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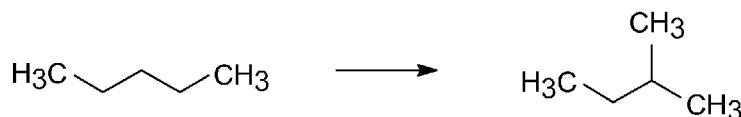
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(54) **Title:** FLEXIBLE UNIT FOR ISOMERIZATION AND DISPROPORTIONATION OF HYDROCARBONS USING SOLID ACID CATALYSTS

**FIG. 1**

(57) **Abstract:** A flexible hydrocarbon conversion process utilizing the same reaction zone for isomerization and disproportionation is described. The feed and type of products are selected. The hydrocarbon feed is contacted with a catalyst and in the presence of hydrogen and an added chloride promoter. The catalyst comprises a solid catalyst comprising a refractory inorganic oxide having a metal halide dispersed thereon. The operating conditions are varied depending on whether isomerization or disproportionation is desired.



FLEXIBLE UNIT FOR ISOMERIZATION AND DISPROPORTIONATION
OF HYDROCARBONS USING SOLID ACID CATALYSTS

STATEMENT OF PRIORITY

This application claims priority to U.S. Application No. 14/562,411 which was
5 filed December 05, 2014, the contents of which are hereby incorporated by reference in its
entirety.

BACKGROUND OF THE INVENTION

The isomerization of light naphtha has become an important process for the
upgrading of petroleum refiners' gasoline pool. The removal of lead antiknock additive from
10 gasoline and the rising demands of high-performance internal-combustion engines increased
the need for "octane," or knock resistance, in the gasoline pool. Isomerization processes have
been used to improve the low octane numbers (RON) of light straight run naphtha.
Isomerization processes involve reacting one mole of a hydrocarbon (e.g., normal pentane) to
form one mole of an isomer of that specific hydrocarbon (e.g., isopentane), as shown in Fig.
15 1. The total number of moles remains the same throughout this process, and the product has
the same number of carbons as the reactant.

However, with the increase in isomerization, there is also an increase in the
Reid vapor pressure (RVP) of the product. The RVP of gasoline has been utilized by the
Environmental Protection Agency as a means of regulating volatile organic compounds
20 emissions by transportation fuels and for controlling the formation of ground level ozone, and
it is stricter in the summer months. As these regulations become more stringent and as more
ethanol (which has a high vapor pressure) is blended into gasoline, C5 paraffins need to be
removed from the gasoline pool. Moreover, the need to remove components may also extend
to some C6 paraffins. This may result in refiners being oversupplied with C5 paraffins and
25 possibly C6 paraffins.

Disproportionation reactions offer a possible solution to the problem of excess
C5 and C6 paraffins during these time periods. The disproportionation of paraffins (e.g.,
isopentane (iC5)) involves reacting two moles of hydrocarbon to form one mole each of two
different products, one having a carbon count greater than the starting material and the other

Disproportionation reactions differ from cracking reactions in which one mole of a hydrocarbon forms two moles of product, each with a lower carbon number than the starting material.

During the winter months, when the RVP specifications are more relaxed, isomerization of light naphtha would become more favorable for the refiner.

SUMMARY OF THE INVENTION

One aspect of the invention is a flexible hydrocarbon conversion process utilizing the same reaction zone for isomerization and disproportionation. In one embodiment, the process includes selecting a hydrocarbon feed, and isomerization products or disproportionation products. If the isomerization products are selected, the hydrocarbon feed is contacted in the reaction zone with a catalyst in the presence of hydrogen and a first added chloride promoter under isomerization conditions to obtain the selected isomerization products. The catalyst comprises a solid catalyst comprising a refractory inorganic oxide having a metal halide dispersed thereon. The hydrogen is present in a mole ratio of hydrogen to hydrocarbon feed of 0.05:1 to 5:1, the first added chloride promoter is present in an amount in a range of 30 ppm to 400 ppm, and a mole ratio of hydrogen to chloride from the added chloride promoter is in a range of 100:1 to 5000:1. If the disproportionation products are selected, the hydrocarbon feed is contacted in the reaction zone with the catalyst in the presence of hydrogen and a second added chloride promoter under disproportionation conditions to obtain disproportionation products. The hydrogen is present in a mole ratio of hydrogen to hydrocarbon feed of greater than 0:1 to less than 0.1:1, the second added

SUMMARY OF THE INVENTION

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chloride promoter is present in an amount of at least 100 ppm to 5000 ppm, and a mole ratio of hydrogen to chloride from the added chloride promoter is in a range of greater than 0:1 to 100:1.

BRIEF DESCRIPTION OF THE DRAWINGS

- 5 Fig. 1 illustrates the isomerization reaction of n-pentane.
 Fig. 2 illustrates the disproportionation reaction of iso-pentane.
 Fig. 3 is a schematic of one embodiment of the process of present invention.

DETAILED DESCRIPTION OF THE INVENTION

- 10 The present invention provides a process that can be switched between isomerization and disproportionation by changing the operating conditions. As a result, the same reaction zone and catalyst can be used. This would allow the refiner to modify the operating conditions as the seasons change or as product demands change to go from isomerization to disproportionation and back.

- 15 During a first time period, for example, in the summer months, light naphtha would be separated into C_5 and C_6 stream in a splitter. The C_6 stream could be sent to a reformer, a standard isomerization zone, or directly to a gasoline stream. The C_5 stream would be sent to the reaction zone utilizing catalyst described below.

- 20 As used herein, C_x means hydrocarbon molecules that have "X" number of carbon atoms, C_x^+ means hydrocarbon molecules that have "X" and/or more than "X" number of carbon atoms, and C_x^- means hydrocarbon molecules that have "X" and/or less than "X" number of carbon atoms.

- 25 As used herein, the term "stream" can include various hydrocarbon molecules and other substances. Moreover, the term "stream comprising C_x hydrocarbons" can include a stream comprising hydrocarbon with "x" number of carbon atoms, suitably a stream with a majority of hydrocarbons with "x" number of carbon atoms and preferably a stream with at least 75 wt % hydrocarbons with "x" number of carbon atoms. Where a stream is identified as comprising C_x and $C_{x'}$ hydrocarbons, the stream preferably has at least 75 wt % hydrocarbons with "x" and "x'" number of carbon atoms. Moreover, the term "stream comprising C_{x+}
30 hydrocarbons" can include a stream comprising a majority of hydrocarbon with more than or equal to "x" carbon atoms and suitably less than 10 wt % and preferably less than 1 wt %

hydrocarbon with $x-1$ carbon atoms. Lastly, the term " C_x -stream" can include a stream comprising a majority of hydrocarbon with less than or equal to " x " carbon atoms and suitably less than 10 wt % and preferably less than 1 wt % hydrocarbon with $x+1$ carbon atoms.

5 As used herein, the term "zone" can refer to an area including one or more equipment items and/or one or more sub-zones. Equipment items can include one or more reactors or reactor vessels, heaters, exchangers, pipes, pumps, compressors, controllers and columns. Additionally, an equipment item, such as a reactor, dryer, or vessel, can further include one or more zones or sub-zones.

10 As used herein, the term "about" means within 10% of the value, or within 5%, or within 1%.

It has been found that solid acid catalysts can be used to catalyze hydrocarbon disproportionation reactions. The catalyst comprises a refractory inorganic oxide having a metal halide dispersed thereon. There can optionally be a Group VIII metal component
15 dispersed thereon. The reaction takes place in the presence of hydrogen and a chloride promoter.

Fig. 3 illustrates one embodiment of the process 100. The hydrocarbon feed
105 is introduced into the disproportionation reaction zone 110.

The hydrocarbon feed 105 comprises hydrocarbons capable of isomerization
20 or disproportionation. One example of a suitable hydrocarbon feed 105 comprises alkanes having 4 to 7 carbon atoms. These may be contained in streams from petroleum refining, synthetic-fuel production, and biomass conversion, for example. Suitable streams from petroleum refining include, but are not limited to, natural gas liquids (NGLs), liquefied petroleum gas (LPGs), light straight-run naphtha, light naphtha, light natural gasoline, light
25 reformate, light raffinate from aromatics extraction, light cracked naphtha, butanes, normal-butane concentrate, field butanes and the like. An especially preferred feedstock is light straight-run naphtha, containing more than 50% of C_5 and C_6 paraffins with a high concentration of low-octane normal paraffins. The light straight-run naphtha and other feedstocks also may contain naphthenes, aromatics, olefins, and hydrocarbons heavier than
30 C_6 . The olefin content should be limited to a maximum of 10% and the content of

hydrocarbons heavier than C₆ to 20% for effective control of hydrogen consumption, cracking reactions, heat of reaction and catalyst activity.

The hydrocarbon feed 105 may need to be treated to remove sulfur-, nitrogen- and oxygen-containing compounds to prevent them from poisoning the disproportionation catalyst. The feedstock may be treated by any method that will remove water, sulfur-, nitrogen- and oxygen-containing compounds. Sulfur may be removed from the feed stream by hydrotreating. Adsorption systems for the removal of sulfur-, nitrogen- and oxygen-containing compounds and water from hydrocarbon streams are well known to those skilled in the art.

The isomerization or disproportionation reaction takes place in the presence of hydrogen 115 which has been shown to increase the catalyst stability significantly. The hydrogen 115 can be introduced into the system dissolved in the hydrocarbon feed 105 or directly into the disproportionation reaction zone 110. The hydrogen 115 may be supplied totally from outside the process or supplemented by hydrogen recycled to the feed after separation from reactor effluent. Light hydrocarbons and small amounts of inerts such as nitrogen and argon may be present in the hydrogen. Water should be removed from hydrogen supplied from outside the process, preferably by an adsorption system as is known in the art.

For isomerization reactions, the mole ratio of hydrogen 115 to hydrocarbon feed 105 is in the range of 0.05:1 to 5:1, or 0.1:1 to 5:1, or 0.15:1 to 5:1, or 0.2:1 to 5:1, or 0.05:1 to 2:1, or 0.05:1 to 1:1, or 0.05:1 to 0.5:1.

For disproportionation reactions, the mole ratio of hydrogen 115 to hydrocarbon feed 105 is in the range of greater than 0:1 to 2:1, or 0:1 to 1.5:1, or 0:1 to 0.75:1, or 0:1 to 0.5:1, or 0:1 to 0.3:1, or 0:1 to 0.1:1, or 0:1 to 0.05:1, or 0:1 to 0.02:1, or 0:1 to 0.01:1, or 0.01:1 to 0.05:1.

The isomerization and disproportionation reaction take place in the presence of an added chloride promoter 120. The chloride promoter typically comprises carbon tetrachloride, tetrachloroethylene, propyldichloride, butylchloride, chloroform, 2-chloro-2-methylpropane, 2-chloropropane, 2-chloro-2-methylbutane, 2-chloropentane, 1-chlorohexane, 3-chloro-3-methylpentane, 2-chlorobutane, or combinations thereof.

For isomerization reactions, the chloride concentration of the added chloride promoter is typically in the range of greater than 0 to 5000 ppm, or greater than 0 to 1000 ppm, or greater than 0 to 500 ppm, or greater than 0 to 400 ppm, or 30 to 400 ppm, or 30 to 300 ppm.

5 For disproportionation reactions, the chloride concentration of the added chloride promoter is typically in the range of greater than 0 to 5000 ppm, and it typically ranges from 100 ppm to 5000 ppm, or 200 ppm to 5000 ppm, or 400 ppm to 5000 ppm, or 600 ppm to 5000 ppm, or 800 ppm to 5000 ppm, or 1000 ppm to 5000 ppm, or 1200 ppm to 5000 ppm, or 1400 ppm to 5000 ppm, or 1600 ppm to 5000 ppm.

10 The chloride promoter 120 can be added to the hydrocarbon feed 105, for example being dissolved in the hydrocarbon feed, or directly to the disproportionation reaction zone 110.

For isomerization reactions, the mole ratio of hydrogen to chloride from the added chloride promoter is in the range of greater than 0:1 to 5000:1, or 50:1 to 5000:1, or 15 75:1 to 5000:1, or 100:1 to 5000:1, or 150:1 to 5000:1, or 175:1 to 5000:1, or 200:1 to 5000:1, or 225:1 to 5000:1.

For disproportionation reactions, the mole ratio of hydrogen to chloride from the added chloride promoter is in the range of greater than 0:1 to 5000:1, or 0:1 to 2500:1, or 0:1 to 1000:1, or 0:1 to 750:1, or 0:1 to 500:1, or 0:1 to 250:1, or 0:1 to 225:1, or 0:1 to 200:1, or 0:1 to 175:1, or 0:1 to 150:1, or 0:1 to 125:1, or 0:1 to 100:1, or 0:1 to 75:1, or 0:1 20 to 50:1, or 0:1 to 25:1, or 0:1 to 15:1, or 0:1 to 5:1, or 1:1 to 10:1, or 1:1 to 5:1.

In some embodiments for isomerization reactions, the mole ratio of hydrogen to hydrocarbon is 0.05:1 to 5:1, the chloride concentration is 30 ppm to 400 ppm, and the mole ratio of hydrogen to chloride is 100:1 to 5000:1.

25 In some embodiments for disproportionation reactions, the mole ratio of hydrogen to hydrocarbon is greater than 0:1 to 0.1:1, the chloride concentration is 100 ppm to 5000 ppm, and the mole ratio of hydrogen to chloride is greater than 0:1 to 100:1.

By selecting an appropriate combination of mole ratio of hydrogen to hydrocarbon feed, chloride concentration, and mole ratio of hydrogen to chloride for a given catalyst, the selectivity for isomerization products can be at least 5 %, or at least 10 %, or at least 15 %, or at least 20 %, or at least 25 %, or at least 30% or at least 35%, or at least 40%,
 5 or at least 45%, or at least 50%, or at least 55%, or at least 60%, or at least 65%, or at least 70%, or at least 75%, or at least 80%. The % selectivity for the disproportionation reaction is defined as: $[(\text{sum of the wt.\% } C_{x-} \text{ and } C_{x+} \text{ compounds}) / (100 - \text{wt.\% } C_x \text{ feed})] \times 100$. When the feed contains n- C_x and i- C_x , part of the n- C_x or i- C_x can isomerize depending on the initial feed concentrations and the equilibrium constant. In the case where isomerization of n- C_x to
 10 i- C_x occurs, the % selectivity for the disproportionation reaction is $(\text{wt.\% } C_{(x-1)-} \text{ in product} + \text{wt.\% } C_{(x+1)+} \text{ in product} - \text{wt.\% } C_{(x-1)-} \text{ in feed} - \text{wt.\% } C_{(x+1)+} \text{ in feed}) / (\text{wt.\% } nC_x \text{ in feed} - \text{wt.\% } nC_x \text{ in product}) \times 100$. As the feed composition increases in complexity, a simple equation similar to these may not be adequate. The % selectivity for the C_{x+} disproportionation products is defined as: $[(\text{sum of the } C_{x+} \text{ compounds}) / (100 - \text{wt.\% } C_x \text{ feed})] \times 100$ and can be at
 15 least 5 %, or at least 10 %, or at least 15 %, or at least 20 %, or at least 25 %.

By selecting an appropriate combination of mole ratio of hydrogen to hydrocarbon feed, chloride concentration, and mole ratio of hydrogen to chloride for a given catalyst, the selectivity for disproportionation products can be at least 5 %, or at least 10 %, or at least 15 %, or at least 20 %, or at least 25 %, or at least 30% or at least 35%, or at least
 20 40%, or at least 45%, or at least 50%, or at least 55%, or at least 60%, or at least 65%, or at least 70%, or at least 75%, or at least 80%.

For example, with an nC5 feed, at a mole ratio of hydrogen to hydrocarbon of 0.02, a mole ratio of hydrogen to chloride of 5, and a chloride concentration of 1600 ppm, the selectivity for the disproportionation products was over 50%.

25 The hydrocarbon feed 105 in admixture with hydrogen 115 and the chloride promoter 120 contacts the catalyst in a reaction zone 110 to obtain the isomerization or disproportionation products. The hydrocarbon feed 105 can be pre-heated with heat exchangers 125 and 130 and heater 135, for example.

The reaction zone 110 may be in a single reactor or two or more separate
 30 reactors with suitable heaters between them to ensure that the desired temperature is

maintained at the entrance to each reactor. The reactants may be contacted with the catalyst in upward, downward, or radial flow fashion. The reactants may be in the liquid phase, a mixed liquid-vapor phase, or a vapor phase when contacted with the catalyst, with excellent results being obtained with primarily liquid-phase operation. Contacting may be effected using the catalyst in a fixed-bed system, a moving-bed system, a fluidized-bed system, or in a batch-type operation.

As illustrated, the reaction zone 110 includes two reactors 140, 145. The hydrocarbon feed 105 with the hydrogen 115 and chloride promoter 120 enters reactor 140 where it contacts the catalyst. The effluent 150, which contains unreacted hydrocarbon feed and reaction products, is sent to heat exchanger 130 to exchange heat with the incoming hydrocarbon feed 105 and then to reactor 145 where it contacts the catalyst. Effluent 155, which contains unreacted hydrocarbon feed and reaction products from reactor 145 as well as from reactor 140, is sent to heat exchanger 125 and then to separation zone 160.

Suitable isomerization reaction conditions include a temperature in the range of 40°C to 300°C, or 40°C to 250°C, or 40°C to 200°C, or 110°C to 250°C. The pressure is generally in the range of 0 MPa (g) to 13.8 MPa (g), or 0 MPa (g) to 10.0 MPa (g), or 0 MPa (g) to 7.5 MPa (g), or 0 MPa (g) to 5.0 MPa (g), or 0 MPa (g) to 3.5 MPa (g), or 1 MPa (g) to 4 MPa (g). The liquid hourly space velocity (LHSV) is generally in the range of 0.25 hr⁻¹ to 10 hr⁻¹, or 0.25 hr⁻¹ to 7 hr⁻¹, or 0.25 hr⁻¹ to 5 hr⁻¹, or 0.25 hr⁻¹ to 3 hr⁻¹, or 0.25 hr⁻¹ to 2 hr⁻¹, or 0.5 hr⁻¹ to 2 hr⁻¹, or 1 hr⁻¹ to 2 hr⁻¹. The contacting time is in the range of a few seconds to hours, or 0.5 min to 10 hr, or 0.5 min to 8 hr, or 0.5 min to 6 hr, or 0.5 min to 4 hr, or 0.5 min to 2 hr, or 0.5 min to 1 hr, or 1 min to 1 hr, or 5 min to 1 hr.

Suitable disproportionation reaction conditions include a temperature in the range of 100°C to 300°C, or 150°C to 300°C, or 175°C to 300°C, or 200°C to 300°C, or 225°C to 300°C, or 250°C to 300°C. The pressure is generally in the range of 0 MPa (g) to 13.8 MPa (g), or 0 MPa (g) to 10.0 MPa (g), or 0 MPa (g) to 7.5 MPa (g), or 0 MPa (g) to 5.0 MPa (g), or 0 MPa (g) to 3.5 MPa (g). The liquid hourly space velocity (LHSV) is generally in the range of 0.25 hr⁻¹ to 10 hr⁻¹, or 0.25 hr⁻¹ to 7 hr⁻¹, or 0.25 hr⁻¹ to 5 hr⁻¹, or 0.25 hr⁻¹ to 3 hr⁻¹, or 0.25 hr⁻¹ to 2 hr⁻¹, or 0.5 hr⁻¹ to 2 hr⁻¹, or 1 hr⁻¹ to 2 hr⁻¹. The contacting time is in the

range of a few seconds to hours, or 0.5 min to 10 hr, or 0.5 min to 8 hr, or 0.5 min to 6 hr, or 0.5 min to 4 hr, or 0.5 min to 2 hr, or 0.5 min to 1 hr, or 1 min to 1 hr, or 5 min to 1 hr.

The reaction zone 110 contains a catalyst. The catalyst is a solid acid catalyst comprising a refractory inorganic oxide having a metal halide dispersed thereon. There can optionally be a Group VIII metal component dispersed thereon.

Suitable refractory inorganic oxides include, but are not limited to, alumina, titania, zirconia, chromia, zinc oxide, magnesia, thoria, boria, silica, aluminum phosphate, silica-alumina, silica-magnesia, chromia-alumina, alumina-boria, silica-zirconia and other mixtures thereof.

Alumina is a suitable refractory inorganic oxide for use in the process. Suitable alumina materials are the crystalline aluminas known as gamma-, eta-, and theta-alumina. Zirconia, alone or in combination with alumina, comprises an alternative inorganic-oxide component of the catalyst. In some embodiments, the refractory inorganic oxide can have an apparent bulk density of 0.3 to 1.01 g/cc and surface area characteristics such that the average pore diameter is 20 to 300 angstroms, the pore volume is 0.05 to 1 cc/g, and the surface area is 50 to 500 m²/g.

The alumina can be formed into any desired shape or type of carrier material known to those skilled in the art such as rods, pills, pellets, tablets, granules, extrudates, and like forms by methods well known to the practitioners of the catalyst material forming art. Spherical carrier particles may be formed, for example, from this alumina by: (1) converting the alumina powder into an alumina sol by reaction with a suitable peptizing acid and water and thereafter dropping a mixture of the resulting sol and a gelling agent into an oil bath to form spherical particles of an alumina gel which are easily converted to a gamma-alumina carrier material by known methods; (2) forming an extrudate from the powder by established methods and thereafter rolling the extrudate particles on a spinning disk until spherical particles are formed which can then be dried and calcined to form the desired particles of spherical carrier material; and (3) wetting the powder with a suitable peptizing agent and thereafter rolling the particles of the powder into spherical masses of the desired size.

The extrudate particle form of the carrier material may be prepared by mixing alumina powder with water and suitable peptizing agents such as nitric acid, acetic acid, aluminum nitrate, and the like material until an extrudable dough is formed. The amount of water added to form the dough is typically sufficient to give a Loss on Ignition (LOI) at 500°C of 30 to 65 mass %. The acid addition is generally sufficient to provide 2 to 7 mass % of the volatile-free alumina powder used in the mix. Preferably from 0.1 to 10 mass-% of an extrusion aid such as Methocel, and more preferably from 1 to 5 mass-%, is included in the mix. The resulting dough optimally is then mulled and extruded through a suitably sized die to form extrudate particles as described hereinabove.

The extrudate particles are dried at a temperature of 150°C to 200°C, and then calcined at a temperature of 400°C to 800°C for a period of 0.2 to 10 hours to create the preferred form of the refractory inorganic oxide catalyst base. The calcination is typically effected within a temperature range of from 545°C to 610°C, or 560°C to 580°C. In some embodiments, the calcination conditions are established to provide a finished-catalyst surface area of 150 to 280 m² /g (or 150 to 230 m² /g) with an average pore diameter of from 35 to 60 angstroms.

Another component of the catalyst of the present invention is a metal halide, such as a Friedel-Crafts type metal halide. Suitable metal halides of the Friedel-Crafts type include aluminum chloride, aluminum bromide, ferric chloride, ferric bromide, zinc chloride and the like compounds, with the aluminum halides and particularly aluminum chloride ordinarily yielding the best results. Generally, this component can be incorporated into the catalyst using any of the conventional methods for adding metallic halides of this type. Good results are obtained when the metallic halide is sublimed onto the surface of the support. Further details concerning one method of sublimation are disclosed in U.S. Pat. No. 2,999,074, for example.

In some embodiments, when the calcined refractory inorganic-oxide support is loaded with a metal halide component, the presence of chemically combined hydroxyl groups in the refractory inorganic oxide allows a reaction to occur between the metal halide and the hydroxyl group of the support. For example, aluminum chloride reacts with the hydroxyl groups in the preferred alumina support to yield Al-O-AlCl₂ active centers which enhance the

catalytic behavior of the catalyst. Since chloride ions and hydroxyl ions occupy similar sites on the support, more hydroxyl sites will be available for possible interaction with the metal halide when the chloride population of the sites is low. In some embodiments, the metal halide may be impregnated onto the catalyst by sublimation of the metal halide onto the calcined support under conditions to combine the sublimed metal halide with the hydroxyl groups of the calcined support. This reaction is typically accompanied by the elimination of 0.5 to 2.0 moles of hydrogen chloride per mole of metal halide reacted with the inorganic-oxide support. In subliming aluminum chloride, which sublimates at 184°C, suitable loaded temperatures range from 190°C to 750°C, with a preferable range being from 200°C to 650°C. The sublimation can be conducted at atmospheric pressure or under increased pressure and in the presence or absence of diluent gases such as hydrogen or light paraffinic hydrocarbons or both. The impregnation of the metal halide may be conducted batch-wise. One preferred method for impregnating the calcined support is to pass sublimed AlCl_3 vapors, in admixture with a carrier gas such as hydrogen, through a calcined catalyst bed. This method both continuously deposits and reacts the aluminum chloride and also removes the evolved HCl.

The amount of metal halide combined with the calcined support may range from 0.1 up to 30 mass % to the metal-halide-free, calcined composite, or 0.1 up to 25 mass %, or 0.1 up to 20 mass %, or 0.1 up to 15 mass %. The final composite containing the sublimed Friedel-Crafts metal halide is treated to remove the unreacted metal halide by subjecting the composite to a temperature above the sublimation temperature of the metal halide for a time sufficient to remove from the composite any unreacted metal halide. In the case of AlCl_3 , temperatures of 400°C to 650°C, and times of from 1 to 48 hours are sufficient.

In some embodiments, the refractory inorganic oxide support can be pretreated with HCl to convert the Al-OH bonds to Al-Cl before loading with the AlCl_3 .

An optional ingredient of the catalyst is a Group VIII metal component. Of the Group VIII metals, platinum group metals, e.g., platinum, palladium, rhodium, ruthenium, osmium and iridium, are preferred, particularly platinum. Mixtures of Group VIII metals can also be used. This component may exist within the final catalytic composite as a compound

such as an oxide, sulfide, halide, or oxyhalide, in chemical combination with one or more of the other ingredients of the composite, or as an elemental metal. Best results are obtained when substantially all of this component is present in the elemental state. This component may be present in the final catalyst composite in any amount which is catalytically effective, but relatively small amounts are preferred. In fact, the surface-layer Group VIII metal component generally will comprise 0.01 to 2 mass % of the final catalyst, calculated on an elemental basis. Excellent results are obtained when the catalyst contains 0.05 to 1 mass % of platinum.

Typical platinum-group compounds which may be employed in preparing the catalyst of the invention are chloroplatinic acid, platinum dichloride, ammonium chloroplatinate, bromoplatinic acid, platinum tetrachloride hydrate, dicarbonylplatinum dichloride, dinitrodiaminoplatinum, palladium chloride, palladium chloride dihydrate, palladium nitrate, etc. Chloroplatinic acid is preferred as a source of the preferred platinum component. A surface-layer platinum component may be impregnated onto the catalyst from a solution of chloroplatinic acid in the absence of strong mineral acids such as hydrochloric and nitric acid.

In some embodiments, the platinum-group metal component is concentrated in the surface layer of each catalyst particle. A "surface-layer" component has a concentration in the micron surface layer of the catalyst particle that is at least 1.5 times the concentration in the central core of the catalyst particle. Preferably, the surface-layer concentration of platinum-group metal is at least twice the concentration in the central core. As exemplified herein below, the surface layer may be 100 or 150 microns deep and the central core may be 50% of the volume or 50% of the diameter of the particle; however, other quantitative criteria are not excluded thereby. Further details of the characteristics and preparation of a surface-layer platinum-group metal component are contained in U.S. Pat. No. 5,004,859, for example.

The catalyst may contain other metal components known to modify the effect of the Group VIII metal component. Such metal modifiers may include rhenium, tin, germanium, lead, cobalt, nickel, indium, gallium, zinc, uranium, dysprosium, thallium, and mixtures thereof. Catalytically effective amounts of such metal modifiers may be

incorporated into the catalyst by any means known in the art. In some embodiments, the catalyst consists essentially of the alumina support, a metal halide, and a platinum-group metal component. This formulation is free of modifier metals, such as tin or indium or halogen other than in the metal halide.

5 If a Group VIII metal is included, it can be added before the metal halide. In this case, the composite of the alumina and Group VIII metal is dried and calcined before addition to the metal halide. The drying is carried out at a temperature of 100°C to 300°C, followed by calcination or oxidation at a temperature of from 375°C to 600°C in an air or oxygen atmosphere for a period of 0.5 to 10 hours in order to convert the metallic
10 components substantially to the oxide form.

 In some embodiments, the resultant oxidized catalytic composite is subjected to a substantially water-free and hydrocarbon-free reduction step prior to its use in the conversion of hydrocarbons. This step is designed to selectively reduce the platinum-group metal component to the corresponding elemental metal and to insure a finely divided
15 dispersion of the metal component throughout the carrier material. Preferably, substantially pure and dry hydrogen (i.e., less than 20 vol. ppm H₂O) is used as the reducing agent in this step. The reducing agent is contacted with the oxidized composite at conditions including a temperature of 425°C to 650°C and a period of time of 0.5 to 2 hours to reduce substantially all of the platinum-group component to its elemental metallic state. This reduction treatment
20 may be performed in situ as part of a start-up sequence if precautions are taken to pre-dry the plant to a substantially water-free state and if substantially water-free and hydrocarbon-free hydrogen is used. Contact with water in general is to be avoided as water will deactivate the catalyst. Thus, both catalyst treatment and operation should be substantially water free.

 The catalyst may contain an additional halogen component. The halogen
25 component may be either fluorine, chlorine, bromine or iodine or mixtures thereof or an organic polyhalo component. Chlorine is the preferred halogen component. The halogen component is generally present in a combined state with the inorganic-oxide support. Although not essential to the invention, the halogen component is preferably well dispersed throughout the catalyst. The halogen component may comprise from more than 0.2 to 15
30 mass-%, calculated on an elemental basis, of the final catalyst. Further details of halogen

components and their incorporation into the catalyst are disclosed in U.S. Pat. No. 5,004,859 referenced above.

The catalyst can be characterized by a pore-acidity index, calculated as $100 \times (\text{PD} \times \text{Acidity} / \text{SA})$ wherein PD=average pore diameter in angstroms; Acidity=mmols TMP/g @ 120°C and SA=surface area in m²/g. In some embodiments, the catalysts may have a pore-acidity index of at least 7.0.

Surface area is measured using nitrogen by the well-known BET (Brunauer-Emmett-Teller) method, which also indicates average pore diameter. Acidity is measured by loading the sample as powder in a glass tube and pretreating under high vacuum (ca. 10⁻⁶ torr) at 600°C for 2 hours. The samples are then cooled to 120°C and exposed to trimethylphosphine (TMP) for 15 minutes followed by a 45-minute equilibration time, and then degassed with high vacuum. The TMP exposed to the sample is stored in a known volume of gas line and is exposed to the sample by opening a valve connecting this line to sample chamber. The amount of adsorbed TMP is calculated from the vapor-pressure drop caused by adsorption on the sample from the known volume of the gas line, compared to the change in vapor pressure with no sample present.

The effluent 155 from reactor 145 containing the reaction products and unreacted hydrocarbon feed is sent to a separation zone 160 where it is separated into at least two streams 165, 170. Suitable separation processes include, but are not limited to, distillation columns and adsorption processes.

In some embodiments, there can be one or more recycle streams 175 which can be combined with the hydrocarbon feed 105 and recycled to the disproportionation reaction zone 110.

For example, the isomerization of a light naphtha feed comprising C₅ and C₆ hydrocarbons can produce products which can be separated into at least an iso-C₆ stream, an nC₆ stream, and a C₇₊ stream. The nC₆ stream (which may contain methylcyclopentane from the light naphtha feed) can be recycled back to the reaction zone. The iso-C₆ stream can be recovered and blended into gasoline or with any suitable refinery stream. The C₇₊ stream can be recycled to the reaction zone and/or sent to product recovery. Alternatively, the products

from the reaction zone could be separated into at least a normal paraffin stream comprising nC₅ and nC₆ and a branched paraffin stream comprising iC₅ and iC₆ by using separation processes using molecular sieves. The normal paraffin stream could be recycled back to the reaction zone and the branched paraffin stream could be recovered and blended in with gasoline or any suitable refinery stream.

For example, the disproportionation of C₅ paraffins can produce a stream of lighter C₄ hydrocarbons which can be used as a feed for an alkylation unit and a stream of higher boiling C₆₊ hydrocarbons, suitable for gasoline blending or reformer feed. In some embodiments, there could also be a C₅ stream. At least a portion of the C₅ stream could be recycled to the disproportionation reaction zone. In one example, a light naphtha feed can be separated into a C₅ stream and a C₆ stream in a splitter (not shown). The C₆ stream could be sent to a reformer, a standard isomerization unit, or a sent directly to a gasoline stream. The C₅ stream from the splitter can be used as the hydrocarbon feed for the disproportionation reaction zone.

As another example, the disproportionation of iso-pentane (iso-C₅) produces products which can be separated into a C₄ stream and a C₅₊ stream. The C₄ stream contains isobutane (iso-C₄), which can be used as a feed for an alkylation process. The C₅₊ stream contains C₆₊ isoparaffins, which could be blended with gasoline. The RVP of the C₅₊ fraction product would be lower than the RVP of the iso-C₅ feed.

Since disproportionation is an equilibrium limited reaction, equilibrium amounts of C₅ will be present with the products; it is desirable to recycle the C₅ material to increase the C₅ conversion. This can be done by separating the effluent into at least a C₄ stream, a C₅ stream and a C₆₊ stream. The C₅ stream could be recycled to the disproportionation reaction zone, and the C₆₊ stream could be used as gasoline blendstock.

In some embodiments, the separation could yield at least an iso-C₄ stream, an iso-C₅ stream, and an n-C₅₊ stream. In some embodiments, there could also be a separate n-C₄ stream, or the n-C₄ stream could be combined with the iso-C₄ stream. The stream of unconverted iso-C₅ could be recycled to the disproportionation reaction zone.

In some embodiments, the separation could result in at least an iso-C₄ stream, a C₅ stream comprising iso-C₅ and n-C₅, and an n-C₆₊ stream. In some embodiments, there could also be a separate n-C₄₋ stream, or the n-C₄₋ stream could be combined with the iso-C₄₋ stream. The C₅ stream could be recycled to the disproportionation reaction zone.

5 In some embodiments, the separation could yield at least an iso-C₄ stream, a stream comprising n-C₄ and iso-C₅, and an n-C₅₊ stream. The stream comprising n-C₄ and iso-C₅ could be recycled to the disproportionation reaction zone. Recycling the n-C₄ to the disproportionation reaction zone will result in it being isomerized to iso-C₄.

10 When the hydrocarbon feed is a C₄ feed, the separation could yield at least a C₃₋ stream, a C₄ stream, and a C₅₊ stream. The C₄ stream could be recycled to the disproportionation reaction zone. In some embodiments, the C₄ stream could also be separated into an n-C₄₋ stream and an iso-C₄₋ stream.

15 With a C₇ feed, the separation could result in at least a C₆₋ stream, a C₇ stream, and a C₈₊-rich stream, with the C₇ stream being recycled to the disproportionation reaction zone.

Additional separations could be made as would be understood by those of skill in the art.

20 After a period of use, the catalyst will become deactivated due to coke formation. The deactivated catalyst can be regenerated. Once the catalyst reaches a predetermined level of deactivation, the regeneration process could be initiated. The feed would be flushed from the reaction zone. One method of regeneration involves heating the catalyst, desirably in the presence of hydrogen and optionally a hydrocarbon. The hydrocarbon has a higher heat capacity than hydrogen and can assist in increasing the reaction temperature within the reactor. Any suitable hydrocarbon can be used, including but
25 not limited to, isobutane. The molar ratio of hydrogen to hydrocarbon is typically in the range of 1:20 to 20:1. In some embodiments, the catalyst can be heated to a temperature in the range of 100°C to 300°C, or 125°C to 275°C, or 150°C to 250°C, or 150°C to 225°C, or 150°C to 200°C, or 175°C to 300°C. The catalyst is typically heated for at least 1 h, or in the range of 0.25 to 24 hr.

Examples

Example 1: Catalyst

The catalyst is a chlorided alumina catalyst containing platinum made for example by US Patent 5,004,859. The concentration of platinum ranged from 0.002 wt.% to 2 wt.%, the
5 chloride concentration ranged from 0.1 to 10 wt.% and the alumina phase was one of alpha, gamma, eta or theta.

Example 2: Experimental Set Up

The catalytic reactions were typically run using a 7/8" inner diameter stainless steel tube reactor. Prior to catalyst loading, the reactor was dried by heating the reactor to at
10 least 150°C with a three-zone clam shell furnace under a stream of flowing nitrogen for at least four hours. After the drying procedure was completed, the reactor was cooled to ambient temperature, connected to a nitrogen line, and the reactor opened under flowing nitrogen. The reactor was inserted through a hole in a nitrogen glovebag, and the connection of the glovebag with the reactor was sealed with electrical tape. The top of the open re
15 actor was enclosed within a glovebag and had nitrogen blowing through it. The catalyst from Example 1 was loaded under nitrogen in the glovebag to the reactor under this positive flow of nitrogen. The reactor was sand packed with 50-70 mesh sand, the sand having been previously calcined to 700°C for 7 h. Typically, 40 ccs of catalyst was loaded into the reactor, and the reaction was run downflow. The feed had a 1.4 MPa(g) (210 psig)
20 hydrogen header and the concentration of dissolved hydrogen in the feed was determined from the literature values reported in the IUPAC Solubility Data Series volumes 5/6 "Hydrogen and Deuterium" (1981) for pentane and butane. It was assumed that the value for pentane would remain constant for the iC5, iC5/nC5 and iC5/nC5/cyclopentane (CP) feeds. The feed was passed through a high surface sodium dryer prior to introduction to the reactor
25 and was added to the reactor by means of a Quizzix pump. . A second pump controlled the chloride addition rate. The chloride was dissolved in the feed, and the chloride source (2-chlorobutane) had previously been dried with activated 3A molecular sieves. The two feed streams were introduced to the reactor by joining the two separate feed streams with a Tee connector immediately prior to their introduction to the reactor. The temperature was
30 measured using K-type thermocouples, and the pressure was controlled by means of a backpressure regulator. The effluent was sent directly to an Agilent 6890N gas chromatograph (GC), and the product was analyzed by means of flame ionization detection.

A 60 m, 0.32 mm inner diameter, 1.0 μm film thickness DB-1 column was used. The initial oven temperature was 40°C, with a 4 minute hold time at this temperature. The oven was then ramped to 135°C at a 5°C/min ramp rate, and the program was completed once this temperature was reached. The GC inlet was 250°C with a hydrogen carrier gas. The product was then sent directly to a product charger and collected.

Example 3: Disproportionation of iC5 with regeneration

The catalytic reaction was run according to the procedure outlined above, except 30 ccs of catalyst was used and a header of nitrogen was present on the feed chargers. The conditions and results are listed in Table 1 below. After the catalyst had deactivated, the catalyst was regenerated by flushing the feed out of the reactor, purging the reactor with hydrogen and pressurizing with hydrogen to 193 kPa (g) (28 psig) and then heating to 175°C for 2 h. The regeneration occurred after 30 h on stream. After the regeneration, the reactor was cooled to the desired temperature, the pressure was adjusted, and then feed was reintroduced to the system. The results are shown below in Table 1 and demonstrate that the disproportionation of iC5 occurs with this type of catalyst, but deactivates with time on stream (TOS).

Table 1. Disproportionation of iC5 and regenerations results

TOS (h)	12	21	30	47 ^a	55 ^a
T (°C)	145	145	145	146	146
P (psig)	449	454	456	455	454
Cl (ppm)	1700	1600	1100	1600	1600
LHSV (hr ⁻¹)	1.9	2.0	2.8	2.0	2.0
H ₂ /HC ^b	0.0	0.0	0.0	0.0	0.0
H ₂ /Cl ^c	0.0	0.0	0.0	0.0	0.0
% iC5 Conv. ^d	25	10	1	18	12
% C5P Conv. ^e	18	7	< 1	13	10
% Selec. Disp. ^f	72	74	42 ^g	74	76
Compound					
Methane	0.00	0.00	0.00	0.00	0.00
Ethane	0.00	0.00	0.00	0.00	0.00

Propane	0.04	0.01	0.00	0.02	0.01
iC4	7.38	2.99	0.17	5.26	3.90
nC4	0.37	0.13	0.01	0.16	0.14
iC5	74.83	89.89	98.82	82.45	87.44
nC5	6.93	2.65	0.69	4.63	3.00
Neopentane	0.02	0.01	0.01	0.01	0.01
22DMB	0.27	0.04	0.00	0.12	0.06
23DMB	1.33	0.54	0.03	0.98	0.70
2MP	4.42	2.02	0.14	3.43	2.63
3MP	2.57	1.17	0.08	1.99	1.52
nC6	0.71	0.15	0.00	0.36	0.20
C7+	1.14	0.39	0.04	0.56	0.38
Unknown	0.00	0.01	0.00	0.02	0.00

^a After the regeneration procedure, ^b molar ratio of hydrogen to hydrocarbon in feed, ^c molar ratio of hydrogen to chloride, ^d % iC5 Conv. = 100 - wt.% iC5, ^e % C5P Conv. = 100 - wt.% iC5 - wt.% nC5, ^f % Selec. Disp. = (wt.% C₄₋ + wt.% C₆₊)/(100 - wt.% iC5)x100 and ^g selectivity may be off due to increased error from low conversion and the assumption of exactly 100 wt.% iC5.

Example 4: Disproportionation of iC5

The catalytic reaction was run according to the procedure outlined above. The conditions and results are listed in Table 2 below and demonstrate that the presence of small amounts of hydrogen increase the stability of the catalyst.

Table 2. Disproportionation of iC5

TOS (h)	15	20	25
T (°C)	172	172	172
P (psig)	608	610	611
Cl (ppm)	1600	1600	1600
LHSV (hr ⁻¹)	1.0	1.0	1.0

H ₂ /HC ^a	0.02	0.02	0.02
H ₂ /Cl ^b	5	5	5
% iC5 Conv. ^c	52	53	54
% C5P Conv. ^d	41	42	42
% Selec. Disp. ^e	80	80	77
Compound			
Methane	0.00	0.00	0.00
Ethane	0.00	0.00	0.00
Propane	0.53	0.62	0.63
iC4	21.07	21.67	20.18
nC4	2.54	2.54	2.51
iC5	48.28	47.06	45.62
nC5	10.51	10.89	12.36
22DMB	1.06	1.08	1.34
23DMB	1.77	1.75	1.79
2MP	5.81	5.73	5.91
3MP	3.45	3.41	3.55
nC6	1.49	1.47	1.63
C7P	2.32	2.42	2.45
C8+	1.17	1.37	1.40
Unknown	0.00	0.00	0.00

^a Molar ratio of hydrogen to hydrocarbon in feed, ^b molar ratio of hydrogen to chloride, ^c % iC5 Conv. = 100 - wt.% iC5, ^d % C5P Conv. = 100 - wt.% iC5 - wt.% nC5 and ^e % Selec. Disp. = (wt.% C₄ + wt.% C₆₊)/(100 - wt.% iC5)x100.

5 Example 5: Disproportionation of nC5

The catalytic reaction was run according to the procedure outlined above. The conditions and results are listed in Table 3 below and demonstrate that the disproportionation of nC5 readily occurs with these types of catalysts and that with small amounts of hydrogen being present, the catalyst stability is increased.

Table 3. Disproportionation of nC5

TOS (h)	8	13	28
T (°C)	176	175	171
P (psig)	619	618	622
Cl (ppm)	1600	1600	1600
LHSV (hr ⁻¹)	1.0	1.0	1.0
H ₂ /HC ^a	0.02	0.02	0.02
H ₂ /Cl ^b	5	5	5
% nC5 Conv. ^c	69	68	67
% C5P Conv. ^d	35	35	33
% Selec. Disp. ^e	50	52	50
Compound			
Methane	0.00	0.00	0.00
Ethane	0.00	0.00	0.00
Propane	0.81	0.81	0.66
iC4	15.49	15.83	15.19
nC4	3.70	3.32	2.54
iC5	34.05	32.70	33.60
nC5	31.26	32.06	33.18
22DMB	1.47	1.35	1.33
23DMB	1.30	1.36	1.37
2MP	4.09	4.25	4.25
3MP	2.54	2.64	2.62
nC6	1.44	1.45	1.32
C7P	2.46	2.64	2.44
C8+	1.39	1.60	1.50
Unknown	0.00	0.00	0.00

^a Molar ratio of hydrogen to hydrocarbon in feed, ^b molar ratio of hydrogen to chloride, ^c % nC5 Conv. = 100 - wt.% nC5, ^d % C5P Conv. = 100 - wt.% iC5 - wt.% nC5 and ^e % Selec. Disp. = (wt.% C₄ + wt.% C₆₊)/(100 - wt.% nC5)x100.

5

Example 6: Disproportionation of Pentanes in the presence of cyclopentane (CP)

The catalytic reaction was run according to the procedure outlined above. For the first part of the reaction, the feed was a blend of iC5/nC5. Once the reactivity of the paraffinic feed in the absence of significant amounts of naphthenes was established, a new feed was introduced comprising iC5/nC5/CP. The conditions and results are listed in Table 4 below and demonstrate that disproportionation readily occurs in the feed without CP, but upon CP introduction the activity for paraffin disproportionation decreases and the paraffin isomerization activity increases.

10 Table 4. Disproportionation of pentanes in the presence and absence of cyclopentane

Feed	iC5/nC5	iC5/nC5	iC5/nC5	iC5/nC5/CP	iC5/nC5/CP	iC5/nC5/CP
TOS (h)	0	10	25	0	41	51
T (°C)	NA	170	168	NA	166	165
P (psig)	NA	454	454	NA	452	451
Cl (ppm)	NA	1600	1600	NA	1600	1600
LHSV (hr ⁻¹)	NA	1.0	1.0	NA	1.0	1.0
H ₂ /HC ^a	NA	0.02	0.02	NA	0.02	0.02
H ₂ /Cl ^b	NA	5	5	NA	5	5
% nC5 Conv. ^c	NA	55	52	NA	56	56
% C5P Conv. ^d	NA	27	28	NA	14	15
% Selec. Disp.	NA	96 ^e	100 ^f	NA	51 ^e	53 ^e
Compound	Feed			Feed		
Methane	0.00	0.01	0.00	0.00	0.00	0.00
Ethane	0.00	0.01	0.01	0.00	0.01	0.01
Propane	0.00	0.39	0.77	0.00	0.11	0.11
iC4	0.02	11.58	12.96	0.01	6.52	6.62
nC4	0.02	2.05	3.13	0.02	0.93	0.93
iC5	49.18	50.28	47.19	40.35	51.89	51.29

nC5	50.13	22.31	24.05	41.72	18.34	18.25
22DMB	0.00	1.40	1.43	0.31	0.80	0.83
23DMB	0.07	1.27	1.04	0.24	0.63	0.66
2MP	0.11	4.04	3.29	0.47	2.04	2.12
3MP	0.08	2.48	2.02	0.13	1.12	1.16
nC6	0.26	1.22	1.10	0.29	0.62	0.65
C7P	0.08	1.72	1.76	0.03	0.99	1.00
C8+	0.03	1.26	1.23	0.04	2.19	2.39
Unknown	0.00	0.00	0.00	0.00	0.00	0.00
CP ^g	0.00	0.00	0.00	16.26	13.83	13.97

^a Molar ratio of hydrogen to hydrocarbon in feed, ^b molar ratio of hydrogen to chloride, ^c % nC5 Conv. = (wt.% nC5 in feed - wt.% nC5 in product)/(wt.% nC5 in feed)x100, ^d % C5P Conv. = (wt.% nC5 in feed + wt.% iC5 in feed - wt.% nC5 in product - wt.% iC5 in product)/(wt.% nC5 in feed + wt.% iC5 in feed)x100, ^e % Selec. Disp. = (wt.% C₄ in product + wt.% C₆₊ in product - wt.% C₄ in feed - wt.% C₆₊ in feed)/(wt.% nC5 in feed - wt.% nC5 in product)x100, ^f % Selec. Disp. = 100 since net loss of both iC5 and nC5 and ^g CP overlapped with 23DMB in the GC, the concentration was estimated by quantifying the peak area for 22DMB and back-calculating the concentration for 23DMB assuming a 22DMB/23DMB ratio of 1.27 and then subtracting that value from the overlapped signal to arrive at the estimated CP concentration.

Example 7: Disproportionation of nC4

The catalytic reaction was run according to the procedure outlined above. The conditions and results are listed in Table 5 below and demonstrate that the disproportionation of nC4 readily occurs with these types of catalysts and that with small amounts of hydrogen being present, the catalyst is stable.

Table 5. Disproportionation of nC4 and regenerations results

TOS (h)	0	18	40
T (°C)	NA	165	165
P (psig)	NA	1036	1036

Cl (ppm)	NA	1600	1600
LHSV (hr ⁻¹)	NA	1	1
H ₂ /HC ^a	NA	0.02	0.02
H ₂ /Cl ^b	NA	6	6
% nC4 Conv. ^c	NA	66	66
% C4P Conv. ^d	NA	20	21
% Selec. Disp. ^e	NA	30	31
Compound			
Methane	0.00	0.11	0.10
Ethane	0.00	0.16	0.16
Propane	0.01	9.00	9.23
iC4	0.16	45.98	45.54
nC4	99.37	33.45	33.34
iC5	0.00	7.15	7.35
nC5	0.01	2.24	2.32
22DMB	0.00	0.45	0.48
23DMB	0.00	0.15	0.16
2MP	0.00	0.47	0.51
3MP	0.00	0.27	0.29
nC6	0.30	0.19	0.20
C7P	0.04	0.21	0.15
C8+	0.07	0.16	0.15
Unknown	0.03	0.00	0.00

^a Molar ratio of hydrogen to hydrocarbon in feed, ^b molar ratio of hydrogen to chloride, ^c % nC4 Conv. = ((wt.% nC4 in feed – wt.% nC4 in product)/wt.% nC4 in feed)x100, ^d % C4P Conv. = ((wt.% iC4 in feed + wt.% nC4 in feed – wt.% iC4 in product – wt.% nC4 in product)/(wt.% iC4 in feed + wt.% nC4 in feed))x100 and ^e % Selec. Disp. = ((wt.% C₃₋ in product + wt.% C₅₊ in product - wt.% C₃₋ in feed - wt.% C₅₊ in feed)/(wt.% nC4 in feed – wt.% nC4 in product)x100.

5

SPECIFIC EMBODIMENTS

While the following is described in conjunction with specific embodiments, it will be understood that this description is intended to illustrate and not limit the scope of the preceding description and the appended claims.

5 A first embodiment of the invention is a flexible hydrocarbon conversion process utilizing the same reaction zone for isomerization and disproportionation comprising selecting a hydrocarbon feed; selecting isomerization products or disproportionation products for the hydrocarbon feed; and if the isomerization products are selected, contacting the hydrocarbon feed in the reaction zone with a catalyst in the presence of hydrogen and a first added chloride promoter under isomerization conditions to obtain the selected isomerization products; wherein the catalyst comprises a solid catalyst comprising a refractory inorganic oxide having a metal halide dispersed thereon; wherein the hydrogen is present in a mole ratio of hydrogen to hydrocarbon feed of 0.051 to 51; wherein the first added chloride promoter is present in an amount in a range of 30 ppm to 400 ppm; and 10 wherein a mole ratio of hydrogen to chloride from the added chloride promoter is in a range of 1001 to 50001; or if the disproportionation products are selected, contacting the hydrocarbon feed in the reaction zone with the catalyst in the presence of hydrogen and a second added chloride promoter under disproportionation conditions to obtain disproportionation products; wherein the hydrogen is present in a mole ratio of hydrogen to hydrocarbon feed of greater than 01 to 0.11; wherein the second added chloride promoter is present in an amount of 100 ppm to 5000 ppm; and wherein a mole ratio of hydrogen to chloride from the added chloride promoter is in a range of greater than 01 to 1001. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein the catalyst further comprises a 25 Group VIII metal component dispersed thereon. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein the hydrocarbon feed comprises alkanes having 4 to 7 carbon atoms. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein the isomerization conditions include a 30 temperature in a range of 40°C to 300°C, a pressure in a range of 0 MPa (g) to 13.8 MPa (g), and a liquid hourly space velocity of 0.25 hr⁻¹ to 12 hr⁻¹, or the disproportionation conditions

include a temperature in a range of 100°C to 300°C, a pressure in a range of 0 MPa (g) to 13.8 MPa (g), and a liquid hourly space velocity of 0.25 hr⁻¹ to 10 hr⁻¹. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein at least one of the first added chloride promoter and the second added chloride promoter comprises carbon tetrachloride, tetrachloroethylene, propyldichloride, butylchloride, chloroform, 2-chloro-2-methylpropane, 2-chloropropane, 2-chloro-2-methylbutane, 2-chloropentane, 1-chlorohexane, 3-chloro-3-methylpentane, 2-chlorobutane, or combinations thereof. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein the hydrogen is dissolved in the hydrocarbon feed. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph further comprising fractionating an effluent from the reaction zone into at least two streams, the effluent containing the isomerization products or the disproportionation products. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein the isomerization products are selected, wherein the hydrocarbon feed comprises a light naphtha feed comprising C₅ and C₆ hydrocarbons, wherein contacting the hydrocarbon feed in the reaction zone with the catalyst comprises contacting the light naphtha feed in the reaction zone with the catalyst, and wherein fractionating the effluent from the reaction zone into the at least two streams comprises fractionating the effluent from the reaction zone into at least an nC₆ stream and an iC₆- stream; and optionally recycling a portion of the nC₆ stream to the reaction zone. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein the disproportionation products are selected, and wherein the paraffin feed comprises a light naphtha feed comprising C₅ and C₆ hydrocarbons, further comprising separating the light naphtha feed into a C₅ stream and a C₆ stream; wherein contacting the hydrocarbon feed in the reaction zone with the catalyst comprises contacting the C₅ stream in the reaction zone with the catalyst; and wherein fractionating the effluent from the reaction zone into the at least two streams comprises fractionating the effluent from the reaction zone into at least an iso-C₄ stream, a C₅ stream comprising iso-C₅ and n-C₅, and a C₆₊ stream; and optionally recycling at least a portion of the C₅ stream to the reaction zone. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph

wherein the disproportionation products are selected, and wherein the hydrocarbon feed comprises a light naphtha feed comprising C₅ and C₆ hydrocarbons, further comprising separating the light naphtha feed into a C₅ stream and a C₆ stream; wherein contacting the hydrocarbon feed in the reaction zone with the catalyst comprises contacting the C₅ stream in the reaction zone with the catalyst, and wherein fractionating the effluent from the reaction zone into the at least two streams comprises fractionating the effluent from the reaction zone into at least an iso-C₄ stream, an n-C₄ and iso-C₅ stream, and a n-C₅₊ stream; and optionally recycling at least a portion of the n-C₄ and iso-C₅ stream to the reaction zone. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein the disproportionation products are selected, and wherein the hydrocarbon feed comprises a C₄ feed, and wherein separating the effluent from the reaction zone into the at least two streams comprises separating the effluent from the reaction zone into at least a C₃₋ stream, a C₄ stream, and a C₅₊ stream; and further comprising optionally recycling at least a portion of the C₄ stream to the reaction zone. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein the disproportionation products are selected, and wherein the hydrocarbon feed comprises a C₇ feed, and wherein separating the effluent from the reaction zone into the at least two streams comprises separating the effluent from the reaction zone into at least a C₆₋ stream, a C₇ stream, and a C₈₊-rich stream; and further comprising optionally recycling at least a portion of the C₇ stream to the disproportionation reaction zone. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph further comprising regenerating the catalyst. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein regenerating the catalyst comprises heating the catalyst to a temperature in a range of 100°C to 300°C in the presence of hydrogen.

A second embodiment of the invention is a flexible hydrocarbon conversion process utilizing the same reaction zone for isomerization and disproportionation comprising selecting a hydrocarbon feed comprising alkanes having 4 to 7 carbon atoms; selecting isomerization products or disproportionation products for the hydrocarbon feed; and if the isomerization products are selected, contacting the hydrocarbon feed in the reaction zone

with a catalyst in the presence of hydrogen and a first added chloride promoter under isomerization conditions including a temperature in a range of 40°C to 300°C to obtain the isomerization products; wherein the catalyst comprises a solid catalyst comprising a refractory inorganic oxide having a metal halide dispersed thereon; wherein the hydrogen is present in a mole ratio of hydrogen to hydrocarbon feed of 0.5:1.0 to 5:1; wherein the first added chloride promoter is present in an amount in a range of 30 ppm to 400 ppm; and wherein a mole ratio of hydrogen to chloride from the added chloride promoter is in a range of 100:1 to 5000:1; or if the disproportionation products are selected, contacting the hydrocarbon feed in the reaction zone with the catalyst in the presence of hydrogen and a second added chloride promoter under disproportionation conditions including a temperature in a range of 100°C to 300°C to obtain disproportionation products; wherein the hydrogen is present in a mole ratio of hydrogen to hydrocarbon feed of greater than 0.1 to 0.11; wherein the second added chloride promoter is present in an amount of at least 100 ppm to 5000 ppm; and wherein a mole ratio of hydrogen to chloride from the added chloride promoter is in a range of greater than 0.1 to 100:1; fractionating an effluent from the reaction zone into at least two streams, the effluent containing the isomerization products or the disproportionation products; . recovering at least one stream; and optionally recycling at least a portion of one stream to the reaction zone. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph wherein the catalyst further comprises a Group VIII metal component dispersed thereon. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph wherein the hydrogen is dissolved in the hydrocarbon feed. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph further comprising regenerating the catalyst by heating the catalyst to a temperature in a range of 100°C 300°C in the presence of hydrogen. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph wherein the isomerization products are selected, wherein the hydrocarbon feed comprises a light naphtha feed comprising C₅ and C₆ hydrocarbons, wherein contacting the hydrocarbon feed in the reaction zone with the catalyst comprises contacting the light naphtha feed in the reaction zone with the catalyst, and wherein fractionating the effluent from the reaction zone into the at least two streams comprises fractionating the effluent from the reaction zone into at least

an nC₆ stream and an iC₆- stream; and optionally recycling a portion of the nC₆ stream to the reaction zone. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph wherein the disproportionation products are selected, and wherein the paraffin feed comprises a light naphtha feed comprising C₅ and C₆ hydrocarbons, further comprising separating the light naphtha feed into a C₅ stream and a C₆ stream; wherein contacting the hydrocarbon feed in the reaction zone with the catalyst comprises contacting the C₅ stream in the reaction zone with the catalyst, and wherein fractionating the effluent from the reaction zone into the at least two streams comprises fractionating the effluent from the reaction zone into at least an iso-C₄ stream, a C₅ stream comprising iso-C₅ and n-C₅, and a C₆₊ stream; recovering the iso-C₄-rich stream, and the C₆₊-rich stream; and optionally recycling at least a portion of the C₅ stream to the reaction zone.

Without further elaboration, it is believed that using the preceding description that one skilled in the art can utilize the present invention to its fullest extent and easily ascertain the essential characteristics of this invention, without departing from the spirit and scope thereof, to make various changes and modifications of the invention and to adapt it to various usages and conditions. The preceding preferred specific embodiments are, therefore, to be construed as merely illustrative, and not limiting the remainder of the disclosure in any way whatsoever, and that it is intended to cover various modifications and equivalent arrangements included within the scope of the appended claims.

In the foregoing, all temperatures are set forth in degrees Celsius and, all parts and percentages are by weight, unless otherwise indicated.

While at least one exemplary embodiment has been presented in the foregoing detailed description of the invention, it should be appreciated that a vast number of variations exist. It should also be appreciated that the exemplary embodiment or exemplary embodiments are only examples, and are not intended to limit the scope, applicability, or configuration of the invention in any way. Rather, the foregoing detailed description will provide those skilled in the art with a convenient road map for implementing an exemplary embodiment of the invention. It being understood that various changes may be made in the

function and arrangement of elements described in an exemplary embodiment without departing from the scope of the invention as set forth in the appended claims.

CLAIMS

1. A flexible hydrocarbon conversion process utilizing the same reaction zone for isomerization and disproportionation comprising:

selecting a hydrocarbon feed;

5 selecting isomerization products or disproportionation products for the hydrocarbon feed; and

if the isomerization products are selected,

10 contacting the hydrocarbon feed in the reaction zone (110) with a catalyst in the presence of hydrogen and a first added chloride promoter under isomerization conditions to obtain the selected isomerization products;

wherein the catalyst comprises a solid catalyst comprising a refractory inorganic oxide having a metal halide dispersed thereon;

wherein the hydrogen is present in a mole ratio of hydrogen to hydrocarbon feed of 0.05:1 to 5:1;

15 wherein the first added chloride promoter is present in an amount in a range of 30 ppm to 400 ppm; and

wherein a mole ratio of hydrogen to chloride from the added chloride promoter is in a range of 100:1 to 5000:1;

or

20 if the disproportionation products are selected,

contacting the hydrocarbon feed in the reaction zone (110) with the catalyst in the presence of hydrogen and a second added chloride promoter under disproportionation conditions to obtain disproportionation products;

25 wherein the hydrogen is present in a mole ratio of hydrogen to hydrocarbon feed of greater than 0:1 to 0.1:1;

wherein the second added chloride promoter is present in an amount of 100 ppm to 5000 ppm; and

wherein a mole ratio of hydrogen to chloride from the added chloride promoter is in a range of greater than 0:1 to 100:1.

- 30 2. The process of any of claims 1-2 wherein the catalyst further comprises a Group VIII metal component dispersed thereon.
3. The process of any of claims 1-2 wherein the hydrocarbon feed comprises alkanes having 4 to 7 carbon atoms.
4. The process of any of claims 1-2 wherein the isomerization conditions
35 include a temperature in a range of 40°C to 300°C, a pressure in a range of 0 MPa (g) to 13.8 MPa (g), and a liquid hourly space velocity of 0.25 hr⁻¹ to 12 hr⁻¹, or the disproportionation conditions include a temperature in a range of 100°C to 300°C, a pressure in a range of 0 MPa (g) to 13.8 MPa (g), and a liquid hourly space velocity of 0.25 hr⁻¹ to 10 hr⁻¹.
5. The process of any of claims 1-2 wherein at least one of the first added
40 chloride promoter and the second added chloride promoter comprises carbon tetrachloride, tetrachloroethylene, propyldichloride, butylchloride, chloroform, 2-chloro-2-methylpropane, 2-chloropropane, 2-chloro-2-methylbutane, 2-chloropentane, 1-chlorohexane, 3-chloro-3-methylpentane, 2-chlorobutane, or combinations thereof.
6. The process of any of claims 1-2 wherein the hydrogen is dissolved in
45 the hydrocarbon feed.
7. The process of any of claims 1-2 further comprising:
 fractionating an effluent (155) from the reaction zone (110) into at least two streams (165, 170), the effluent (155) containing the isomerization products or the disproportionation products.
- 50 8. The process of claim 7 further comprising recycling at least a portion of one of the streams (165, 170) to the reaction zone (110).
9. The process of any of claims 1-2 further comprising regenerating the catalyst.
10. The method of claim 9 wherein regenerating the catalyst comprises
55 heating the catalyst to a temperature in a range of 100°C to 300°C in the presence of hydrogen.

1/2

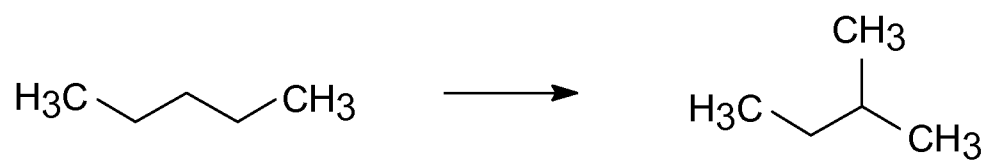


FIG. 1

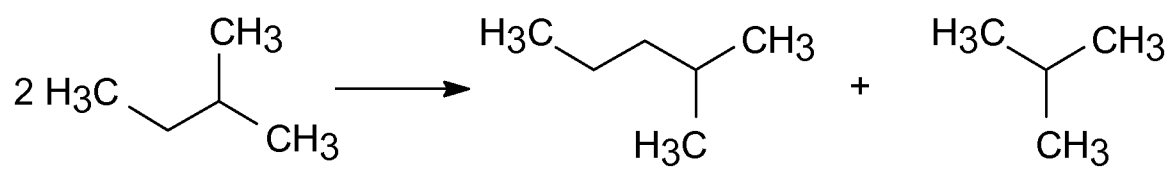


FIG. 2

2/2

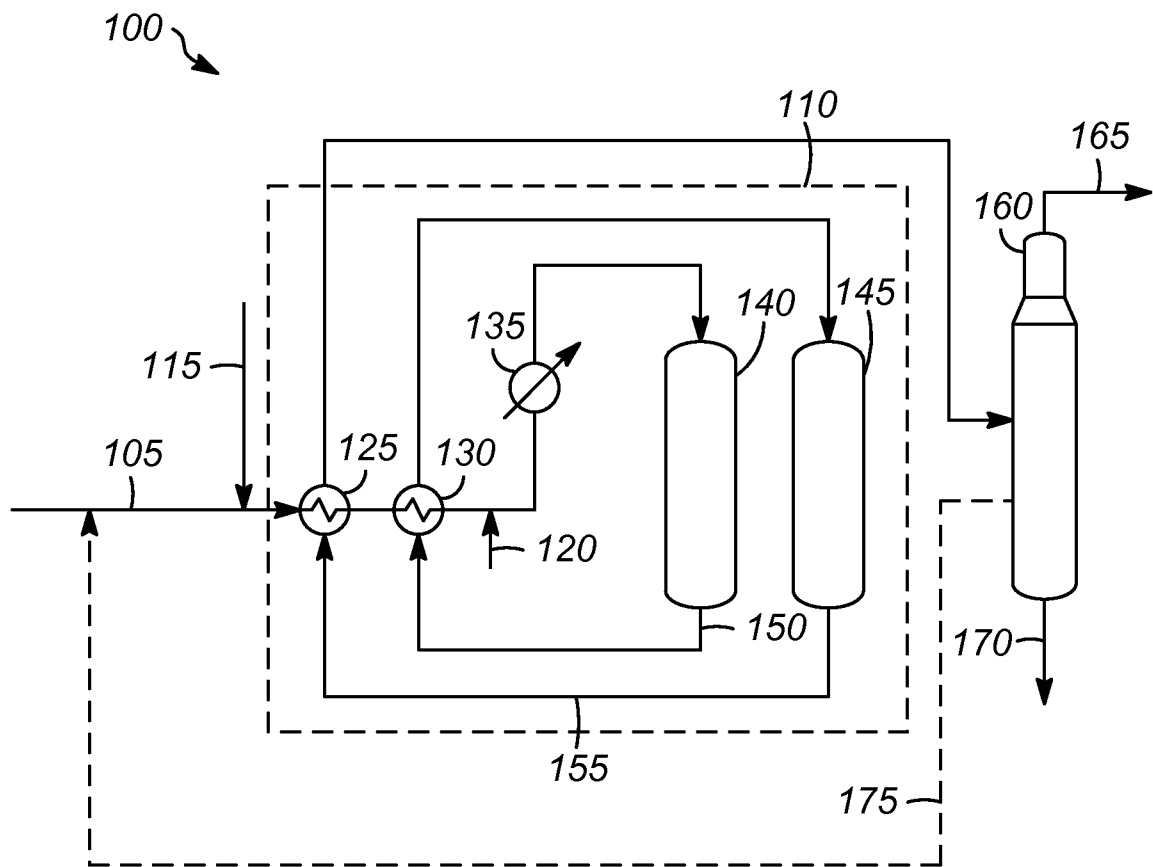


FIG. 3

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 2015/062999

A. CLASSIFICATION OF SUBJECT MATTER <i>C07C 5/22 (2006.01)</i> <i>C07C 6/08 (2006.01)</i> According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) <i>C07C 5/22, 6/08</i> Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) PatSearch (RUPTO internal), USPTO, PAJ, Esp@cenet, DWPI, EAPATIS, PATENTSCOPE		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5004859 A (UOP) 02.04.1991, abstract, claims, col. 10, lines 33-37, col. 11, line 1-col. 13, line 22	1-9
Y		10
Y	US 5654247 A (PHILLIPS PETROLEUM COMPANY) 05.08.1997, claims	10
A	WO 2001/016059 A1 (CHEVRON U.S.A. INC.) 08.03.2001	1-10
A	US 6025293 A (PHILLIPS PETROLEUM COMPANY) 15.02.2000	1-10
☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.		
*	Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family
"A"	document defining the general state of the art which is not considered to be of particular relevance	
"E"	earlier document but published on or after the international filing date	
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	
"O"	document referring to an oral disclosure, use, exhibition or other means	
"P"	document published prior to the international filing date but later than the priority date claimed	
Date of the actual completion of the international search 18 February 2016 (18.02.2016)		Date of mailing of the international search report 10 March 2016 (10.03.2016)
Name and mailing address of the ISA/RU: Federal Institute of Industrial Property, Berezhkovskaya nab., 30-1, Moscow, G-59, GSP-3, Russia, 125993 Facsimile No: (8-495) 531-63-18, (8-499) 243-33-37		Authorized officer A. Sedov Telephone No. 499-240-25-91

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 2015/062999

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

Independent claim 1 discloses two inventions not associated to each other by single inventive conception, since they apply to different subjects.

1st object is a process for isomerization.

2nd object is a process for disproportionation.

These objects use different raw materials to give two different products.

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☒ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.