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3,221,078

SELECTIVE HYDROGENATION OF
OLEFINS IN DRIPOLENECarl D. Keith, Summit, and Paul N. Rylander, Newark,
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Our invention relates to a method whereby diolefin hydrocarbons can be substantially hydrogenated when admixed with monoolefin hydrocarbons and aromatic hydrocarbons, without substantial hydrogenation of the aromatic hydrocarbons. In a more limited aspect, our invention relates to a method whereby both diolefin hydrocarbons and monoolefin hydrocarbons can be substantially hydrogenated when admixed with aromatic hydrocarbons without substantial hydrogenation of the aromatic hydrocarbons.

Normally liquid hydrocarbon mixtures which contain diolefins, monoolefins and aromatics can be produced by a variety of processes which are known in the art. Such processes can involve the pyrolysis or cracking of crude petroleum or fractions derived therefrom containing at least two carbon atoms on the average, for example, ethane, propane, propylene, butane, natural gasoline, light straight run gasoline (for example, one having a boiling range of from about 90 to 215° F.), straight run naphtha (for example, one having a boiling range of from about 215 to 430° F.), kerosene naphthenic catalytic light cycle stock produced in the cracking of gas oil by the fluid process to produce gasoline, straight run gas oil, and the like. The aforementioned pyrolysis operations can be carried out with or without the aid of a catalyst and in the presence or absence of steam. Generally, they are carried out at temperatures within the approximate range of 1350° F. to 1550° F., although somewhat lower and somewhat higher temperatures can also be used, and at pressures within the approximate range from zero p.s.i.g. to fifty p.s.i.g. although in some instances considerably higher pressures can be used. The pyrolysis operations are generally carried out primarily for the production of ethylene, the normally liquid hydrocarbon mixture containing diolefins, monoolefins and aromatics being obtained as a by-product. Usually the normally liquid hydrocarbon mixtures which are hydrogenated in accordance with our process will have a boiling point at atmospheric pressure within the range from approximately 0° F. to approximately 500° F.

Materials which can be subjected to the hydrogenation operation of our invention include dripolene or fractions thereof. Dripolene is a normally liquid mixture of hydrocarbons obtained as a by-product in the high temperature pyrolysis of normally gaseous hydrocarbons to produce ethylene. In the production of dripolene, a gaseous hydrocarbon such as ethane, propane, propylene, or a mixture thereof (for example, by-product refinery gas) is pre-heated and passed through an alloy tube at a high space velocity and at a pyrolysis temperature between about 1200° F. and 1800° F., preferably between about 1350° F. and 1550° F. Low pressures up to about 85 p.s.i.g. are ordinarily employed in this operation, a pressure below about 20 p.s.i.g. being satisfactory. The time of exposure to the high temperature is usually about 0.05 to 5 seconds, contact times of 0.1 to 1 second being preferred.

The pyrolysis produces normally gaseous products containing unsaturated hydrocarbon such as ethylene, normally liquid hydrocarbons rich in unsaturated hydrocarbons including olefins and diolefins of varying boiling points and structural configuration, and various aromatic hydrocarbons, as well as tar. The unsaturated hydro-

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carbons such as ethylene which are contained in the normally gaseous product are usually the desired product of the pyrolysis process. The normally liquid hydrocarbons and tar which are obtained are considered to be by-products of the pyrolysis operation. High temperature pyrolysis products are rapidly cooled, usually by quenching with water to a temperature of about 400° F. A viscous tarry material condenses out of the gas during the quenching. The gases from the quenching operation are compressed and cooled and a liquid material which boils between about 100° and 400° F. condenses out of the gases during the compressing-cooling step. This liquid is dripolene. The amount of tar and dripolene produced is dependent upon the feed, temperature, contact time and pressure. The quantity of liquid hydrocarbons produced in this way is ordinarily about 3 percent by weight of the total quantity of gas charged to the pyrolysis reactor. As a charge stock to the hydrogenation process of our invention, it is desirable to use an overhead cut or fraction taken in a distillation of the total dripolene, such cut or fraction being generally free of those high boiling fractions of the dripolene which have heretofore been used in the manufacture of resins by thermal or catalytic polymerization. The dripolene overhead cut will generally have a boiling point at atmospheric pressure not exceeding 375° F. and will generally amount to not more than 90 percent by volume of the dripolene from which it has been obtained by distillation. Potential resin-forming ingredients present in the dripolene can also be removed from the dripolene by passing it through a bed of activated alumina at room temperature.

As has been stated, the normally liquid hydrocarbon mixtures which are hydrogenated in accordance with our invention contain two types of hydrocarbons which are desirable motor fuel ingredients, namely, monoolefins and aromatics, and one type which are not, namely, diolefins. Diolefins are undesirable motor fuel ingredients because they are unstable and lead to gum formation. In its broader aspect, our invention provides a means whereby the diolefins can be hydrogenated, so that the hydrogenated product contains monoolefins and a large proportion of the aromatics originally present in the hydrocarbon mixture subjected to hydrogenation. When this is done, the hydrogenated normally liquid hydrocarbon mixture is upgraded in its utility as a motor fuel ingredient.

The normally liquid hydrocarbon mixtures which we employ as a starting material are a valuable source of aromatics. Aromatics are conventionally recovered from mixtures containing them by the use of solvent extraction procedures. For such procedures to be used most advantageously, the mixtures subjected to extraction should be essentially free from both diolefins and monoolefins, since the presence of such olefins interferes with the solvent extraction. In its more limited aspect, our invention provides a method for the substantially complete hydrogenation of both diolefins and monoolefins.

It has heretofore been proposed (U.S. Patent No. 2,953,612 to Haxton et al. and U.S. Patent No. 2,799,627 to Haensel mentioned therein) to hydrogenate aromatic-containing hydrocarbon fractions to remove diolefins and monoolefins therefrom using a platinum-alumina or palladium-alumina catalyst. In accordance with the process of our invention, we employ a palladium-alumina catalyst, the use of this type of catalyst making for selectively. In other words, by using a palladium-alumina catalyst we obtain less hydrogenation of aromatics, in comparison with the amount of aromatics hydrogenation which takes place when a platinum-alumina catalyst is used. Moreover, in order to minimize the hydrogenation of aromatics and also to provide for long catalyst life, we conduct the

hydrogenation at an average temperature not exceeding 210° F. Furthermore, in our operation using the palladium-alumina catalyst, the hydrogenation is carried out with the dripolene or other hydrocarbon mixture being hydrogenated at least 90 percent by weight in the liquid phase while the hydrocarbon mixture undergoing hydrogenation is contacted with the catalyst. In the process of Haxton et al., although when the dripolene first contacts the catalyst it is almost entirely in the liquid phase, the dripolene vaporizes during operation as a result of the heat generated by the hydrogenation, so that in its later stages the operation is a vapor phase hydrogenation. In the operation described by Haensel, the hydrogenation is a vapor phase one.

The catalyst which is used in practicing our process is one which consists essentially of palladium supported on an activated or gamma-alumina base, preferably a base which is essentially free of components which react with alumina to form an acidic catalyst, such as chlorine, fluorine, silica, boria, and the like. The catalyst will generally contain from 0.05 to 10.0 percent by weight of palladium, preferably from 0.1 to 1.0 percent by weight and preferably deposited on the superficial surface of the alumina. Preferably, the base will be of relatively high surface area, for example, from 25 to 500 square meters per gram or higher as measured by the BET method. Catalysts which can be utilized in accordance with our process are well-known in the art. For example, suitable catalysts can be prepared by impregnating commercially available activated alumina pellets with an aqueous solution of a suitable palladium salt, for example, palladium chloride admixed with hydrochloric acid, followed by precipitation of the palladium in situ by the use of aqueous hydrogen sulfide solution or gaseous hydrogen sulfide. After this has been done, the pellets can be dried and calcined in air. Catalysts suitable for use in our process can also be prepared by the general procedure described in U.S. Patent No. 2,475,155 to Rosenblatt.

The hydrocarbon mixture hydrogenated in accordance with our invention will generally have a bromine number (ASTM-D-1158-55T) of at least about 10, and generally within the range from about 30 to about 100. In the aspect of our invention wherein the diolefins are hydrogenated to provide a reaction product containing monoolefins and aromatics, the hydrogenation can be carried out under a wide variety of operating conditions, depending upon the particular stock being treated, the intended use of the product and the activity of the catalyst used. In general, however, the hydrogenation will be conducted at a pressure with the range from about zero p.s.i.g. to 2000 p.s.i.g. (preferably 100 p.s.i.g. to 700 p.s.i.g.) and at a liquid hourly space velocity (LHSV, meaning volume of hydrocarbon mixture being hydrogenated per volume of catalyst per hour) within the range from about 0.1 to about 10. The amount of hydrogen introduced into the reaction zone will generally be from 2 to 20 times that required to saturate completely the olefins (monoolefins plus diolefins) present in the feed being hydrogenated.

As has been stated above, the hydrogenation with the palladium-alumina catalyst is carried out at an average temperature not exceeding 210° F., and generally at an average temperature within the range from 100° F. to 200° F. Under adiabatic conditions, the temperature of the reaction mixture rises as the hydrogenation proceeds. In order to prevent undue temperature increase of the mixture undergoing hydrogenation, various means can be resorted to. For example, the hydrocarbon undergoing hydrogenation can be admixed with an extraneous inert material, for example, the hexane used in the examples below, or with recycled hydrogenated product. On the other hand, the reaction zone can be supplied with cooling means, for example, a cooling jacket or coils, or the catalyst can be disposed in two or more beds with cooling means being provided between the beds.

As has been stated, one aspect of our invention involves the production of a hydrogenated product which is essentially free from both diolefins and monoolefins, that is, has a bromine number not exceeding one. This can be accomplished, in accordance with our invention, by subjecting the product resulting from the hydrogenation step involving the use of palladium-alumina catalyst to vapor phase hydrogenation using a catalyst which consists essentially of cobalt molybdate supported on alumina. When the hydrogenation step with cobalt molybdate is carried out, the hydrogenated product produced in the preceding step is preferably treated in order to remove polymers. This can be accomplished in a variety of ways, for example, by distilling and discarding the bottoms. On the other hand, the hydrogenated product from the first step can be passed through a bed of activated alumina at room temperature.

Various methods for manufacturing cobalt molybdate supported on alumina catalysts are known in the art. Note, for example, U.S. Patent No. 2,325,033 to Byrns and U.S. Patent No. 2,898,308 to Teter et al. Such catalysts generally consist essentially of from about 2 to 5 percent by weight of cobalt oxide and from 5 to 15 percent by weight of molybdic oxide, the balance being alumina. In using the cobalt molybdate-alumina catalyst, temperatures within the range from about 550 to about 950° F., pressures within the range from about 200 to about 1000 p.s.i.g., and weight hourly space velocities (WHSV, meaning weight units of hydrocarbon feed to be hydrogenated per weight unit of catalyst per hour) within the range from about 0.1 to about 10 can suitably be used. Hydrogen to hydrocarbon ratios within the range from about 1 to about 10 can be employed, these ratios being on a molar basis and on the basis of hydrocarbons introduced into the reaction zone. Tungsten-nickel sulfide, nickel-alumina, platinum-alumina and palladium-alumina can also be used in place of the cobalt molybdate-alumina catalyst.

The following examples illustrate our invention.

Example I

A quantity of commercially activated alumina was first obtained. This sample was of 8-14 mesh size (U.S. Standard Sieve), had a surface area of about 250 square meters per gram (BET method), and typically had the following analysis by weight: alumina, 92 percent; Na₂O, 0.80 percent; Fe₂O₃, 0.12 percent; SiO₂, 0.09 percent and TiO₂, 0.01 percent, the remaining being volatile matter.

This commercially activated alumina was employed in the manufacture of a catalyst containing 0.3 percent by weight of palladium by making the catalyst in the manner described in U.S. Patent No. 2,475,155 to Rosenblatt.

A 0.500 inch outside diameter reactor tube with a 0.0049 inch wall was charged with 5 ml. or 4.1 grams of the palladium-alumina catalyst which was mixed with 19 ml. of corundum pellets of a size similar to that of the palladium-alumina catalyst. The reactor tube was surrounded with a liquefied paraffin bath maintained at 70° C., and nitrogen gas was bubbled through the bath to equalize its temperature.

In this example a fraction obtained by fractionating a quantity of dripolene was hydrogenated. This fraction had a boiling range at atmospheric pressure of from 93° F. to 295° F., had a specific gravity (measured at 20° C. and referred to water at 4° C.) of about 0.865, and had a bromine number of 50. The fraction contained 0.0045 percent by weight of sulfur and analyzed as follows by volume: isoprene, 0.5 percent; cyclopentadiene, 9.2 percent; cyclohexadiene, 1.3 percent; benzene, 71.1 percent; toluene, 17.0 percent; xylene, 0.6 percent; and styrene 0.3 percent.

As the dripolene fraction had been standing a considerable period of time before being used in this example, it was passed through a bed containing 65 ml. of the same kind of activated alumina as was used in preparing

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the palladium-alumina catalyst. Prior to passage through the bed, the dripolene fraction was diluted with an equal volume of normal hexane.

In carrying out the hydrogenation, the dripolene fraction which was diluted with an equal volume of normal hexane and which had been passed through the bed of activated alumina was delivered as feed upward through the catalyst reactor bed at the rate of 10.0 ml. per hour (liquid hourly space velocity of one, based upon the dripolene fraction). Hydrogen was introduced concurrently with the dripolene fraction at a rate of 2.40 liters per hour, measured at 25° C. and one atmosphere. A hydrogen rate of 0.32 liter per hour was necessary to hydrogenate all of the olefins present in the dripolene fraction. The reactor pressure was maintained at 400 p.s.i.g. with the hydrogen being delivered from a pressurized tank and with the dripolene fraction being supplied by means of a pump.

The bromine number of the hydrogenated product dropped to a low level during the first few hours of operation and then levelled off at 4-5 (8-10 on the basis of the dripolene fraction hydrogenated). This life study was continued for more than 2500 hours, indicating a favorable life for the palladium catalyst in selectively removing diolefins from the dripolene fraction.

A sample of the dripolene fraction-n-hexane mixture hydrogenated with the palladium-alumina catalyst was distilled to yield a fraction containing 46 percent by volume of aromatics and 52 parts per million of sulfur. This distilled fraction had a bromine number of 4.3 and had the following ASTM distillation: initial boiling point, 148° F.; 10 percent, 156° F.; 50 percent, 163° F.; 90 percent, 184° F.; and end point, 247° F.

The distillate fraction described in the preceding paragraph was hydrogenated over a cobalt molybdate-alumina catalyst at 5 WHSV and 500 p.s.i.g. In carrying out this operation, the catalyst used was in the form of 1/16-inch pellets and analyzed approximately 3 percent by weight of cobalt oxide and approximately 10 percent by weight of molybdc oxide, the remainder being alumina. Hydrogen gas was introduced into the reaction zone at the rate of five moles per mole of total hydrocarbon feed, including the n-hexane present therein. When the reaction temperature was 600° F., the hydrogenated product had a bromine number of 0.2. A reaction temperature of 700° F. was also found to be suitable for use in the hydrogenation step with the cobalt molybdate-alumina catalyst, inasmuch as essentially no hydrocracking or loss of aromatics occurred when the hydrogenation was conducted at this temperature.

We claim:

1. A method for the hydrogenation of diolefins present in a liquid hydrocarbon mixture containing diolefins, monoolefins and aromatics and boiling at atmospheric pressure within the range from about 0° F. to 500° F. which comprises passing the hydrocarbon mixture and hydrogen into contact with a palladium-alumina catalyst under hydrogenation conditions of pressure and space velocity and at an average temperature not exceeding 210° F. whereby the diolefins present in the hydrocarbon mixture are hydrogenated, the hydrocarbon mixture being hydrogenated being at least 90 percent by weight in the liquid phase at all times while it is in contact with the catalyst.

2. The method of claim 1 wherein the liquid hydrocarbon mixture is dripolene and the dripolene and hydrogen are passed concurrently upwardly through the catalyst.

3. The method of claim 1 wherein the palladium-alumina catalyst consists essentially of activated alumina

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having supported thereon from 0.05 to 10 percent by weight of palladium.

4. The method of claim 1 wherein the pressure is within the range from zero p.s.i.g. to 2000 p.s.i.g. and wherein the liquid hourly space velocity is within the range from 0.1 to 10.

5. A method for the hydrogenation of diolefins and monoolefins present in a liquid hydrocarbon mixture containing diolefins, monoolefins and aromatics and boiling at atmospheric pressure within the range from about 0° F. to 500° F. which comprises passing the hydrocarbon mixture and hydrogen into contact with a palladium-alumina catalyst under hydrogenation conditions of pressure and space velocity and at an average temperature not exceeding 210° F. whereby the diolefins present in the hydrocarbon mixture are hydrogenated, the hydrocarbon mixture being hydrogenated being at least 90 percent by weight in the liquid phase at all times while it is in contact with the catalyst, and thereafter passing the hydrocarbon mixture in vapor phase together with hydrogen into contact with a cobalt molybdate-alumina catalyst under hydrogenation conditions of temperature, pressure and space velocity whereby the monoolefins are hydrogenated without substantial hydrogenation of aromatics present in the hydrocarbon mixture and whereby a hydrogenated product having a bromine number not exceeding one is produced.

6. The method of claim 5 wherein the liquid hydrocarbon mixture is dripolene.

7. The method of claim 5 wherein the palladium-alumina catalyst consists essentially of activated alumina having supported thereon from 0.05 to 10 percent by weight of palladium.

8. The method of claim 5 wherein, in the first hydrogenation step the pressure is within the range from zero p.s.i.g. to 2000 p.s.i.g. and the liquid hourly space velocity is within the range from 0.1 to 10 and wherein, in the second hydrogenation step, the temperature is within the range from 550 to 950° F., the pressure is within the range from 200 to 1000 p.s.i.g. and the weight hourly space velocity is within the range from 0.1 to 10.

9. The process of claim 5 wherein the hydrocarbon mixture after having been hydrogenated using the palladium-alumina catalyst is treated to remove polymers prior to being hydrogenated using the cobalt molybdate-alumina catalyst.

10. The process of claim 9 wherein the treatment to remove polymers is effected by distillation.

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