

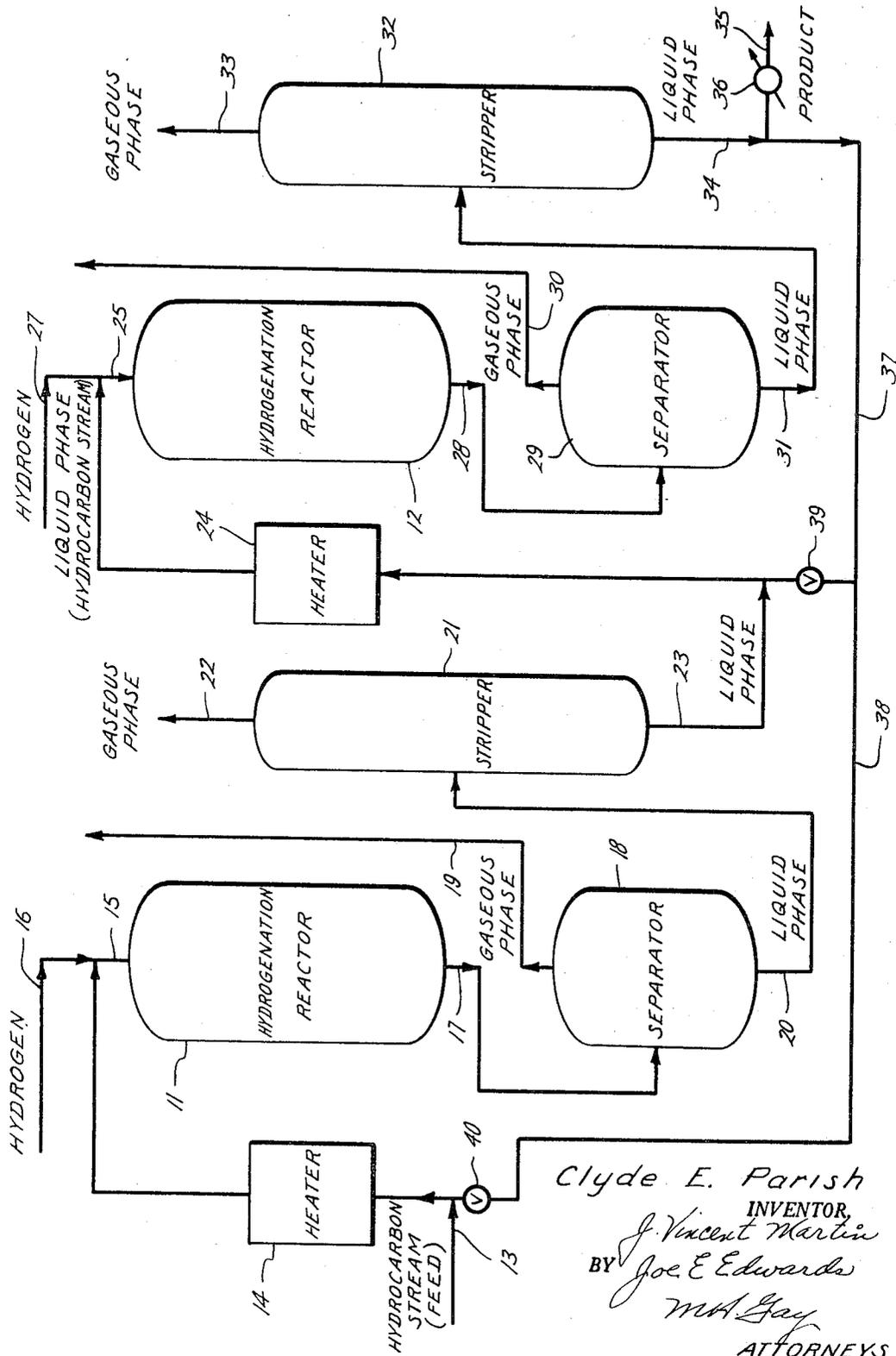
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TWO-STAGE HYDROGENATION OF AROMATIC-HYDROCARBONS

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1

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**TWO-STAGE HYDROGENATION OF AROMATIC
HYDROCARBONS**

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This is a continuation-in-part of my prior co-pending United States patent application Serial No. 135,516, filed September 1, 1961, now abandoned, entitled Hydrogenation Process.

The present invention generally relates to a process for hydrogenating aromatic hydrocarbons and more particularly relates to an improved process for converting monocyclic aromatics into the corresponding cycloaliphatic hydrocarbons.

Hydrogenation of aromatics in hydrocarbon streams frequently has been carried out to provide saturated hydrocarbons. For example, hydrogenation has been employed to convert benzene into cyclohexane, toluene into methyl cyclohexane and the aromatics in kerosene petroleum fractions into various cycloaliphatics. In addition, several processes are specifically directed to the conversion of polycyclic aromatics into polycyclic aliphatics and derivatives.

Difficulties have been encountered in many known processes for converting aromatics to the corresponding completely saturated hydrocarbons. Thus, in processes directed to conversion of polycyclic aromatics to the corresponding cycloaliphatics, relatively severe reaction conditions are usually required. These conditions usually result in some cracking of feed and loss of product, with deposition of cracked materials upon the catalyst and reduction in catalyst activity. Moreover, difficulties may arise separating the various desired products from undesired by-products.

Present processes which are largely directed to conversion of selected monocyclic aromatics to selected monocyclic aliphatics usually require a relatively large number of steps, selected purified catalyst poison-free feed and other special parameters. Moreover, many of such processes are also characterized by relatively low yields of product, and by cracking of feed and catalyst fouling in the absence of special precautionary measures.

There are also aromatic hydrogenating processes which are of a more general nature and which attempt in a relatively indiscriminate manner to at least partially hydrogenate both monocyclic and polycyclic aromatics. Such processes in general result in relatively low yields of product and are mainly used for general upgrading of feed stocks.

Accordingly the above-described types of hydrogenation processes usually can be readily distinguished from one another on the basis of difficulties to be overcome, types of catalyst, types of process steps, conditions and equipment, and in other ways. Since the hydrogenation of monocyclic aromatics to monocyclic aliphatics is becoming increasingly important to the petroleum industry and since current processes for the same are usually subject to one or more of the described difficulties and/or deficiencies, it would be highly desirable to be able to provide an improved process which features a simplified procedure. Such process should be economical and result in essentially complete conversion of monocyclic aromatics to the corresponding monocyclic aliphatic hydrocarbons for maximum yield under easily controlled, moderate hydrogenation conditions which preserve maximum catalyst activity. Relatively high feed rates and conversion rates are desired, as well as adaptability of such a process to the treatment of the usual grades of monocyclic aromatics without special pretreatment of the feed or other complicated and/or costly steps.

2

Accordingly, it is a principal object of the present invention to provide an improved process for hydrogenating monocyclic aromatics into the corresponding monocyclic aliphatic hydrocarbons.

Another object is to provide an improved hydrogenation process for converting monocyclic aromatics into the corresponding saturated hydrocarbons under moderate operating conditions, including temperature and pressure, and at high feed rates, whereby catalyst fouling and loss of product are reduced.

Yet another object of the present invention is to provide an improved monocyclic aromatic hydrogenation process which employs a minimum number of relatively simple steps, and is capable of providing high yields of monocyclic aliphatics without substantial cracking of the feed and while preserving the activity of at least a portion of the catalyst so as to assure essentially complete hydrogenation of the monocyclic aromatics.

A further object is to provide a process for hydrogenating monocyclic aromatics through the use of platinum catalysts, which process maintains maximum activity of at least a portion of such catalyst.

These and other objects will become more apparent when read in conjunction with the following detailed description, the claims and the attached drawings wherein there is schematically illustrated one embodiment of apparatus for carrying out the process of the present invention.

In accordance with the present invention, the foregoing objects are accomplished by subjecting a low boiling hydrocarbon feed stream containing monocyclic aromatics in a first reaction zone to the action of dry hydrogen under selected hydrogenation conditions of temperature and pressure and space velocity generally characterized as moderate conditions, and which do not result in cracking of the feed. The hydrogenation in the first reaction zone is carried out with the feed in the liquid phase and in the presence of a hydrogenation catalyst containing platinum to substantially hydrogenate the monocyclic aromatics in the feed. The total product of the first reaction zone is then passed from that zone and separated into liquid and gaseous phases, the liquid phase being free of platinum catalyst poisons, while the gaseous phase contains the catalyst poisons, such as sulfur compounds. The gaseous phase, including unreacted hydrogen, is passed out of the primary system and, if desired, unreacted hydrogen can be stripped therefrom and purified for recontacting with incoming feed in the first reaction zone.

The separated purified liquid phase is then hydrogenated in the liquid phase in a separate second reaction zone with dry, platinum catalyst poison-free hydrogen and a poison-free portion of the hydrogenation catalyst containing platinum, under conditions of pressure, temperature and space velocity equivalent to those of the first reaction zone. Such hydrogenation in the second reaction zone is preferably carried out for a time sufficient to fully hydrogenate the monocyclic aromatics to monocyclic aliphatics. Since the flow rates are high and the conditions are mild, cracking of the feed or product is eliminated. Accordingly, with the second reaction zone isolated from catalyst poisons and free of polymeric laydown on the catalyst, the peak efficiency of hydrogenation in the second reaction zone can be maintained, since the catalyst therein is kept in a state of maximum hydrogenation activity. The net result is conversion of up to essentially 100 percent of the monocyclic aromatics to monocyclic aliphatics and at a relatively rapid rate.

Before a specific description of the present process is given, the following definitions and abbreviations will be used for the purposes of convenience in an effort to simplify this disclosure. All temperatures are designated

3

on the Fahrenheit scale as ° F., pressures are given in pounds per square inch gauge and are abbreviated as p.s.i., hydrogen gas flow rates are given as standard cubic feet of hydrogen per barrel of hydrocarbon stream feed, and are abbreviated as s.c.f. per barrel, and space velocity is given as liquid hourly space velocity per volume of catalyst, and is abbreviated as LHSV.

Wherever hydrogen is referred to herein, it will be understood that such hydrogen is conventional hydrogen in that it is dry. It has been found that the yield of desired product usually is lowered if the hydrogen contains substantial proportions of water vapor or is saturated therewith. Moreover, the hydrogen which is passed into the second reaction zone is free of both moisture and platinum catalyst poisons, including nitrogen compounds and sulfur compounds. Preferably, the dry hydrogen which passes into the first reaction zone is also free of platinum catalyst poisons, although this is not essential, inasmuch as the feed to the first reaction zone usually contains platinum catalyst poisons.

It will be further understood that the hydrogen referred to herein can be recycle hydrogen or hydrogen from any source, as long as it meets the described criteria so far as moisture and platinum catalyst poisons are concerned. Thus, for example, the waste hydrogen in the gaseous phase from the stripping zone between the first and second reaction zones can be passed to a separator and completely separated from platinum catalyst poisons and moisture and then can be reused, as previously described. As another example, dry hydrogen containing platinum catalyst poison could be recycled from the stripping zone between the first and second reaction zone and can be recycled to the first reaction zone. Moreover, dry, poison-free hydrogen from a stripping zone subsequent to the second reaction zone could be recycled to either the first or second reaction zone, or both.

It will be further understood that the present process is directed to hydrogenation of monocyclic aromatics rather than polycyclic aromatics and that the monocyclic aromatics are converted to the corresponding monocyclic aliphatics and are not cracked to non-cyclic aliphatics. Such monocyclic aromatics can be present in platinum catalyst poison-containing, low boiling point mixed feed streams such as a kerosene feed stream having a top boiling point not in excess of about 450° F.-500° F. Moreover, platinum catalyst poison-containing monocyclic aromatics, for example, benzene, toluene, xylene and the like can be used as the feed streams to the first reaction zone. Obviously, platinum catalyst poison-free feed streams can also be used but, from the standpoint of the present process, no substantial advantage is to be gained by employing the same.

In any event, if a mixed feed stream containing monocyclic aromatics is treated, the present process can essentially completely convert the monocyclic aromatics to the corresponding monocyclic aliphatics, but usually does not result in substantial conversion of polycyclic aromatics to polycyclic aliphatics. This is because the hydrogenation conditions utilized in both reaction zones are relatively mild, and are optimal only for hydrogenation of monocyclic aromatics. Such conditions include a pressure of between about 300 and about 500 p.s.i., which is sufficient to maintain the low boiling point feed in the liquid phase during the hydrogenation at the temperatures employed within both reaction zones. If the hydrogenation were to be carried out with the monocyclic aromatics in the gaseous phase, the rate of conversion would be substantially lowered, and the ultimate yield of desired product might be impaired.

Relatively high feed rates can be used in the present process, due to liquid phase treatment of the feed, and such feed rates result in negligible cracking of the feed, with negligible polymeric laydown on the catalyst. Accordingly, catalyst activity can be more readily maintained. The reaction temperature in each of the two

4

reaction zones can be up to about 600° F., with excursions permitted up to as high as 700° F., or slightly more, but below those temperatures at which substantial aromatization of aliphatics occurs, and with the qualification that the main portion of the hydrogenation takes place at temperatures usually not in excess of about 600° F. and generally within the range of between about 400° F. and about 600° F. Within the described range, temperature rises of up to 150° F. during hydrogenation are permissible.

A high hydrogen flow rate into each reaction zone is desirable so as to minimize the chances of any cracking of the feed stream. It has been found that it is desirable that the hydrogen flow rate into each reactor zone not be below about 800 s.c.f. per barrel of hydrocarbons but that flow rates for the hydrogen in excess of about 3200 s.c.f. per barrel of hydrocarbons do not provide any further advantages. Moreover, hydrogen flow rates greatly in excess of 3200 s.c.f. per barrel may so reduce the residence time of the monocyclic aromatics in each reactor zone as to reduce the rate of conversion thereof. Accordingly, hydrogen flow rates for the present process are between about 800 s.c.f. and about 3200 s.c.f. per barrel of hydrocarbons.

The space velocity of hydrocarbons through the reactors ranges between about 0.5 and about 12 LHSV and can be readily adjusted within the described range.

The temperature, pressure, space velocity, hydrogen flow rate and other conditions in each of the reaction zones are regulated to prevent substantial aromatization of the feed i.e. reversal of the desired hydrogenation process. Some temperature rise does ordinarily take place within each reaction zone due to the exothermic hydrogenation reaction, as previously described, but can be readily controlled by varying reaction conditions within the above-indicated limits and by feed dilution with constituents which do not undergo hydrogenation under the conditions of the process, e.g. monocyclic aliphatics already prepared by the process. Moreover, if aromatization conditions should inadvertently occur in either reaction zone, they act as an inherent safety check against a runaway reaction condition, because aromatization is endothermic and results in a lowering of overall temperature within the particular reaction zone affected.

As previously indicated, the initial concentration of monocyclic aromatics in the feed stream can be varied in order to vary the rate of increase in temperature in the reaction zones. It has been found that optimum monocyclic aromatic concentration in the initial feed stream for the first reaction zone is usually somewhere around 20% by volume, although monocyclic aromatic concentrations of up to about 40% or 50% by volume can be used, depending upon the hydrogenation conditions. It is usually preferable to reduce the hydrogenation conditions towards the minimum values when the monocyclic aromatic content of the initial feed of the first reaction zone is substantially reduced to below about 20% by volume.

In adjusting the monocyclic aromatic concentration in the feed to the first reaction zone, one means which can be employed is admixing the feed with a preselected proportion of the monocyclic aromatic-free liquid phase product of the second reaction zone before the feed passes to the second reaction zone. This dilutes the monocyclic aromatic concentration of the feed stream to the desired degree. It is also possible to adjust the concentration of monocyclic aromatics in the liquid feed to the second reaction zone in the same manner, provided that the diluent is moisture-free and platinum catalyst poison-free, such as the liquid product of the second reaction zone. Accordingly the LHSV and/or the maximum temperature rise in each reaction zone can be readily controlled.

The platinum-containing catalyst used in both reaction zones can be any conventional platinum-containing catalyst such as that which is ordinarily used in reforming

operations where saturated hydrocarbons are dehydrated and/or cyclized into aromatic hydrocarbons. One specific example of such catalyst is commercially available under the trade designation R5 from the Universal Oil Products Company, Des Plaines, Illinois. The catalysts for the present process usually contain platinum in a concentration of between about 0.01% and about 5.0%, by weight, supported on an alumina base, and may optionally contain from about 0% to about 8%, by weight, of a halogen, such as chlorine or fluorine combined therewith. However, the presence of such halogen is not necessary for the purposes of the catalyst of the present invention. Thus the present process is not limited to any particular platinum hydrogenation catalyst but is suitable for use with all those hydrogenation catalysts which contain platinum and which are capable of effecting the requisite hydrogenation under mild conditions in accordance with the present process. Various such platinum catalysts, with or without other constituents, are well known in the art.

When the present process is carried out in accordance with the foregoing, substantially complete, that is, up to 100% conversion of monocyclic aromatics into the corresponding monocyclic aliphatics can be obtained. For example, yields generally not less than about 97% and in some instances as high as 100% of cyclohexane can be obtained from benzene. Similar yields of methyl cyclohexane can be obtained from toluene. This is also true of the hydrogenation of most other monocyclic aliphatics by the present process. In the case of mixed low boiling feeds, such as 450° F. B.P. kerosene, the present process results in equally high conversion of monocyclic aromatics therein and in low conversion of other materials. Accordingly, the present process is solely directed to maximum conversion of monocyclic aromatics to monocyclic aliphatics.

Referring now to the accompanying drawing, one embodiment of a hydrogenation system for the present process is schematically illustrated. The apparatus contains two reactors 11 and 12, each containing a catalyst containing platinum. A hydrocarbon feed stream containing, for example, 30% by volume of benzene, is supplied through pipe 13 under a pressure of 400 p.s.i. and is first passed through a heater 14, wherein it is heated to a suitable temperature, e.g. 425° F., whereupon it is discharged through a pipe 15 into the top of reactor 11. Dry hydrogen gas is supplied to the reactor 11 by means of pipe 16 and in a suitable amount, for example 2000 s.c.f. per barrel of hydrocarbons. The hydrogen commingles with the hydrocarbon feed stream and hydrogenation of the monocyclic aromatics in the feed, for example, benzene, occurs in reactor 11 at, for example, 425°–475° F. and 400 p.s.i. The sulfur-bearing materials from the feed are converted into gaseous derivatives such as hydrogen sulfide, etc.

The total products of reactor 11 exit through pipe 17 at the bottom of reactor 11 and pass into a phase separator 18 wherein they are separated into a liquid phase which exits therefrom through pipe 20 and a gaseous phase which passes out of the system through pipe 19.

The separator 18 can be operated under any desired physical conditions but preferably under conditions which are milder than the hydrogenation conditions, with respect to the temperature and pressure. If desired, an even more thorough separation can be obtained by passing the liquid phase via pipe 20 into a fractionating stripper 21 whereby the hydrocarbon stream can be further separated into liquid hydrocarbons and gaseous products. The gaseous phase is exited through pipe 22 and the liquid phase through pipe 23 from stripper 21. The gaseous phases in pipes 19 and 22 comprise unused hydrogen, nitrogen and gaseous hydrogen derivatives of contaminants, such as hydrogen sulfide. Thus platinum catalyst poisons of various types and quantities are removed from the liquid phase so that the resulting purified platinum

catalyst poison-free stream is ready for contacting with the poison-free platinum catalyst in a second reactor. By this procedure, at least half of the platinum catalyst, i.e. that in the second reactor, is always fully protected against poisoning and reduction of activity.

The described purified liquid phase which may contain, for example, about 10%–15% benzene, in pipe 23, passes under a suitable pressure, e.g. 400 p.s.i., through a heater 24 and is heated therein to a suitable temperature, e.g. 437° F., then passes therefrom through pipe 25 and into the top of the second reactor 12 containing the poison-free platinum catalyst. Dry, platinum catalyst, poison-free hydrogen gas passes in an amount of 2000 s.c.f. per barrel of liquid into the top of the reactor 12 via pipe 27 and commingles with the liquid therein under hydrogenation conditions, for example, 435–485° F. and 400 p.s.i., preferably to hydrogenate essentially all of the remaining monocyclic aromatics in the liquid to the corresponding monocyclic aliphatics. For example, the benzene can be essentially completely converted into cyclohexane. The monocyclic aromatic-free or lowered aromatic content liquid product of reactor 12 is passed out of the bottom of the reactor 12, along with the diluent and unreacted hydrogen, by way pipe 28 to a separator 29 and this total product is separated into a gaseous phase, comprising unreacted hydrogen, which exits the separator by pipe 30, and a liquid phase containing the monocyclic aliphatics, any unreacted aromatics and diluent, which liquid phase exits the separator by pipe 31. The separator 29 can be operated under similar or milder conditions than those of the reactor 12. A further separation of the liquid phase can be made by use of a fractionating stripper 32 to provide a product liquid phase which exits through pipe 34 or cooler 36, etc. to suitable storage by means of pipe 35 and a gaseous phase which exits by means of pipe 33.

The preferably monocyclic aromatic-free liquid phase from the product of reactor 12 and pipe 34 can be admixed with the hydrocarbon stream in line 13 and the liquid phase of the products of the first reactor 11 in pipe 23 in order to control the monocyclic aromatic concentration supplied to each reactor. For example, if benzene is to be hydrogenated, the amount of benzene in such feeds can thus be controlled to prevent an undue increase in the reactor temperature as a result of the exothermic hydrogenation reaction. The flow of the liquid in line 34 to the lines 13 and 23 by way of the pipes 37 and 38 can be controlled by valves 40 and 39. As an example, the admixing of the described liquid phases can be adjusted readily to provide a suitable hydrocarbon stream feed rate, e.g. an LHSV of 2.4, and a suitable aromatic-free liquid phase recycle rate e.g. an LHSV of 5.6 to the reactor 11, and to provide a liquid phase feed rate in pipe 23 of e.g. an LHSV of 6.0, with no monocyclic aromatic-free liquid phase recycle to pipe 23 from line 37.

The various gaseous phases in pipes 19, 22, 30 and 33 containing hydrogen can be reclaimed by conventional methods to provide dry, platinum catalyst poison-free hydrogen for reuse in the reactors 11 and 12. Various pumps, controllers, heat exchangers, etc. which can be used in the present system are not illustrated in the drawing, for purposes of simplicity, but their arrangement, placement and construction will be obvious to those skilled in the art.

Because the liquid phase of the product of the first reactor 11 is platinum catalyst poison-free before it is charged to the second reactor 12 and because dry, platinum catalyst poison-free hydrogen is used exclusively in the second reactor 12, essentially complete conversion of the monocyclic aromatics can be obtained in the second reactor 12 without any depreciation of the activity of the platinum catalyst therein, and without cracking and polymer formation therein and deposition on such catalyst. Moreover, 10 percent less catalyst can be used than is ordinarily required in conventional catalytic hydro-

generation processes. Furthermore, the moderate operating conditions of the present process promote a long catalyst life, with at least one-half of the total platinum catalyst always being completely protected against poisoning and reduction of activity.

The catalyst in the first reaction zone (reactor 11) is, of course, exposed to poisoning and suffers some loss of activity during the process, but can be regenerated by known regeneration techniques, such as steam and the like. Accordingly, it is not irreparably damaged. The present process employs the same or a substantially identical platinum-containing catalyst in both the first and the second reaction zones in order to allow standardization of process parameters. It will be appreciated that in commercial operation, the process has improved simplicity by reason of substantially the same parameters for both reaction zones. Accordingly, a simplified control system can be employed during such commercial use of the process.

Moreover, should an accident occur wherein the catalyst in the second reaction zone does become contaminated to some degree or loses its reactivity to some small extent, such catalyst can be readily transferred to the first reaction zone and can be used as the catalyst therein in addition to or in replacement of catalyst of the first reaction zone. In addition, the regeneration technique for the catalyst, in such event, is advantageously standardized through the use of the single type of catalyst in both reaction zones.

The following examples further illustrate certain features of the present invention:

Example I

A hydrocarbon feed stream consisting of 30% by volume of benzene containing about 50 p.p.m. sulfur-bearing contaminants, calculated as sulfur, and 70% by volume of cyclohexane was hydrogenated in a first reaction zone, substantially as indicated in the accompanying drawing, in the presence of platinum-containing (R-5) catalyst and with dry, platinum catalyst poison-free hydrogen entering the reaction zone at 200 s.c.f. per barrel of hydrocarbon. A pressure of about 400 p.s.i. and a temperature of about 425° F. were substantially maintained in the first reaction zone with a maximum exothermically caused temperature rise of about 60° F., for a maximum temperature in the first reaction zone of 460° F. The benzene was hydrogenated to cyclohexane in the first reaction zone under liquid phase conditions, and the total product of the first reaction zone was passed therefrom and separated into liquid and gaseous phases.

The liquid phase contained only poison-free benzene and cyclohexane, while the gaseous phase contained unused hydrogen, hydrogen sulfide, nitrogen and other platinum catalyst poisons. The gaseous phase was passed out of the system and into a separator wherein the unused hydrogen was completely separated from the other gaseous constituents and saved for reuse.

The liquid phase was passed into a second reaction zone, along with dry hydrogen which contained no platinum catalyst poisons, and the benzene therein was hydrogenated in that second reaction zone at a hydrogen flow rate of 2000 s.c.f. per barrel of hydrocarbon, at a pressure of 400 p.s.i. and a temperature of 437° F. in the presence of a platinum-containing catalyst (R-5). The reaction exhibited an exothermically caused temperature rise of 29° F. to a maximum temperature of 466° F.

The product of the second reaction zone was passed therefrom and was then separated into liquid and gaseous phase, unused hydrogen being stripped therefrom. The remaining liquid phase was found to be aromatic-free and was admixed with the incoming hydrocarbon stream feed to the first reaction zone to provide a feed LHSV of 2.4 and liquid phase recycle of 5.6. The liquid phase in the first reaction zone provided feed to the second reaction zone in amounts such that the feed was 6.0 LHSV and no

liquid phase recycle was added to the feed to the second reaction zone. Conversion of the benzene to cyclohexane in the first reaction zone was approximately 6 percent and the overall conversion of benzene to cyclohexane in the process was 99 percent.

Example II

A hydrocarbon feed stream consisting of 40% toluene containing about 40 p.p.m. sulfur-bearing contaminants, calculated as sulfur, and 60% methyl cyclohexane by volume was passed into a first reaction zone, and contacted with dry hydrogen and subjected to hydrogenation therein at 400 p.s.i., 600° F. and a hydrogen flow rate of 1072 s.c.f. barrel of hydrocarbon in the presence of a platinum-containing R-5 catalyst. The products of the first reaction zone were separated into liquid and gaseous phases in a liquid-gaseous phase separator, and the resulting platinum catalyst poison-free liquid phase was then passed into a second reaction zone and contacted with dry platinum catalyst poison-free hydrogen entering the reaction zone at a rate of 2403 s.c.f. per barrel of hydrocarbon. The reaction zone was maintained at a pressure of 400 p.s.i. and a temperature of 575° F. in the presence of poison-free platinum-containing catalyst. Both the first reaction zone conditions and the second reaction zone conditions were liquid phase for the monocyclic aromatic being hydrogenated.

The products of the second reaction zone were then separated into liquid and gaseous phases and the aromatic-free liquid phase was admixed with the hydrocarbon feed stream passing to the first reaction zone so as to provide a feed LHSV of 3.2 and a liquid phase recycle of 4.8. The liquid phase of the second reaction zone was admixed with the liquid phase of the first reaction zone to provide a feed to the second reaction zone at an LHSV of 0.6 and a liquid phase recycle of 5.4. The conversion of toluene to methyl cyclohexane in the first reaction zone was about 50 percent and the overall conversion between the two reaction zones of the present process was 100 percent conversion of toluene to methyl cyclohexane.

Example III

A hydrocarbon feed stream comprising kerosene containing about 50 p.p.m. of sulfur-bearing contaminants, calculated as sulfur, and having a boiling range between 344° F. and 520° F. was passed into a first reaction zone. The kerosene consisted predominantly of monocyclic aromatics and contained only a minor proportion of polycyclic aromatics, approximately 3% by weight. It was subjected in the first reaction zone to hydrogenation conditions for converting the monocyclic aromatics therein to the corresponding monocyclic aliphatics. Those conditions comprised 2000 s.c.f. of dry hydrogen per barrel of hydrocarbon, a pressure of 400 p.s.i., and a temperature of 590° F., R-5 platinum catalyst being present as a fixed bed in the reaction zone.

The total product of the first reaction zone was then removed from the first reaction zone and separated into liquid and gaseous phases, the liquid phase being totally free of catalyst poison. This liquid phase was then passed to a second reaction zone for completion of hydrogenation of monocyclic aromatics therein. In the second reaction zone the liquid phase was subjected to liquid phase hydrogenation in the presence of a poison-free platinum-containing R-5 catalyst and dry platinum catalyst poison-free hydrogen at 2000 s.c.f. per barrel of hydrocarbons, at a pressure of 400 p.s.i. and a temperature of 550° F. The total product of the second reaction zone was then passed from the second reaction zone, and separated into liquid and gaseous phases to remove unreacted hydrogen. The substantially aromatic-free liquid phase of the second reaction zone was then admixed with the hydrocarbon feed to the first reaction zone to provide a feed rate LHSV of 2.4, with a liquid phase recycle rate LHSV of 2.0. The liquid phase of the second reaction zone was also re-

cycled to the liquid phase product from the first reaction zone to provide a feed for the second reaction zone at a feed rate LHSV of 2.0, with a liquid phase recycle rate LHSV of 2.0. The monocyclic aromatic content of the feed in the first reaction zone was reduced from about 20 percent to about 13 percent, and was reduced from about 13 percent to about 3-4 percent in the second reaction zone.

The preceding examples clearly illustrate that substantially complete conversion of monocyclic aromatics can be accomplished in accordance with the process of the present invention utilizing a two reactor system, with the second reactor completely isolated, catalyst poisonwise, from the first reactor. Liquid phase hydrogenation is carried out at moderate temperature and pressure and at relatively high hydrogen flow rates, by passing the feed and hydrogen through a fixed bed of platinum-containing catalyst in each of two separate reaction zones employing corresponding reaction conditions. The process is simple, effective and economical and is capable of batch, semi-continuous or continuous operation. The process can provide essentially complete conversion of monocyclic aromatics to monocyclic aliphatics without substantial cracking of the feed product or aromatization of the product.

It is completely unnecessary to employ more than two reactors in the present process in order to accomplish complete hydrogenation of all monocyclic aromatics in the hydrocarbon feed stream. However, it will be understood that the present process can be modified to employ more than two reaction zones. It will be further noted that no special pretreatment of the feed stream need be carried out before passage of the feed stream into the first reactor zone. Thus, usual refinery feed streams containing monocyclic aromatics and which normally contain platinum catalyst poisons, such as sulfur compounds in concentrations of as much as 50 parts per million or more can be used without prior separation of the sulfur compounds therefrom. Thus it is wholly unnecessary to first desulfurize the feed stream before hydrogenation in the present process. This obviously results in substantial savings in processing time, labor and equipment. Moreover, inasmuch as substantially complete conversion of the monocyclic aromatics can take place by the present process, separation of the desired product may be facilitated, especially for feeds which initially contain only a selected monocyclic aromatic such as benzene, together with usual contaminants.

From the foregoing it will be seen that the present invention is one which is adapted to attain all of the ends and objects hereinbefore set forth, together with other advantages which are obvious and which are inherent to the system and which can be implied from the foregoing.

Various changes, alterations, additions and modifications can be made in the present process, and its steps and conditions, and all such changes, alterations, additions and modifications which are within the scope of the appended claims form a part of the present invention.

What is claimed is:

1. A process for hydrogenating monocyclic aromatics in a hydrocarbon stream comprising the steps of subjecting a platinum catalyst contaminant-containing hydrocarbon stream, the aromatic content thereof containing a major proportion of monocyclic aromatics, in a first reaction zone to the action of hydrogen in an amount above 800 s.c.f. per barrel of hydrocarbons, a pressure from about 300 p.s.i. to about 500 p.s.i., a temperature from about 400° F. to just below the temperature at which reforming of the non-aromatic hydrocarbons occurs, in the presence of a hydrogenation catalyst containing platinum and at a LHSV of hydrocarbons between about 0.5 and 12, regulated to provide hydrogenation of cyclic aromatics without cracking, separating the products of said first reaction zone into liquid and gaseous phases, and subjecting only the liquid phase

in a second isolated reaction zone to the action of contaminant-free hydrogen under conditions equivalent to those of the first reaction zone, including hydrogen in an amount above 800 s.c.f. per barrel of hydrocarbons, a pressure from about 300 p.s.i. to about 500 p.s.i., a temperature from just below 400° F. to about the temperature at which reforming of the non-aromatic hydrocarbons occurs, in the presence of a contaminant-free hydrogenation catalyst containing platinum and a LHSV of hydrocarbons between about 0.3 and 12, regulated to provide essentially complete hydrogenation of monocyclic aromatics without cracking thereof.

2. The process of claim 1 wherein the products of the second reaction zone are separated into liquid and gaseous phases and wherein said second reaction zone's liquid phase products are admixed in such amounts with the hydrocarbon stream passing to said first reaction zone that an exothermic reaction-caused temperature rise in said first reaction zone does not exceed about 150° F.

3. A process for hydrogenating monocyclic aromatics to monocycloaliphatics, without cracking, in a hydrocarbon stream having an end boiling point of not more than about 500° F., which process comprises passing a hydrocarbon stream having an end boiling point of up to about 500° F. to a first reaction zone, the aromatics of said stream containing predominantly monocyclic aromatics and also containing substantial concentrations of catalyst poisons, hydrogenating said stream in said first reaction zone in the liquid phase in the presence of dry hydrogen and a poison-sensitive hydrogenation catalyst containing platinum and under hydrogenation conditions of pressure, temperature and space velocity insufficient to effect cracking or aromatization of said hydrocarbons for a time sufficient to substantially hydrogenate said monocyclic aromatics, separating the total products of said first reaction zone into a liquid phase free of said catalyst poisons and a gaseous phase containing said catalyst poisons and passing only said separated liquid phase to and hydrogenating only said separated liquid phase in a separate isolated second reaction zone in the liquid phase with dry platinum catalyst poison-free hydrogen and poison-free platinum hydrogenation catalyst under conditions of pressure, temperature and space velocity equivalent to those conditions of said first reaction zone, and continuing said hydrogenation in said second reaction zone for a time sufficient to essentially fully hydrogenate said monocyclic aromatics to monocyclic aliphatics without cracking thereof, while maintaining the activity of said catalyst in said second reaction zone by keeping it in a deposit-free, poison-free condition.

4. The process of claim 3 wherein said hydrogenation conditions comprise a pressure of from about 300 p.s.i. to about 500 p.s.i., a temperature of from about 400° F. to less than that temperature at which substantial aromatization occurs, a feed LHSV below about 12 but sufficiently high to inhibit cracking, and a hydrogen flow rate of between about 800 s.c.f. and about 3200 s.c.f. per barrel of hydrocarbons.

5. The process of claim 4 wherein the hydrogen utilized in said first reaction zone is platinum catalyst poison-free, wherein the maximum temperature rise in each of said reaction zones is 150° F. and the main proportion of said hydrogenation is effected at a temperature not in excess of about 600° F., and wherein the monocyclic aromatic concentration of said stream passing to said first reaction zone does not exceed about 40 percent by volume of said hydrocarbons.

6. The process of claim 3 wherein the total product of said second reaction zone is separated into a liquid phase and a gaseous phase, and a proportion of the liquid phase product of said second reaction zone is recycled to said stream passing to said first reaction zone, whereby the concentration of monocyclic aromatics in said stream passing to said first reaction zone is maintained at a pre-

11

determined value for improved temperature control in said first reaction zone.

7. The process of claim 6 wherein a proportion of said liquid phase product of said second reaction zone is recycled to said liquid phase passing into said second reaction zone, whereby the concentration of monocyclic aromatics passing into said second reaction zone is maintained at a predetermined level for improved temperature control in said second reaction zone.

8. The process of claim 3 wherein said stream passing to said first reaction zone consists essentially of sulfur-bearing benzene diluted with cyclohexane.

9. The process of claim 4 wherein said stream passing to said first reaction zone consists essentially of sulfur-bearing benzene diluted with cyclohexane and wherein said benzene is essentially completely converted to cyclohexane without substantial production of cracked cycloaliphatic products.

10. The process of claim 3 wherein said stream passing to said first reaction zone consisting essentially of sulfur-bearing toluene diluted with methylcyclohexane.

12

11. The process of claim 4 wherein said stream passing to said first reaction zone consists essentially of sulfur-bearing toluene diluted with methylcyclohexane and wherein said toluene is essentially completely converted to methylcyclohexane without substantial production of cracked cycloaliphatic products.

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