

Process for the Dimerization/Oligomerization of Mixed Butenes Over an Ion-  
Exchange Resin Catalyst

Technical Field

5           The present invention relates to a process for dimerizing/oligomerizing olefins and more particularly, to a single step process for dimerizing/oligomerizing a feed stream that includes butene isomers (mixed butenes) to produce highly branched olefins having 8 carbons and olefins having more than 8 carbons using an ion-exchange resin catalyst under mild conditions.

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Background

Gasoline continues to be a leading energy source for internal combustion engines, which are commonly used to power machines such as motor vehicles for the transportation of people and goods. The standard measure for the performance  
15 of gasoline is octane rating. The most common measurement methods for octane rating are the Research Octane Number (RON), the Motor Octane Number (MON), and the Anti-Knock Index (AKI)—the average of the RON and MON numbers. Fuel with a higher octane rating can be used in higher-compression, higher performance engines. Thus, there is an incentive for scientists to develop new ways of increasing  
20 the octane rating of gasoline.

In addition, increasingly restrictive fuel legislation throughout the world has only strengthened this incentive. The challenge has now become maintaining the quality of the fuel while lowering its harmful emissions. One group of harmful

substances present in gasoline that have been reduced via legislation is aromatics (e.g., benzene emissions). The aromatic content of gasoline must now be reduced to below 35 vol% level due to emissions-limiting legislation (the United States has even lowered it below 25 vol%). Aromatic compounds have the greatest contribution to RON, and thus the legislatively-mandated reductions to aromatic content of gasoline will cause significant reduction in the quantity of gasoline as well as RON deficiencies. In addition, fuel producers must also be cognizant of the fuel's Reid Vapor Pressure (RVP), a way to measure how quickly fuel evaporates. The higher a fuel's RVP is, the quicker its rate of evaporation is, and consequently, the more it contributes to the ozone layer. RVP for fuel typically should be below 14.7 psi, which is the normal atmospheric pressure. RVP is a particularly important measurement for fuel during the summer months, when the EPA strictly regulates the RVP of gasoline sold in retail stores. During the summer, the RVP in gasoline typically cannot exceed 9.0 psi. As aromatic compounds also have a low RVP, the reduction in aromatic content in gasoline will also result in an increased RVP. Thus, there is now an incentive to find new ways to retain a high octane rating in gasoline, while staying within the framework of the new emissions regulations and maintaining a low RVP.

Decades ago, lead was used as an additive to gasoline in order to increase its octane rating. However, lead has since been removed from gasoline blends in most countries due to its harmful environmental effects. For the past twenty years or so, partly in response to the need to increase octane ratings in the absence of lead, gasoline sold in the United States and elsewhere has been blended with up to 15% volumes of methyl-tertiary-butyl-ether (MTBE), an oxygenate, in order to reduce environmentally harmful exhaust emissions while still raising the octane rating.

While MTBE has low RVP, MTBE itself has been classified as a pollutant and a potential human carcinogen. To make matters worse, many gasoline storage tanks have developed leaks and because MTBE is highly soluble in water and low in biodegradability, MTBE has polluted the ground water in many communities. Thus, the use of MTBE in gasoline sold in the United States has practically halted in recent years.

Presently, the planned replacement for MTBE is fermented grain ethanol from wheat or sugarcanes. For example, US 4398920(A) revealed a blended fuel comprising a mixture of ethanol, acetone, and methanol from fermentation. The use of ethanol in gasoline blends is advantageous in several ways, including its higher blending RON and the fact that its toxicology is known in the industry. However, the production of ethanol is costly and may only be economically sustainable when tax reductions are granted. In addition, producing sufficient quantities of grain ethanol to satisfy the needs of the transportation industry has the adverse effect of interfering with the use of grain crops for food. Further, ethanol has relatively low energy content when compared to gasoline. Specifically, ethanol contains about 76,000 Btu's/gallon while gasoline contains about 113,000 Btu's/gal. Ethanol also has a high affinity towards water and it cannot be mixed together with the gasoline directly in the refinery, and thus it can only be added just before the last distribution point in the network. Moreover, ethanol easily forms low-boiling azeotropic mixtures with the components of gasoline which leads to higher RVP, varying from 17 to 22 psi at 10-15% blending levels. The higher RVP associated with ethanol blends is problematic, especially in the summer months. Additionally, excessively high concentrations of ethanol (about 10% of ethanol by volume) seem to cause increases in the emissions of NO<sub>x</sub>.

Alkylates (e.g., iso-octane and trimethyl pentanes) are also an extremely desirable substitute for MTBE due to their higher RON, low RVP, and positive influence on the emissions. Alkylation is a refinery process which consists of the formation of highly branched paraffins by the catalytic alkylation reaction of isobutane with light olefins such as propylene and butenes in the presence of sulfuric acid or hydrogen fluoride. From an environmental standpoint, both sulfuric acid and hydrogen fluoride are strong acids. Thus, the handling of enormous volumes of either acid in routine operations, disposal of their by-products, and transporting either acid for their recovery are high risk due to their corrosive nature. As a result, the production of alkylates is not environmental friendly process.

Overall, taking into account costs and environmental concerns, along with the need to maintain higher RON and lower RVP, methods for the production of additional octane enhancers are needed.

One such method for producing octane enhancers is the dimerization and oligomerization of butenes to create high-octane hydrocarbon components. The major compounds obtained from the dimerization and oligomerization of mixed butenes are C8 and C12 olefins. Among these C8 olefins, diisobutenes (DIBs) are the most preferred. DIB is a non-oxygenated fuel component with many advantages such as higher RON, better anti-knock quality, and higher energy content compared with MTBE and alkylates, as well as a lower RVP than MTBE and ethanol. More specifically, highly branched octenes derived from butene dimerization and oligomerization tend to (a) give very similar RON increases as MTBE when the same volume is added to a low RON gasoline; (b) have higher RON sensitivities compared to MTBE and alkylates, and hence a better anti-knock quality and higher combustion

efficiency in modern and future spark ignition engines; and (c) have a higher energy content and lower RVP compared to MTBE.

There are two main types of light aliphatic olefin dimerization mechanisms: a metal-catalyzed coordinative mechanism and an acid-catalyzed ion mechanism.

5 The coordinative metal complex-catalyzed processes often use nickel, cobalt, or Ziegler-type catalysts among others. These processes normally use n-butene as starting material, and generally produce largely linear olefins or mainly head-tail and head-head dimerization and oligomerization of double bonds of the olefins. The coordinative metal complex-catalyzed processes have been studied extensively;  
10 however, they are not the subject of this invention.

In contrast, the acid-catalyzed processes produce strongly branched olefins. The dimerization of isobutene is typically performed using acid catalysts, including sulfonic acid derivatives, zeolites, and ion exchange resins. Sulfuric acid and hydrogen fluoride have often been used to catalyze the dimerization of isobutene;  
15 however, as mentioned above, these catalysts tend to be highly corrosive in nature.

Nickel oxide catalysts have also been used in butene oligomerization processes. These catalysts, however, are deactivated quickly due to the coke formation, despite the fact that C8 olefins can be selectively obtained with 85% selectivity. These supported nickel-based catalysts also tend to produce less  
20 branched dimers or oligomers.

Catalysts based on zeolite were reported to dimerize or oligomerize olefins in 1970s. For example, DE 2347235 A1 teaches that the dimerization of 1-butene at 170°C/40 atm over a zeolite with 5% Ni loadings catalyst gave linear octene at 40.5% conversion and 81.8% selectivity. However, even at 150°C, low n-butenes

dimerization activity and fast deactivation due to coking were detected. The small amount of hard coke is sufficient to block the access of reactants to internal acid sites of zeolites. Cracking is often observed when using zeolite-based catalyst.

Ion (ionic) exchange resin catalysts reduce the negative environmental effects of acidic waste streams compared with mineral acid catalysts. Additionally, ion exchange resin catalysts are minimally corrosive and are easily separated from products. Up until now, ion exchange resin catalysts have only been used in selective isobutene dimerization processes to produce DIBs and isooctenes, because these products are useful octane enhancers. In other words, the feedstock was limited to isobutene (one isomer of butene) which results in DIB being essentially exclusively formed. Other catalysts, such as Nickel oxides and zeolites with or without nickel, appear inferior to the ion exchange resin catalyst of the present invention in activity, selectivity, and catalyst life for mixed light olefin dimerizations.

Therefore, there is a need for the efficient production of hydrocarbon components that show many advantages over presently used MTBE, ethanol, or alkylates as RON enhancers. Additionally there is a need for such a process that utilizes an ion exchange resin catalyst because they are minimally corrosive and separate easily from the products post reaction. Finally, there is a strong incentive to find inexpensive ways to produce octane enhancers, due to the high production costs of other octane enhancers such as ethanol.

### Summary

The present invention is directed to a process for producing octane-enhancing fuel components that overcomes the disadvantages of other fuel components such as MTBE, ethanol, and alkylates. Specifically, the present invention in one embodiment is directed to a process for producing C8 and C8+ olefins from the dimerization and oligomerization reactions of a mixed olefin (butene) feed. The process comprises introducing a mixed butenes liquid feed containing at least two butene isomers into a reactor with an acidic ion exchange resin catalyst under mild conditions.

In one embodiment, the mixed butenes feed consists of all four butene isomers. In another embodiment, the mixed butenes feed consists of at least two butene isomers and, optionally, can incorporate other C2-C5 olefins, such as ethylene, propylene and pentene.

The mixed butenes feed interacts with the ion exchange resin based catalyst in the reactor, converting mixed butenes into higher olefins. The use of an ion exchange resin based catalyst under mild reaction conditions will prevent cracking products and catalyst deactivation, which is a distinct advantage over other commercial oligomerization processes that utilize nickel oxide or zeolite-based catalysts. Additionally, the use of an ion-exchange resin catalyst in butene dimerization/oligomerization reactions under mild conditions leads to more highly branched C8 and C8<sup>+</sup> olefin products—specifically highly branched octenes that are very important RON enhancers—compared with nickel oxide and zeolite-based catalysts. In one embodiment, the ion exchange resin based catalyst is a sulfonic acid cation exchanger in the hydrogen form. In another embodiment, a polar compound such as a butanol or water may be added to the catalyst to promote the chemical reaction.

In one embodiment, the temperature maintained in the reactor is 30-160°C, the pressure maintained in the reactor is 20-100 bar, and the Liquid Hourly Space Velocity (LHSV) for the reactor is maintained at approximately 0.33 hr.

5    Brief Description of the Drawing Figures

A more complete understanding of the invention and its many features and advantages will be attained by reference to the following detailed description and the accompanying drawing. It is important to note that the drawing illustrates only one embodiment of the present invention and therefore should not be considered to limit  
10    its scope.

Fig. 1 shows a diagram of a fixed bed process in accordance with an embodiment of the invention.

Detailed Description of Certain Embodiments

15        As mentioned hereinbefore, the prior art contains a number of processes for the dimerization/oligomerization of iso-butene; however, these processes contain associated deficiencies, such as being highly selective towards one type of olefin (e.g., C8 olefins), with other higher number olefins being present in very small amounts. In particular, the prior art is directed to the dimerization/oligomerization of  
20    one butene isomer (e.g., isobutene). In addition, some of these processes are technically complex and require multiple steps for processing a feed stream.

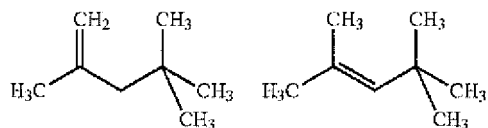
The present invention overcomes the deficiencies and limitations of the prior art and is directed to a process for the dimerization and oligomerization of mixed olefins (in particular mixed butenes) over an ion-exchange resin based catalyst to produce highly branched C8 and C8+ olefins. More specifically, the present invention is a single stage (single pass) process that is performed under mild conditions resulting in high conversion rates as discussed below. For selective dimerization/oligomerization of isobutene in the mixture of mixed olefins, an exemplary reaction temperature is between about 30-100°C. For dimerization/oligomerization of mixed butenes, an exemplary reaction temperature is from about 80°C to about 180°C.

#### Mixed Olefins (Butenes)

Mixed butenes have four structural isomers, 1-butene, 2-cis-butene, 2-trans-butene, and isobutene. Optionally, other low olefins, such as propylene and ethylene, can also be present in the feed as described below. In addition, the term "higher olefins" refers to olefins that are formed as a product as part of the present process and have a greater carbon number than the olefins in the initial feedstock introduced into the reactor.

#### Diisobutanes (DIBs) or Isooctenes

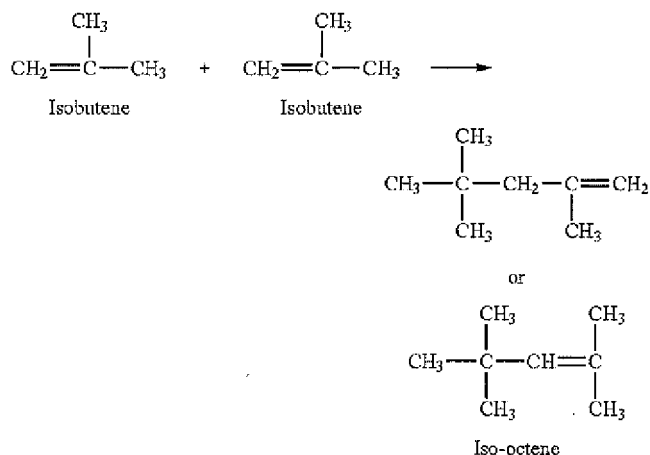
Diisobutenes include two isomers of 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene.



### Oligomerization

- Oligomerization of mixed butenes includes oligomerization of all butene
- 5 isomers including the oligomerization (dimerization) of isobutene, as well as the other isomers of butene.

### Dimerization of Isobutene



### 10 Ion-exchange Resin

Typically, ionic (ion) exchange resins are very small plastic beads and accordingly, the structure of the resin is a polymer on which a fixed ion has been permanently attached. To preserve the electrical neutrality of the resin, each fixed

ion is neutralized with a counterion. This counterion is mobile and can get into and out of the resin bead. Each ion going into the bead (resin) has to be replaced by an ion getting out of the bead, again to preserve electrical neutrality. This is what is called ion exchange. Only ions of the same electric sign are exchanged. Resins can thus come in both a cation resin form and an anion resin form. For ion exchange to be efficient, there must be a difference in affinity between the ion in the resin and the ion or ions that one seeks to remove from the solution. The resin must have a higher affinity for the ion in the solution compared to the ion in the resin.

In accordance with the present invention, an ion-exchange resin is broadly defined as an insoluble matrix containing labile ions capable of exchanging with ions in the surrounding medium without major physical change taking place in its structure. Suitable resins for use in the practice of the present invention include but are not limited to sulfonic acid cation exchangers in the hydrogen form. However, it will be appreciated that other ion-exchange resins can be used so long as they are capable of performing the intended functions and are suitable for use in the dimerization/oligomerization scheme described herein.

#### C8 olefins:

The mixture of C8 olefins mentioned in the present invention is mixed octenes, which are dimers of mixed butenes. There are total 72 isomers of the octenes and only a few of them have high RON values. There are two types of olefins, namely branched and linear (straight chained). Highly branched octenes are very important RON enhancers for gasoline and thus, the production of these types of octenes is desirable. Some of the C8 olefins are highly branched such as

dimethyl-hexene and trimethyl-pentene. C8 olefins may also be linear or with fewer branches which are not the subject of this invention. It will also be appreciated that cyclic products can also be formed by this process.

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#### C8+ olefins:

C8+ olefins stand for the oligomers of mixed butenes with a carbon number of 12 or more. The cyclic products can also be formed by this process.

#### 10 The Present Dimerization/Oligomerization Process

As described herein, effective processes for producing highly branched C8 and C8+ olefins from olefins are provided as embodiments of the present invention and more particularly, highly branched olefins are formed. Additionally, processes for producing fuel compositions that include oligomers prepared from butene and/or  
15 other olefins are also provided as embodiments of the present invention.

For example, in one embodiment of the present invention, a mixed olefin feedstock is contacted with a catalyst at the appropriate reaction conditions and preferably as part of a single stage process (single pass) to produce a product stream that includes oligomers. In another embodiment of the present invention, the  
20 un-reacted olefin can be recycled to produce the product stream of said oligomers. More specifically, a mixed butenes feedstock is contacted with a catalyst at the appropriate reaction conditions to produce a product stream that includes highly

branched C8 and C8+ olefins, including DIBs. The product stream can be combined with a fuel component to produce the fuel composition. The fuel component of the fuel composition can be selected from gasoline, diesel, jet fuel, aviation gasoline, heating oil, bunker oil, or a combination thereof, or other suitable fuel components within the spirit of the present invention. In certain embodiments including preferred embodiments, the resultant fuel composition has an increased RON and reduced RVP, without the presence of other chemicals that can have deleterious effects on the environment.

The source of the mixed olefin stream can vary and can encompass any number of different sources of feedstocks (streams) that are suitable for use in the present invention. For example, in some embodiments of the present invention, the mixed olefin stream can be a discharge stream from an FCC unit or thermal cracking unit, a raffinate stream from an MTBE process, a raffinate stream from TBA process, liquid petroleum gas (LPG) stream or a combination thereof. It will further be understood that other sources of the mixed olefin stream are within the scope of the present invention. In accordance with the disclosed embodiments, the mixed olefin stream can include a mixed butene stream. In another embodiment, the mixed olefin stream can be in the form of a mixed C3 to C5 olefins feed stream. In yet other embodiments, the mixed olefin stream can include one or more of polypropylene, n-butylene, 2-butene, isobutylene, pentenes, hexenes, olefins having more than six carbons, etc. Other suitable sources for the mixed olefin stream and types of olefins will be apparent to those of skill in the art and are to be considered within the scope of the present invention.

In accordance with one preferred embodiment of the present invention, the mixed butenes feed (stream/feedstock) used in this invention is a liquid mixture of at

least two and preferably all four of the isomers of 1-butene, isobutene, 2-trans-butene and 2-cis-butene. These relatively low value mixed butenes feeds can come directly from refinery tail gases.

Different butene isomers have different activities toward dimerization or  
5 oligomerization. For example, isobutene is predisposed to being dimerized or oligomerized. In contrast, it is generally very difficult for 2-butenes, especially 2-trans-butenes, to form the correspondent dimers or oligomers. Thus, most traditional processes focus on the selective dimerization of one butene isomer in that the process is specifically tailored to dimerizing one isomer of butene. This process  
10 limitation thus results in a product stream being formed that is of predominantly one olefin type. As mentioned herein, it is desirable to form a product stream that not only contains DIBs but also contains other highly branched higher olefins.

In accordance the present invention, the present process allows all four isomers of butene to be effectively dimerized or oligomerized under relatively mild  
15 conditions with high single pass conversion rates and high selectivity towards C8 olefins (along with production of C12 olefins and smaller amounts of C12+ olefins).

In one embodiment, the mixed butenes feed consists of all four butene isomers in varying quantities as will be appreciated by a review of the Examples presented herein. However, as previously mentioned and in accordance with  
20 another embodiment of the present invention, the feed can include at least two butene isomers, as well as other C3–C5 olefins, such as propylene and ethylene.

Fig. 1 illustrates one exemplary system 100 for performing dimerization/oligomerization of mixed butenes in accordance with the present invention. Fig. 1 likewise shows an exemplary process flow. Fig. 1 shows the

implementation of the present invention in a fixed bed process. The system 100 includes a reactor 110 which can be in the form of a fixed bed reactor vessel. A catalyst is loaded within a zone or region 112 that is within the reactor 110 as shown. In the illustrated embodiment, the catalyst is centrally located within the reactor 110.

5 The reactor 110 itself is disposed within a hotbox which is generally shown at 120.

The reactants are delivered to the reactor 110 in the following manner. A source of feedstock (e.g., the mixed butenes feed) is identified at 130 and the source 130 is fluidly connected (e.g., by means of a fluid conduit 131 (such as a pipe)) to a storage receptacle 140 to allow the feedstock to be stored in the storage receptacle

10 140. As mentioned herein, the feedstock is typically a liquid stream.

A valve or flow control device 145 is disposed along the conduit to control the flow of the feedstock to both the storage receptacle 140 and the reactor 10. In addition, a means 150 for delivering the feedstock (mixed butenes) into the reactor 110 at a desired rate is provided. The means 150 is in communication with the

15 storage receptacle 140 via a conduit 141 and is configured to operatively cause the feedstock to be delivered at a desired flow rate to the reactor 110. In one embodiment, the means 150 is in the form of a gas source (such as  $N_2$ ) that is used to press the liquid feedstock into the reactor 110 at a desired rate (flow rate). The gas source 150 is connected to the storage receptacle 140 by means of a conduit

20 (e.g., pipe) that can include a valve or the like 155 for controlling the flow of the gas to the storage receptacle 140.

The valve 145 can be placed into a position that closes off the flow from the source 130 to the storage receptacle 140; however, the combined gas (from source 150) and the stored feedstock within the storage receptacle 140 are permitted to flow

through the valve 145 toward the reactor 110. A conduit 151 can lead from valve 145 to an inlet of the reactor 110. Within the conduit 151, there can be a valve 153 that controls the flow the feedstock to the inlet of the reactor 110.

Before entering an inlet of the reactor 110, the feedstock passes through a  
5 heat exchange device 160 that is located between valve 145 and the reactor 110. The heat exchange device 160 is configured to adjust the temperature of the feedstock to a preselected temperature (e.g., a selected reactor temperature) prior to the feedstock entering the reactor 110. After passing through the reactor 110 and into contact with the catalyst in region 112, olefin products are formed as discussed  
10 herein and these products exit an outlet of the reactor 110 via a conduit 171 and are introduced to a separator 170. As described herein, the reactor 110 can be a single stage reactor in which the feedstock flows once therethrough and into contact with the catalyst to form the product stream. The conversion rates can thus be described as being single pass conversion rates.

15 The separator 170 can be in the form of a liquid/gas separator in which the olefin products with high boiling points are cooled down and flow through a conduit 173 before being collected as a liquid sample which is generally indicated at 180. Unreacted feedstock is removed from the separator 170 via a different outlet for further processing and/or collection. For example, the unreacted feedstock (e.g.,  
20 unreacted butenes) can flow through a conduit 175 be analyzed by an online gas chromatograph 190 or can simply be vented through a conduit/line 177 that leads to a vent 179. One or more valves can be included in the line 177 as shown.

It will be appreciated that the products (liquid sample 180) can be then further processed and/or transported to another location.

As mentioned herein and in accordance with one embodiment, the fixed bed reactor 110 has at least one region 112 that is loaded with a solid ion exchange catalyst which is suitable for use in the particular present invention. One exemplary solid ion exchange catalyst is a solid Brønsted acid catalyst. Accordingly, the solid ion exchange catalyst can be of a type that is suitable for use in the present invention and is of type that results in the dimerization/oligomerization of the mixed olefins to form the desired highly branched olefins (C8 and C8+ olefins).

Under mild reaction conditions which are described herein, this type of catalyst will prevent cracking products and will be less susceptible to catalyst deactivation—a problem often encountered in other commercial oligomerization processes using nickel oxide or zeolite-based catalysts. Further, the ion-exchange resin catalyst leads to the production of more highly branched C8 and C8+ olefins with milder reaction conditions compared with nickel oxide and zeolite-based catalysts.

In some embodiments, the catalyst resins employed are sulfonic acid cation exchangers in the hydrogen form. A specific exemplary strong acid cation exchange resin is described below with reference to the disclosed examples. A stream of a polar compound can also be added to the catalyst in the reactor to promote the oligomerization/dimerization reaction. In one embodiment, the promoter feed can be an alcohol, such as a butanol. In another embodiment, the promoter feed consists of water.

The reaction in the present invention takes place under mild reaction temperatures. For selective dimerization/oligomerization of isobutene in the mixture of mixed olefins, the reaction temperature is between 30-100°C. For

dimerization/oligomerization of mixed butenes, the reaction temperature is from 80°C to 180°C. More specifically, use of an ion exchange resin catalyst and mild conditions in the reactor 110 results in a non-corrosive, environmentally-friendly reaction, in contrast to those typically observed in the production of alkylates. For example, in one embodiment, the temperature at which the reaction is conducted is about 30°C to achieve high selectivity toward isobutene dimerizations.

The system and process described herein is a continuous flow process in which the feed stream is continuously fed into the reactor.

The products of the present invention is in the form of a stream that includes mainly C8 olefins and C12 olefins, with a small amount of C16 olefins, C16+ olefins, and cyclic compounds. Among the C8 olefins produced, the preferred one is DIB since as described herein, DIB has advantageous properties in terms of acting as an octane enhancer. The reaction in the present invention has high selectivity for C8 olefins—including DIB—as well as C12 olefins. However, unlike previous processes that produced DIB via selective dimerization of isobutene, the present invention utilizes relatively low value mixed butenes feeds to produce DIB and other valuable, highly-branched C8 and C8+ olefins. In other words, the mixed butenes feeds for use in the present process are not specifically customized to achieve high selective dimerization of isobutene (i.e., the feedstock is not solely isobutene) but rather, the mixed butenes feeds produce not only DIB but other desirable olefins (e.g., highly branched higher olefins) as a result of operation conditions and process steps described herein.

The products of the present invention, namely highly branched C8 and C8+ olefins with high RON values, are extremely valuable in the fuel industry. With the

increasingly restrictive regulations on gasoline as mentioned above, highly branched C8 and C8+ olefins provide an alternative non-oxygenated octane enhancer that meets those restrictions. Specifically, highly branched C8 and C8+ olefins can increase RON and lower RVP in fuel without the negative environment impact seen with MTBE or aromatics. The process of the present invention thus achieves this objective by producing a product that includes not only highly branched C8 olefins but also produces other highly branched olefins that have a carbon number more than 8.

The C8 and C8+ olefins produced through the present invention can also be used as valuable feedstock. Specifically, the C8 and C8+ olefin products can be utilized as premium feeds for Fluid Catalytic Cracking (FCC) processes such as Deep Catalytic Cracking (DCC) and High Severity Fluid Catalytic Cracking (HSFCC) processes to produce highly demanded light olefins such as ethylene and propylene. A mixture of dimers and trimmers which have a large number of allylic hydrogens are considerably more reactive and have proven to be the most desirable feeds for FCC based cracking processes such as HSFCC and DCC. These C8 and C8+ products may also be used as intermediates in synthesizing detergent, plasticizer, pesticide, lubricants, additives, flavors, medicine and many other fine industrial chemicals.

## EXAMPLES

The following examples are provided to better illustrate embodiments of the present invention. However, it is to be understood that these examples are merely illustrative in nature, and that the process embodiments of the present invention are not necessarily limited thereto.

The following experiments were conducted at a pilot plant having the configuration and characteristics of the system 100 illustrated in Fig. 1. In Examples 1-3, the feedstream was comprised of mixed butenes (mixed olefins) and more particularly, the composition of the mixed butenes is: 1-butene 21%; isobutene 35%;  
5 2-cis-butene 19%; and 2-trans-butene 25%. The mixed butenes can be obtained from any number of different commercial sources and in the present experiments, the mixed butenes were obtained from Abdullah Hashim Gas Ltd. and was used without any purification. The catalyst was an ion-exchange resin and more particularly, the catalyst was an ion-exchange resin that is commercially available  
10 under the trade name 0008-3 from Kairui Chemicals Co. Ltd of China. This exemplary resin is a macroporous strong acid cation exchange resin which is made up of opaque beads and is a sulfonic acid cation exchanger in hydrogen form.

A total of 30 mL of the catalyst was loaded into region 112 of the reactor 110 and the liquid hourly space velocity (LHSV) was approximately  $0.33 \text{ hr}^{-1}$ . The  
15 reaction conditions are listed in Table 1.

In the first example, the reactor was maintained at a pressure of about 20 bar and at a temperature of approximately  $150^{\circ}\text{C}$ . The mixed butenes feed was comprised of all four butene isomers in the following percentages: 2-trans-butene (25%), 1-butene (21%), isobutene (35%), and 2-cis-butene (19%). Unless otherwise  
20 indicated, the percentages mentioned herein are by weight. The test period was approximately 930 minutes. The results of the first example are found in Table 1 below.

Table 1 – Example 1

|                          |                                                                                          |                                              |                 |                        |
|--------------------------|------------------------------------------------------------------------------------------|----------------------------------------------|-----------------|------------------------|
| Reaction Conditions      | Temperature: 150°C; pressure: 20 bar; LHSV: 0.33 hr <sup>-1</sup> ; test period: 930 min |                                              |                 |                        |
| <u>Feed (percentage)</u> | <u>Conversion (%)</u>                                                                    |                                              | <u>Products</u> | <u>Selectivity (%)</u> |
| 2-trans-butene (25%)     | 51.1                                                                                     | <u>Average Conv.</u><br><br>(%)<br><br>59.5% | C8 olefins      | 66.4                   |
| 1-butene (21%)           | 62.3                                                                                     |                                              | C12 olefins     | 27.6                   |
| Isobutene (35%)          | 64.6                                                                                     |                                              | C16 olefins     | 5.4                    |
| 2-cis-butene (19%)       | 57.9                                                                                     |                                              | C20 olefins     | 0.6                    |

In the second example, the reactor was maintained at a pressure of about 20 bar and a temperature of approximately 160°C. The mixed butenes feed was comprised of all four butene isomers in the following percentages: 2-trans-butene (25%), 1-butene (21%), isobutene (35%), and 2-cis-butene (19%). The test period was approximately 1020 minutes. The results of the second example are found in Table 2 below.

Table 2 – Example 2

|                          |                                                                                           |                 |                        |
|--------------------------|-------------------------------------------------------------------------------------------|-----------------|------------------------|
| Reaction conditions      | Temperature: 160°C; pressure: 20 bar; LHSV: 0.33 hr <sup>-1</sup> ; test period: 1020 min |                 |                        |
| <u>Feed (percentage)</u> | <u>Conversion (%)</u>                                                                     | <u>Products</u> | <u>Selectivity (%)</u> |

|                           |      |                                              |             |      |
|---------------------------|------|----------------------------------------------|-------------|------|
| 2-trans-butene<br>(25.2%) | 73.5 | <u>Average Conv.</u><br><br>(%)<br><br>78.2% | C8 olefins  | 58.5 |
| 1-butene (21.5%)          | 79.7 |                                              | C12 olefins | 31.9 |
| Isobutene (32.4%)         | 81.2 |                                              | C16 olefins | 8.2  |
| 2-cis-butene<br>(20.7%)   | 77.4 |                                              | C20 olefins | 1.4  |

For the third example, the reactor was maintained at a pressure of about 20 bar and a temperature of approximately 150°C. The mixed butenes feed was comprised of all four butene isomers in the following percentages: 2-trans-butene (25%), 1-butene (21%), isobutene (35%), and 2-cis-butene (19%). A water promoter feed was also added to the reactor at a rate of 0.01 g/min. The test period was approximately 480 minutes. The results of the third example are found in Table 3 below.

10 Table 3 – Example 3

|                           |                                                                                                                  |                                 |                 |                        |
|---------------------------|------------------------------------------------------------------------------------------------------------------|---------------------------------|-----------------|------------------------|
| Reaction conditions       | Temperature: 160°C; pressure: 20 bar; LHSV: 0.33 hr <sup>-1</sup> ; test period: 480 min; water feed: 0.01 g/min |                                 |                 |                        |
| <u>Feed (percentage)</u>  | <u>Conversion (%)</u>                                                                                            |                                 | <u>Products</u> | <u>Selectivity (%)</u> |
| 2-trans-butene<br>(25.2%) | 80.6                                                                                                             | <u>Average Conv.</u><br><br>(%) | C8 olefins      | 59.9                   |

|                         |      |        |             |      |
|-------------------------|------|--------|-------------|------|
| 1-butene (21.5%)        | 89.0 | 84.5 % | C12 olefins | 30.5 |
| Isobutene (32.4%)       | 90.5 |        | C16 olefins | 8.6  |
| 2-cis-butene<br>(20.7%) | 73.5 |        | C20 olefins | 1.0  |

The average single pass conversion rate of mixed butenes of this invention reached 84.5% (Example 3), while the selectivity towards C8-C12 olefins reached 94% (Example 1). The single pass conversion rates of this invention are significantly higher than what have been reported in the literature for pure isobutene dimerization and 1-butene dimerization. The conversion rate we reported here is very conservative. Based on gas chromatography (GC) analysis of the butene in and butene out of the reaction, the single pass conversion is greater than 90% in certain embodiments<sup>3</sup>.

It will therefore, be appreciated that the present invention describes a single stage process (single pass conversion) in which the mixed butenes undergo dimerization/oligomerization (without being a selective process that is configured to predominantly produce one olefin product and without a hydration step that is configured to product alcohol along with olefins as part of a product stream). As described herein, the process and system of the present invention is directed to the dimerization/oligomerization of four butene isomers together (include n-butene, trans-2-butene, iso-butene and cis-2-butene) (i.e., a mixed light olefin feed) using an ion exchange resin as a catalyst and implemented in a single stage reactor.

The process and the system of the present invention provide a number of advantages over the conventional dimerization/oligomerization processes. These advantages include but are not limited to: (1) providing an alternative non-oxygenated octane enhancer, highly branched C8 and C8+ olefins, to meet the

5 increasingly restrictive regulations and reduction of aromatics in the gasoline; (2) to valorize the relatively low mixed butenes; and (3) to increase the yields of valuable light olefins of ethylene and propylene by recycle of low value butenes to premium cracking feeds (C8-C16 olefins).

While the present invention has been described above using specific

10 embodiments, there are many variations and modifications that will be apparent to those having ordinary skill in the art. As such, the described embodiments are to be considered in all respects only as illustrative, and not restrictive. The scope of the invention is, therefore, indicated by the appended claims, rather than by the foregoing description. All changes that come within the meaning and range of

15 equivalency of the claims are to be embraced within their scope.

What is claimed is:

1. A process for dimerizing and oligomerizing a mixed olefins feed comprising mixed olefins to produce mixed higher olefins, said process comprising the steps of:

introducing the mixed olefins feed into a reactor vessel under oligomerization

5 conditions;

contacting the mixed olefins feed with an ion-exchange resin based catalyst within the reactor to convert the mixed olefins into the mixed higher olefins; and

producing a product stream comprising the mixed higher olefins from the reactor vessel;

10 wherein the hydrocarbon feed comprises at least two different types of olefins having 2 to 5 carbons and the mixed higher olefins comprises: (1) olefins having 8 carbons and (2) olefins having more than 8 carbons.

2. The process of claim 1, wherein the mixed olefins feed comprises at least two butene isomers.

15 3. The process of claim 2, wherein the mixed olefins feed comprises all four isomers of butane.

4. The process of claim 1, where the ion-exchange resin based catalyst comprises a sulfonic acid cation exchanger in the hydrogen form.

20 5. The process of claim 1, wherein the mixed higher olefins comprises olefins having 8 carbons and olefins having more than 8 carbons.

6. The process of claim 5, wherein the mixed higher olefins comprises diisobutene (DIB).

7. The process of claim 5, wherein the mixed higher olefins comprise at least 50% by weight olefins having 8 carbons and at least 20% by weight olefins having 12 carbons.
8. The process of claim 5, wherein the olefins having 12 or more carbons  
5 comprise: (a) olefins having 12 carbons, (b) olefins having 16 carbons; and (c) olefins having 20 carbons.
9. The process of claim 5, wherein a portion of the olefins having 8 carbons that are formed as part of the product comprises highly branched olefins including dimethyl-hexene and trimethyl-pentene.
10. The process of claim 1, where the reactor vessel is maintained at a  
10 temperature of between about 30-180°C.
11. The process of claim 1, further including the step of introducing into the reactor a catalyst promoter which comprises a polar compound.
12. The process of claim 11, wherein the promoter is at least one of water and  
15 butanol.
13. A process for producing a fuel composition from mixed butenes using a butene dimerization/oligomerization system, the process comprises the step of:  
introducing a mixed butenes stream comprising the mixed butenes into a reactor vessel that is part of the dimerization/oligomerization system under  
20 oligomerization conditions;  
  
contacting the mixed butenes stream with an ion-exchange resin based catalyst within the reactor to convert the mixed butenes into a product stream comprising mixed olefins that include highly branched olefins having 8 carbons and olefins having more than 8 carbons; and

combining the product stream with a fuel component to produce the fuel composition;

wherein the mixed butenes comprise n-butene, trans-2-butene, iso-butene, and cis-2-butene; and

5 wherein the fuel component comprises gasoline, diesel, jet fuel, aviation gasoline, heating oil, bunker oil, or a combination thereof.

14. The process of claim 13, wherein the mixed higher olefins comprises olefins having 8 carbons including diisobutene (DIB) and olefins having more than 8 carbons.

10 15. The process of claim 14, wherein the mixed olefins comprise at least 50% by weight olefins having 8 carbons and at least 20% by weight olefins having more than 8 carbons.

16. The process of claim 14, wherein the olefins having more than 8 carbons comprise: (a) olefins having 12 carbons, (b) olefins having 16 carbons; and (c)  
15 olefins having 20 carbons.