced into an isomerization zone.

The isomerization zone utilizes a fixed-bed catalytic composite of alumina, 4.0 percent by weight of aluminum chloride and 0.375 percent by weight of platinum. Operating conditions include a pressure of about 300 psig., a temperature of 330°F. and a hydrogen/hydrocarbon molal ratio of about 1.0:1.0; the reactants traverse the catalyst bed at a liquid hourly space velocity averaging 1.0. Isomeric conversion of about 99.0 percent efficient, and with the volumetric increase due to molecular size, and conversion of some hexane to isopentane, 359 Bbl./day of isopentane, 38 Bbl./day of 2,2-dimethyl butane, 12 Bbl./day of 2,3-dimethyl butane, 36 Bbl./day of 2-methyl pentane and 21 Bbl./day of 3-methyl pentane are introduced.

A butane stream may be processed in a dehydrogenation zone. In order to produce the olefins which are introduced into an alkylation zone to produce a C_4-alkylate having an octane rating of 97.0. In the present situation, sufficient olefins are available from a fluid catalytic cracking unit and, therefore, the butane concentrate is introduced directly into an alkylation zone. The 5,870 Bbl./day of isobutane requires 5,111 Bbl./day of outside butylenes to produce 9,044 Bbl./day of C_4- alkylate which is sent to the clear gasoline pool. The reaction time, utilizing a pumped acid settler/reactor system, is about nine minutes, and the acid to hydrocarbon ratio, using hydrofluoric acid, is 1.5:1.0. Alkylation reactions are effected at a temperature of about 100°F. and a pressure of about 20 atmospheres.

One preferred technique constitutes introducing the 880 Bbl./day of normal butane into an isomerization zone for conversion into additional isobutane which is subsequently alkylated in the alkylation zone. At a conversion efficiency of 99.0 percent, and with the volumetric increase due to molecular size, and additional 904 Bbl./day of isobutane becomes available. Thus, the 6,774 Bbl./day of isobutane will require 5,890 Bbl./day of outside butylenes to produce 10,430 Bbl./day of C_4-alkylate.

The unleaded gasoline pool, including all the C_4-alkylate, has the characteristics shown in the following Table V.

TABLE V

Clear Gasoline Pool, Case II

Component	Bbl./day	Vol.%	Research Octane
Isopentane	1,761	6.81	93
2,2-DiMeBu	93	0.36	92
2,3-DiMeBu	75	0.29	104
2-MePe	321	1.24	74
3-MePe	172	0.66	74
Aromatics	13,016	50.32	115
C_4 Alkylate	10,430	40.32	97
TOTALS:	25,868	100.00	105.3

Based upon the 25,000 Bbl./day of fresh feed charge stock and the additional 5,890 Bbl./day of outside bu-

tylenes, the volumetric yield of the unleaded gasoline pool, having a clear octane rating of 105.3, is 83.7 percent. The foregoing demonstrates the method by which the present invention is effected and the benefits afforded through the utilization thereof.

I claim as my invention:

1. A process for the simultaneous production of an aromatic concentrate and isobutane, from a naphtha boiling range charge stock, which process comprises the steps of:

a. reacting said charge stock, in a low-severity catalytic reforming zone, at reforming conditions including greater than about 90 mol percent conversion of naphthenes to aromatics and less than about 40 mol percent conversion of paraffins to aromatics, to produce a reformate containing aromatic and paraffin hydrocarbons;

b. further reacting at least a portion of the resulting reformed product effluent with hydrogen, in a hydrocracking reaction zone, at hydrocracking conditions and in contact with a hydrocracking catalyst comprising a mordenite carrier material, a palladium component and a nickel component to form isobutane; and,

c, recovering said aromatic concentrate and isobutane from the resulting hydrocracking reaction zone effluent.

2. The process of claim **1** further characterized in that said reformed product effluent is reacted in said hydrocracking reaction zone without intermediate separation thereof.

3. The process of claim **1** further characterized in that said hydrocracking catalyst comprises mordenite carrier material, containing alumina fixed in combination therewith, a sulfided palladium component and a sulfided nickel component.

4. The process of claim **3** further characterized in that said hydrocracking catalyst comprises a carrier material of alumina and from about **60%** to about **90%** by weight of mordenite.

5. The process of claim **1** further characterized in that said hydrocracking catalyst contains from about 0.01 percent to about 2 percent by weight of said palladium component and from about 0.01 percent to about 10 percent by weight of said nickel component, calculated as the elements thereof.

6. The process of claim **1** further characterized in that said hydrocracking conditions include a maximum catalyst bed temperature of from 650°F. to about 850°F., a pressure in the range of 150 to 1,000 psig., a liquid hourly space velocity of about 1.0 to about **10** and a hydrogen circulation rate of 3,000 to about 20,000 scf./Bbl.

7. The process of claim **1** further characterized in that said hydrocracking reaction zone effluent is separated to recover a pentane/hexane concentrate.

8. The process of claim **7** further characterized in that said pentane/hexane is reacted with hydrogen in a hydroisomerization reaction zone at isomerizing conditions selected to produce isomers thereof.

9. The process of claim **1** further characterized in that said isobutane is reacted with an olefinic hydrocarbon, in an alkylation reaction zone, at alkylating conditions selected to produce a normally liquid alkylated hydrocarbon stream.

10. The process of claim **9** further characterized in that said olefinic hydrocarbon is produced by dehydrogenating a propane/butane concentrate separately recovered from said hydrocracking reaction zone effluent.

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