TO:       NASA/Scientific & Technical Information Division
          Attention: Miss Winnie M. Morgan

FROM:      GP/Office of Assistant General Counsel for Patent Matters

SUBJECT: Announcement of NASA-Owned U.S. Patents in STAR

In accordance with the procedures agreed upon by Code GP and Code KSI, the attached NASA-owned U.S. Patent is being forwarded for abstracting and announcement in NASA STAR.

The following information is provided:

U.S. Patent No.: 3,787,904

Government or Corporate Employee: Cal Tech

Supplementary Corporate Source (if applicable): Pasadena, CA

NASA Patent Case No.: NASA-11,673-1

NOTE - If this patent covers an invention made by a corporate employee of a NASA Contractor, the following is applicable:

Pursuant to Section 305(a) of the National Aeronautics and Space Act, the name of the Administrator of NASA appears on the first page of the patent; however, the name of the actual inventor (author) appears at the heading of column No. 1 of the Specification, following the words "... with respect to an invention of ". . . "

Elizabeth A. Carter

Enclosure: Copy of patent cited above
COMPACT HYDROGENATOR

James C. Fletcher, Administrator of the National Aeronautics and Space Administration, with respect to an invention of Peter G. Simmonds, 5200 Palm Drive, La Canada, Calif. 91011

Int. Cl. B01J 9/04; C07F 1/00

U.S. Cl. 23—284

2 Claims

ABSTRACT OF THE DISCLOSURE

A hydrogenating apparatus which includes a reaction chamber of a material such as a palladium alloy that is selectively permeable to atomic hydrogen and catalytically active to hydrogenating reaction and which contains a reactant that is to be hydrogenated, a shell surrounding the chamber and supplied with hydrogen, and a heating coil for heating the shell to thereby heat the hydrogen therein before it passes through the chamber while the reactant remains therein before it passes through the chamber wall. In one device, hydrogen is pumped out of the reaction chamber while the reactant remains therein to remove molecular hydrogen so that more atomic hydrogen can pass through the chamber walls. In another device, the reactant is pumped through the reaction chamber, and hydrogen is removed from the material leaving the chamber, and the reactant is again cycled through the chamber.

ORIGIN OF THE INVENTION

The invention described herein was made in the performance of work under a NASA contract and is subject to the provisions of Section 305 of the National Aeronautics and Space Act of 1958, Public Law 85-568 (72 Stat. 435; 42 USC 2457).

BACKGROUND OF THE INVENTION

(1) Field of the invention

The present invention relates to hydrogenation of compounds and, more particularly, to a compact and convenient method and apparatus for carrying out hydrogenation reactions.

(2) Description of the prior art

Hydrogenation of compounds such as olefinic organic compounds is a process which is practiced for many purposes in the laboratory, pilot plant and on an industrial scale. Traditionally, hydrogenation has been performed using finely divided metal catalysts. The most active catalytic metals are noble metals such as platinum and palladium which are very costly. Such catalysts are provided in a finely divided form and it is relatively difficult to recover the catalyst after completion of the reaction. These catalysts are very sensitive to poisoning from impurities such as sulfur containing compounds and it is difficult to reconvert the catalyst in powder form. Moreover, recovery of the hydrogenated material from the reaction mixture may require several separation and purification steps which invariably are costly and time consuming.

Wahlin, in Pat. No. 2,749,293, has disclosed an electrolytic hydrogenator in which hydrogen evolved adjacent the cathode is permeated through a tubular closed end palladium cathode to collect the hydrogen or to perform reduction of simple olefins contained within the cathode. Permeation is accomplished mainly by electrolytic action, though, temperature may be a factor in the diffusion process. Wahlin prefers to carry such processing at elevated temperature. This also increases the rate of reaction of hydrogen with the sample.

These and many other attendant advantages of the invention will become apparent as the invention becomes better understood by reference to the following detailed description when considered in conjunction with the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic illustration of a first embodiment of a compact hydrogenator of this invention;

FIG. 2 is a schematic illustration of another embodiment according to the invention;

FIG. 3 is a schematic illustration of a multiple-pass hydrogenator; and

FIG. 4 is a schematic illustration of a single-pass continuous hydrogenator.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Previous catalyst studies utilizing palladium-silver alloys have established that compounds containing \( \alpha-\beta \) conjugated ethylenic bonds may be relatively easily quantitatively hydrogenated when in contact with the metal surface in a hydrogen poor atmosphere. However, these studies have shown that at low hydrogen pressure, mono-olefins such as 1-hexene, \( \alpha \)-hexene pressures. Quantitative hydrogenation and other reactions involving substitution or addition of hydrogen or its isotopes, can be effected rapidly, conveniently and in high yield in accordance with the invention by disposing the material to be reacted in a vessel at a first pressure and permeating hydrogen from a higher pressure source through a wall portion of the vessel formed of a hydrogen permeable palladium alloy. The permeation rate of hydrogen through the permeable portion may be increased by heating it to elevated temperature. This also increases the rate of reaction of hydrogen with the sample.

The electrolytic hydrogenator of Wahlin is not a practical commercial means of conducting hydrogenation reactions. The electrochemical cell is unnecessarily complex and requires separate electrodes and electrolyte with the disadvantage of electrolytic dissolution of the expensive platinum or palladium electrodes in the electrolyte and the necessity of handling and utilizing aggressive chemicals such as sulfuric acid. Furthermore, the electrolytic hydrogenator is not adaptable to scaling up to industrial size since that apparatus depends upon the electrolyte for the supply of hydrogen. Thus, the concentration of electrolyte will be continuously changing unless water is continuously replenished to the cell.

SUMMARY OF THE INVENTION

The compact hydrogenator in accordance with the invention provides rapid hydrogenation in a much more convenient and controllable manner. The reaction conditions can be simply and conveniently changed over a wide range of temperatures and pressures. Quantitative hydrogenation and other reactions involving substitution or addition of hydrogen or its isotopes, can be effected rapidly, conveniently and in high yield in accordance with the invention by disposing the material to be reacted in a vessel at a first pressure and permeating hydrogen from a higher pressure source through a wall portion of the vessel formed of a hydrogen permeable palladium alloy. The permeation rate of hydrogen through the permeable portion may be increased by heating it to elevated temperature. This also increases the rate of reaction of hydrogen with the sample.

These and many other attendant advantages of the invention will become apparent as the invention becomes better understood by reference to the following detailed description when considered in conjunction with the accompanying drawings.

••la'dium alloys, for example, palladium-rhodium, palladium-
• -It is preferred to pressurize the outer vessel with hydro-
  "hydrogen-permeable palladium alloy. Increased internal 
  the presence of hydrogen suffers mechanical distortions. 
  in the annular space between the chamber and the vessel 
  wall and only pure hydrogen traverses the wall and re-
  acts with the sample.

"Pure palladium when subject to temperature cycling in 
the presence of hydrogen suffers mechanical distortions. 
However, an alloy of palladium containing 10% to 50% 
silver, preferably between 20% to 40% silver, is as perme-
able to hydrogen and is mechanically stable. Other pal-
adium alloys, for example, palladium-rhodium, palladium-
gold, palladium-ruthenium, or palladium-nickel are gen-
erally less permeable to hydrogen. However, such alloys 
may exhibit different catalytic properties and may be de-
sired for conducting certain reactions.

The palladium reaction chamber may be provided in 
various configurations and lengths of tubing may be con-
ected in parallel to provide increased surface area with 
less flow resistance. Membranes or tubes can also be 
formed from a base structural material such as a porous 
ceramic coated with a thin film of palladium or a suitable 
hydrogen-permeable palladium alloy. Increased internal 
surface area may be provided by etching or provision of 
a spongy palladium material to increase the available sur-
face for reaction.

The hydrogen flux through a film of palladium for a 
given hydrogen pressure is dependent on tube geometry, 
wall thickness and wall temperature. The selectivity of the 
film to permeation of hydrogen is independent of thick-
ness. However, the rate of permeation is inversely propor-
tional to thickness of the film. Thus, the thinnest film 
possible is most desirable for purposes of permeation. 
However, the film must be thick enough to withstand col-
lapse from hydrogen pressure during reaction. Preferably, 
the wall of the reaction chamber should be of the thick-
ness in the range from about 1 mil to about 10 mil.

The permeability of a palladium film is also dependent 
directly upon the pressure differential maintained between 
the high and low pressure side of the film. The higher the 
pressure differential, the greater the permeability of the 
film. Any differential pressure can be utilized in accord-
ance with the invention that will not destroy the film. For 
a 6-mil film, a palladium alloy containing 25% silver can 
withstand a collapse pressure differential of about 300 
PSI.

The temperature of the film also affects its permeability. 
In general, permeation rates through solids increase ex-
ponentially with increase in temperature. At low pressure 
from atmospheric to about 50 p.s.i.g. and room or sub-
ambient temperature, the permeation rate through a 4 to 
6 mil thick palladium film is low but is suitable for con-
ducting certain vigorous reactions in order to prevent de-
polymerization or scission of the compound at the double 
bond. However, for most reactions, it is preferred to in-
ter the permeation rate by raising the temperature to 
at least 50° C. The temperature should be maintained 
below the decomposition temperature of the sample or 
hydrogenated product. However, olefinic compounds have 
successfully hydrogenated in the apparatus of the inven-
tion at temperatures up to 250° C.

The film may be maintained at a more hydrogen per-
meable temperature by external heating means such as 
by placing the device in an oven or by applying an insu-
lated heating coil to the outer shell. In some configurations, 
the wall of the reaction chamber provides a sufficient internal resistance 
to produce the desired heating on passage of electric cur-
rent through the wall.

The hydrogenation apparatus of the invention is prim-
arily applicable to the reduction of carbon double of 
triple bonds such as monoalkenes containing 2 to 30 car-on atoms, conjugated and unconjugated dienes contain-
ing 4 to 30 carbon atoms. Reduction occurs only in ole-
finic bonds in a,b conjugated systems such as unsaturated 
aldehydes, nitriles, esters, ketones and does not occur at 
the functional group. Exemplary compounds reactive in 
the apparatus of the invention at a conversion level of at 
least 90% are listed in the following table.

<table>
<thead>
<tr>
<th>Starting compound</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acrolein</td>
<td>Propionaldehyde</td>
</tr>
<tr>
<td>Acrylonitrile</td>
<td>Propionitrile</td>
</tr>
<tr>
<td>Methyl acrylate</td>
<td>Methyl propanoate</td>
</tr>
<tr>
<td>Methyl vinyl ketone</td>
<td>Methyl ketone,</td>
</tr>
<tr>
<td>2,4-hexadiene</td>
<td>Hexane</td>
</tr>
<tr>
<td>1,3-hexadiene</td>
<td>Hexane</td>
</tr>
<tr>
<td>Styrene</td>
<td>Ethylbenzene</td>
</tr>
<tr>
<td>Acetylene</td>
<td>Ethane</td>
</tr>
</tbody>
</table>

An apparatus suitable for practicing the process of the 
invention is illustrated in FIG. 1. The compact hydrogena-
tor 10 generally includes a closed tube 12 formed of a 
hydrogen-permeable palladium alloy disposed in an outer 
closed vessel 14 which is connected to a source of high 
pressure hydrogen. 16. The lower end 18 of the tube 12 
forms a reservoir for receiving a sample 20 of hydro-
genatable material. The upper open portion 22 of the tube 
12 forms a reaction chamber. The tube 12 forms a reac-
tion chamber which is open to produce the desired heating on passage of electric cur-
rent through the wall. Lower end 18 of the tube 12 is 
vented to the atmosphere. When the reaction is complete, the hydrogen is vented 
from annular chamber 26 through the wall of the tube 12.

The, hydrogen' flux through a film of palladium for a 
given hydrogen pressure is dependent on tube geometry, 
wall thickness and wall temperature. The selectivity of the 
film to permeation of hydrogen is independent of thick-
ness. However, the rate of permeation is inversely propor-
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possible is most desirable for purposes of permeation. 
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polymerization or scission of the compound at the double 
bond. However, for most reactions, it is preferred to in-
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at least 50° C. The temperature should be maintained 
below the decomposition temperature of the sample or 
hydrogenated product. However, olefinic compounds have 
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aldehydes, nitriles, esters, ketones and does not occur at 
the functional group. Exemplary compounds reactive in 
the apparatus of the invention at a conversion level of at 
least 90% are listed in the following table.
olefins. Hexene was quantitatively hydrogenated in less than 30 minutes at a temperature of 100° C. and hydrogen pressure of 30 p.s.i.g. At room temperature, after than- 30 minutes at a temperature of 100° C. and hydrogen pressure and 100° C. temperature. The method has broad application since even sterically hin-
dered olefins may be quantitatively hydrogenated. For ex-
ample, di-tertiary-butyl ethylene was quantitatively hydro-
genated to di-tertiary butyl ethane is about an hour at 100 p.s.i.g. hydrogen pressure and a temperature of 150° C.

After the apparatus is cooled to ambient, and excessive hydrogen has been vented by means of valve 44, the hy-
drogenated product may be poured or pipetted from tube 12. Since the catalyst is in the form of a solid tube, no separation of catalyst and hydrogenated product is re-
quired as has been customary with the processes utilizing powdered catalysts. Since the hydrogen is believed to permeate through the metal lattice of the palladium tube as atomic hydrogen, very efficient catalytic hydrogenation occurs between the ultrapure atomic hydrogen and the unsaturated compound. The palladium-silver alloy tubes can be used for several successive hydrogenations. How-
ever, to maintain maximum efficiency, the tubes should be activated before each hydrogenation by heating in air at 400° C. for approximately 4 hours. This can be conven-
iently accomplished in a furnace. The quantitative uptake of hydrogen can be determined by means of the usual pressure-volume relationships, by accurately measuring pressure on gauges 36 and 48 and knowing the volumes of the inner and outer chambers.

Another embodiment of a compact hydrogenator ap-
paratus, as illustrated in FIG. 2, may be utilized to pro-
vide very rapid hydrogenation of small samples. The com-
pact hydrogenator 10 is generally similar to that shown in FIG. 1. The apparatus further includes a hydrogen pump 50 attached to the vent pipe 46. The hydrogen pump comprises a closed end palladium tube 52, sur-
rounded by a heater coil 54 connected through leads 56 to an independent, variable power supply, not shown. By controlling the maximum efficiency of valve 44 is turned toward tube 52 and coil 54 is energized to heat tube 52 to a hydrogen permeable temperature.

Thus, excess, unused hydrogen which converts to the molecular H2 form is removed through the pump 50, being pumped through the wall of the tube 52 and reacts with the oxygen in the surrounding atmosphere. This affords a very effective pumping action to remove excess molecular hydrogen which is not effective in the reac-
tion and permits freshly diffused atomic hydrogen to pass through the wall of tube 12 where it more readily and efficiently reacts with sample 20 on the interior sur-
face 24 of the reaction chamber tube 12. Since only molecular hydrogen gas can diffuse through the wall of tube 52, none of the vapors of starting material or reacted hydrogenated product are lost. Although the reaction is more rapid with this technique, stoichiometric up-
take cannot be as readily determined.

The embodiments of FIGS. 1 and 2 have been used successively for simple laboratory scale batch hydrogena-
tions of olefinic compounds. These apparatus could be scaled up to the size suitable for pilot plant scale of industrial production. It is also possible to perform hydrogena-
tion according to the method of the invention by either multiple pass recycling or single pass continuous systems.

Referring now to FIG. 3, a batch recycling system is illustrated generally including hydrogenation unit 60, a hydrogenation supply cylinder 62, a gas liquid separator 64 and a sample reservoir 66. The hydrogenation unit 60 includes a coil 68 formed of a hydrogen-permeable mate-
rial such as a palladium-silver alloy having an inlet 70 and an outlet 72. The coil 68 is enclosed within a shell container 74, the outer surface of which is heated by a variable electrical heater supply, not shown, through leads 78. A branch conduit 80 connects the container 74 to the hydrogen supply container 62 through a valve 84. Unhy-
drogenated sample is added to the reservoir container 66 through an inlet 86 containing a valve 88. The recycled sample is pumped through a drain extension 90 con-
taining a valve 92. A recycle conduit 94 including a pump 96 is connected to the inlet 70 to the coil 68. The outlet 72 of the coil is connected to the gas liquid separator 64. Gas is removed from the separator 64 through vent 98 while the liquid flows through outlet pipe 100 into the reservoir 66.

In operation of the recycling system of FIG. 3, unhy-
drogenated sample is placed in reservoir 66 by means of inlet 86 and then valve 88 is closed. The container 74 is pressurized by opening valve 84. After the heating coil 68 is turned on to raise the coil 68 to a more permeable condition, hydrogen permeates into coil 68. Pump 96 is then energized and sample sweeps through the coil 68 and partially reacts with atomic hydrogen permeating into the coil 68. The liquid-gas mixture flows out outlet 72 into the gas liquid separator 66 where molecular hydrogen is removed and reaction product is removed through vent 98. The liquid falls through outlet 100 into the reservoir 66. The liquid mixture is returned by recycle conduit 94 and pump 96 to the coil 68 where it reacts with freshly diffusing atomic hydrogen. The system is maintained in operation until all sample is hydrogenated and recovered in res-
ervoir 66. If necessary, the system is cooled and the hy-
drogenated sample is removed through drain valve 92.

A single pass, continuous hydrogenator is illustrated in FIG. 4. In this embodiment, the sample reservoir has a single inlet 102 for introducing the unhydrogenated sample 104 and for connection to an inert gas pressuring source, if required. The sample 104 flows through conduit 106 to the pump 108 and through a vaporizer 110 such as a heating coil before entering the inlet 70 to the coil 68. The temperature maintained within the coil 68, the pressure applied by means of the hydrogen supply cylinder 92 and the surface area and length of the coil 68 are sufficient such that all of the vaporized sample is reacted with the atomic hydrogen and is quantitatively hydro-
genated before entering outlet 72. The hydrogen-hydro-
genated product mixture flows through outlet conduit 112 into a gas-liquid separator 114 in which all inert gas and hydrogen gas are removed. The hydro-
drogenated liquid product flows through drain 118 into the sample collector 120.

Preferably, the separator 114 includes a second hy-
drogen-permeable palladium coil 122 disposed in an outer container 124 having an inlet 126. The container is sur-
rounded with an insulated electrical heating coil 128 which is connected through leads 130 to a variable power supply, not shown. As air flows through inlet 126 into the annular chamber 132 it acts to pump hydrogen through the wall of coil 120 by reacting with the permeat-
ing hydrogen to form water which leaves through drain 116. The hydrogenated sample flows through tube 118 into the collector 120. The tubes 68 and 120 could be connected as anode and cathode in an electrolyte and the hydrogen collected in the tube 120 could be recycled to the tube 68 as disclosed in the electrolytic hydrogen generator-separator, Pat. No. 3,690,835, issued Sept. 12, 1972.

The last two embodiments of the invention are readily adapted for scaling up to pilot plant and commercial size. The present invention provides rapid hydrogenation under reaction conditions which can be simply and conveniently varied to cover a wide range of temperature and hydrogen pressures. Hydrogenation is conveniently and easily con-
trolled simply by selection of appropriate temperature and pressure for the reaction.
It is to be understood that only preferred embodiments of the invention have been described and that numerous substitutions, modifications and alterations are all permissible without departing from the spirit and scope of the invention as defined in the following claims.

What is claimed is:

1. A hydrogenation reaction apparatus comprising in combination:
   a reaction chamber formed of a material selectively permeable to hydrogen and catalytically active to hydrogenation reactions and having first and second open ends;
   an outer shell surrounding said chamber forming a closed annular compartment;
   supply inlet means for introducing hydrogen into said outer shell;
   pumping means connected to a first end of the chamber for flowing material to be hydrogenated into said chamber;
   a hydrogen separator connected to the second end of the chamber;
   recycle means for returning the output from said separator to said pumping means; and
   product recovery outlet means for removing some of the material which has been hydrogenated in the chamber.

2. A hydrogenation reaction apparatus comprising in combination:
   walls forming a reaction chamber and a gas compartment, one within the other and the walls of the innermost one formed of a material that is selectively permeable to hydrogen and catalytically active to hydrogenation reactions;
   supply inlet means for introducing hydrogen into said gas compartment;
   pumping means connected to said reaction chamber for flowing material to be hydrogenated into said chamber;
   a hydrogen separator connected to the chamber for drawing off material in the chamber and separating at least some of the hydrogen from other material which has been drawn off;
   recycle means for returning the material in the separator from which hydrogen has been removed, to said pumping means; and
   product recovery outlet means for removing some of the material which has been hydrogenated in the chamber.

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JAMES H. TAYMAN, Jr., Primary Examiner
U.S. Cl. X.R.
23—290, 289, 252 R; 55—158, 16; 48—DIG. 005;
260—409, 690