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(54) METHOD OF DEUTERIUM ISOTOPE SEPARATION USING
ETHYLENE AND ETHYLENE DICHLORIDE

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No. OF CLAIMS 12

ABSTRACT

The present invention relates to deuterium isotope separation and enrichment. Presently, multi-stage equilibrium partition methods are employed to concentrate naturally occurring deuterium. Such methods involve bulky equipment and large materials handling problems because of low enrichment factors per stage. Therefore, there is low throughput and long time periods involved in order to attain steady state equilibrium conditions. The present invention overcomes these deficiencies by providing a method of separating deuterium from certain normally commercially available sources such as ethylene, vinyl chloride, 1,2-dichloroethane and propylene using tuned infrared lasers to selectively decompose such compounds into enriched molecular products containing deuterium atoms. The deuterium containing molecules can be easily separated from the starting material by absorption, distillation or other simple chemical separation techniques and methods. After evaporation such deuterium containing molecules can be burned to form water with an enriched deuterium content or pyrolyzed to form hydrogen gas with an enriched deuterium content. The present invention results in obtaining amounts of deuterium or heavy water as a valuable by-product from commercial chemical processes.

METHOD OF DEUTERIUM ISOTOPE SEPARATION USING
ETHYLENE AND ETHYLENE DICHLORIDE
TECHNICAL FIELD

5 The present invention generally relates to deuterium isotope separation and enrichment and more particularly to deuterium isotope separation and enrichment using infra-red laser technology.

BACKGROUND OF THE PRIOR ART

10 Deuterium occurs in nature to the extent of about 0.014%. Presently, multi-stage equilibrium partition methods are employed to concentrate the naturally occurring deuterium. Such methods involve bulky equipment and large materials handling problems because of low enrichment factors per stage. Therefore, there is low throughput and long time
15 periods involved in order to attain steady state equilibrium conditions. The most currently used process handles explosive and highly toxic materials in large quantities; and, thus constitute a serious hazard to public health safety.

20 Prior art systems using counter-current extraction and exchanges are well-known and the principles thereof are described in Kirk-Othmer, "Encyclopedia of Chemical Technology" - 2nd edition. John Wiley & Sons, New York, Vol. 8 - Chapter on "Extraction", E. G. Scheibel (1965) and Vol. 13 - Chapter on "Mass Transfer", A.H.P. Skelland (1967).

25 Also, the following references describe some of the presently known isotope separation techniques: William Spindel, "Isotope Separation Processes", A.C.S. Symposium Series, 11, "Isotope and Chemical Principles", Page 77, Am. Chem. Soc. (1957), Washington, D. C. (including



references contained therein e.g., F. T. Barr and W. P. Drews, Chem. Eng. Progress, 56, 49 (1960)); and P. B. Lumb, Nucl. Eng. Int., Page 64 (June, 1976)).

5 Laser technology has been recently used for producing isotopically selective chemical reactions and isotope separation. Developments in laser technology have demonstrated the use of tuned, infrared lasers to "pump up" the internal energy of a specified molecule to the point where it can decompose. For example, various laser techniques
10 involving separation of isotopes are described in "Experimental and Theoretical Studies of Laser Isotope Separation", by J. P. Aldridge, et al, prepared by The Los Alamos Scientific Laboratory (LA-UR-75-2368) and "Isotopically Selective Photochemistry", by R. V. Ambartzumian and V. S. Letokhov,
15 published in the July, 1975, edition of Laser Focus.

Other patents which Applicant is aware of dealing with infrared laser excitation are discussed and cited below.

U. S. Patent No. 3,941,670 (Pratt, Jr.) deals with sterilization of large molecules (bacteria, DNA, proteins) using infrared lasers in the frequency range of
20 350cm^{-1} to 3500cm^{-1} . While Pratt, Jr., briefly discusses petroleum cracking of large oil molecules, the discussion is built about analogies to the large biochemical molecules.

U. S. Patent No. 3,951,768 (Gurs) discloses the
25 concept of using infrared laser energy to excite or "heat" a bond in a molecule with a single photon. He estimates that the single photon absorption (at about 1000cm^{-1}) will heat a molecule by 1000°C . and thus accelerate its tendency to react by the Arrhenius factor $\exp(E/RT)$. The entire
30 concept and discussions of the Gurs invention is restricted to low power single photon absorption and does not relate to the field of high-power, multiphoton infrared absorption.

U. S. Patent No. 3,983,020 (Moore et al) relates to electronic excitation of molecules with upper electronic
35 states which can predissociate. Thus, it confines itself to single photon absorption and does not involve, or relate to, infrared multiphoton processes, or variations thereto.

In addition, the Applicant wishes to make of record in this application U. S. Patent Nos. 3,904,500

(Jensen) and 3,947,335 (Marling).

None of the prior art techniques known to the inventor teach the presently invented method for deuterium isotope enrichment using high-power intense tuned multiphoton infrared laser technology to selectively dissociate specific organic molecules of some commercially used raw materials having appreciable amounts of deuterium and to separate the deuterium enriched molecular species from the depleted molecular species (without any need for radical scavengers). In some cases the depleted molecular material can be treated with an inexpensive material, such as water, to replenish the deuterium content for recycling purposes.

Applicant's Canadian patent No. 1,085,341 used similar technology primarily for extracting large quantities of deuterium to supply the tremendous demands of heavy water reactors. The present invention provides an attractive method for obtaining smaller quantities of deuterium from commercially used raw materials which contain significant amounts of deuterium and which are readily available since they are used at annual rates in the range of billions of pounds. Because of the prices of organic chemicals and heavy water, the chemical feed stocks contemplated by the present invention can be economically processed on a once-through operational basis without the necessity for recycle or exchange.

BRIEF SUMMARY OF THE INVENTION

The availability of deuterium in large amounts is of great practical importance to the technology of nuclear fission reactors. Deuterium (in heavy water) is used as a moderator in nuclear fission reactors. The present invention makes the production of power from a heavy water moderated reactor much more economical. A heavy water reactor has a major advantage of being able to operate on natural uranium and does not require enriched uranium. Since the cost of pure heavy water is an appreciable portion of the capital costs and a lesser but significant part of the overall operating expenses of a heavy water reactor, the availability of inexpensive heavy water is of great importance in the nuclear fission reactor field.

As described above, laser technology has developed whereby intense tuned, infrared lasers can now be used to cause a specified molecule to selectively decompose. The present invention makes use of this technique to dissociate special classes of organic molecule which will prefer-
5 entially decompose into stable molecular products rather than reactive radicals. If reactive radicals are produced, then one must simultaneously introduce radical scavengers to prevent the "scrambling" of identity between the iso-
10 topically selected, irradiated molecules and the non-isotope bearing molecules in a vessel or container. Stable molecular fragments which do not readily react avoid such "scrambling" problems. The present invention eliminates the reduced yields which are typically inherent when reactive radicals
15 are produced and also eliminates the need to handle large amounts of radical scavengers.

The present invention contemplates as feed stocks use of certain raw materials (i.e., ethylene, vinyl chloride, 1,2 dichloroethane and propylene) which are commercially
20 produced in the range of billions of pounds per year. It is possible, by using the present invention, to obtain attractive yields from such readily available materials by a simple once-through process without the need for recycling or exchange of the deuterium depleted molecules. In some
25 instances, it may be desirable to recycle or exchange the deuterium depleted molecules. However, based upon the quantity of deuterium which can be obtained as a valuable by-product from a typical petroleum plant on a single pass operation, the present invention is economically feasible
30 even when smaller relative yields of deuterium are obtained. For example, a petroleum plant may produce one billion pounds per year of ethylene or propylene. From such a plant it is possible to extract by laser photolysis as much as 200,000 pounds per year of heavy water. Since the ratio of
35 market price of most organic chemicals in this volume are somewhere around 1,000 fold less than for heavy water, the potential market value of such a by-product may be about 10% to 20% of the organic chemicals produced. The profitability can be even higher. Since there are no large economies of

scale in employing the present invention, it can be just as attractive to plants which produce one million pounds of organic chemicals as it is to larger plants.

5 The organic materials which are commercially available in quantity and which lend themselves readily to the selective laser radiation of the present invention are ethylene (C_2H_4), vinyl chloride (CH_2CHCl) 1, 2 dichloroethane (CH_2ClCH_2Cl) and propylene (C_3H_6).

10 Briefly, normal molecules of the aforementioned compounds (i.e., those molecules containing a normal abundance of hydrogen and deuterium) are exposed to suitably focused intense infrared laser beam radiation. The infrared spectra of the molecules having deuterium will differ appreciably from the non-deuterated species. By proper
15 tuning, focusing and pulsing of an infrared laser, substantially all of the deuterium containing molecules exposed to the laser can be selectively dissociated and the deuterium containing products separated from the starting material and other reaction products.

20 Under proper conditions after exposure to the laser radiation a molecular compound containing the deuterium atom and either H_2 or HCl is formed. The molecule with deuterium is stripped from the undecomposed, deuterium depleted stream of organic compounds and H_2 or HCl . The
25 enriched molecular compound can be burned to form water with an enriched deuterium content or pyrolyzed to form hydrogen gas with an enriched deuterium content.

The unreacted molecules depleted of their deuterium containing species can then be handled, treated and/or
30 used in the normal fashion. If desired, the recycle arrangement can be used for the ethylene and propylene deuterium depleted molecules and can be exchanged with normal water or hydrogen to restore the normal isotopic composition and then catalytically recombined, if necessary, to form compounds
35 which can be recycled.

The details of the invented method, as well as the theory of operation, will be better understood in light of the discussions and explanations of the annexed drawing and the preferred methods and techniques described herein-

after.

BRIEF DESCRIPTION OF THE DRAWINGS

The drawing is a block type flow diagram showing in schematic form a preferred form of the invented process for obtaining deuterium isotope enrichment.

DETAILED DESCRIPTION OF THE INVENTION

It is highly desirable to try and increase the initial concentration of deuterium in processes which involve the production of heavy water or any processes which require substantially pure deuterium. The invented method results in increasing the initial concentration of deuterium to about 10% to 20% from the normally available abundance of 0.014% in one step. Such a 1000 fold increase in the magnitude of the initial concentration of deuterium greatly improves the efficiency so that even low temperature distillation techniques could be employed effectively in concentrating the deuterium isotope to about 90% to 99.9% purity (either as D_2O or D_2).

The present invention utilizes certain organic compounds which are commercially manufactured in large quantity and which can be selectively decomposed on a once-through basis into enriched molecular products containing deuterium atoms. The organic compounds which lend themselves to the present invention are ethylene, vinyl chloride, 1, 2-dichloroethane and propylene. The economics of the chemical industry is such that even on a once-through basis the deuterium or heavy water which can be produced as a by-product in the manufacture of the aforementioned organic compounds is quite valuable even on a small scale basis.

The probability of a molecule having a deuterium atom depends generally upon the number of hydrogen atoms and their position in the molecule. All the preferred organic compounds disclosed herein contain between 3 and 6 hydrogen atoms.

The infrared spectra of the deuterated species of molecules for the aforementioned organic compounds will differ appreciably from their respective non-deuterated species. In particular, they will all have a unique stretching frequency at about 2100 cm^{-1} and a unique bending fre-

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quency at about 900 cm^{-1} which will be clearly distinguish-
able from the hydrogen only related deformation frequencies
in the same region. Current CO or HBr lasers are readily
adapted to tuning at the 2100cm^{-1} frequency region while
5 CO₂ and N₂O lasers can be tuned to the appropriate frequency
in the vicinity of 900cm^{-1} . A frequency-doubled CO₂ or N₂O
laser can also be used in the 2100cm region. Suitable spec-
tra data may be found in G. Herzberg, Infrared and Roman
10 Spectra of Polyatomic Molecules, D. van Nostrand Co., New
York (1945); and, in A.P.I. Res. Project 44, "Selected
Infrared Spectral Data". Thermodynamics Research Center,
Texas A & M University, Bryant, Texas.

For each of the selected compounds (i.e., ethylene,
vinyl chloride, 1,2-dichloroethane or propylene) one can
15 determine by conventional methods from available references
its spectroscopy. Then intense tuned infrared laser sources
of optimum wave length can be employed to obtain the desired
separation and increased initial concentrations of deuterium.
For each organic molecule one should do the necessary spectro-
20 scopy both on the non-deuterated and the one or more possible
mono-deuterated species to determine the optimum wave length
to be used in exciting the deuterium containing molecule
with the infrared laser. The identification of suitable
spectral bands involves trial and error procedures. One
25 starts by finding the frequencies at which the monodeuterated
compound absorbs while the non-deuterated is transparent.
Only these frequencies need to be tested to see which lead
to high efficiency decomposition in the laser beam. Once
this is accomplished the normally occurring population of
30 the selected compound is exposed to the properly focused
infrared laser beam. The proper focusing will depend on
the pressure and molecules to be used using conventional
pretesting and optimization techniques known in the infrared
laser field. Standard light pipes may be used, if desired,
35 to make more efficient use of the laser beam.

In operation, a single laser beam can be used in a
pulsed mode with a suitably chosen light pipe so that 50% or
more of the incident energy may be absorbed by the deuterium
containing species in the path length. Alternatively,

two laser beams can be used, one which is a relatively weakly focused beam, but carefully tuned to give high isotopic selectivity and, a second beam which is a more strongly focused beam of higher energy density with lesser requirements on beam quality and tuning to provide the necessary dissociation energy to dissociate the molecules excited by the weaker beam.

The probabilities of obtaining the deuterium atom for a particular compound can be determined from the literature. Pertinent data can be found in the following references: P. J. Robinson and K. A. Holbrook, "Unimolecular Reactions", Chapter 9, (esp. page 303), Wiley-Interscience, London (1972); and C. J. Collins and N. S. Bowman, ed., "Isotope Effects in Chemical Reactions", Am. Chem. Soc. Monograph (1970), Washington, D. C.

Of the chemicals which are currently in large quantity chemical production only a few chemical compounds lend themselves to deuterium separation by the multi-photon laser photolysis technique of the present invention. These compounds are ethylene (C_2H_4), vinyl chloride (CH_2CHCl), 1, 2-dichloroethane (CH_2ClCH_2Cl) and propylene (C_3H_6).

When ethylene is photolyzed in an infrared beam it produces hydrogen (H_2) plus acetylene (C_2H_2). The deuterium atom in the original C_2H_3D will tend to remain in the acetylene rather than the H_2 . This effect has been discussed in the December 1977 issue of Chem. Phys. Letters in an article by A. J. Colussi, R. J. Hwang, H. Tsiee and S. W. Benson. Thus, the process will require separation of acetylene and hydrogen from the unreacted ethylene. This can be done in a number of ways including selective absorption on suitable catalysts such as zeolites or transition metal catalysts.

Vinyl chloride will photolyze into acetylene (C_2H_2) plus hydrogen chloride (HCl). The deuterium atom remaining preferentially in the acetylene. Again the products could be separated from the undecomposed vinyl chloride in the manner described above for ethylene.

Dichloroethane is the best suited of the preferred molecules of the present invention for the deuterium separation. The products after the 1, 2-dichloroethane is photo-

lyzed are vinyl chloride with the deuterium atom plus HCl. The vinyl chloride is easily separated from the undecomposed parent compound using activated charcoal or zeolites as is the HCl. The spectroscopy of dichloroethane is especially
5 simple since all the H atoms are equivalent.

When propylene is photolyzed the products are somewhat more complex, being either hydrogen plus methyl acetylene or hydrogen plus allene. However, as described for previous cases these products can be selectively separ-
10 ated. The deuterium atom again will tend to remain in the methyl acetylene and/or in the allene rather than in the H₂ as was the case for ethylene.

The invented process discussed above will now be described with reference to the annexed drawing which shows
15 in a schematic flow diagram form the presently preferred version of the process. It should be understood that except where otherwise indicated, all the organic compounds (i.e., ethylene, vinyl chloride, 1,2-dichloroethane and propylene) previously identified and discussed behave and
20 function in substantially the same manner. Therefore, we shall sometimes refer to all such organic compounds as the "selected organic molecules".

As explained previously, the various selected organic molecules readily lend themselves to selective radiation of
25 deuterium containing molecules when subjected to intense tuned, infrared lasers, such as CO, CO₂ or N₂O lasers. As shown in the drawing, normal selected organic molecules 10 (i.e., those molecules containing a normal abundance of hydrogen and deuterium) are exposed to a suitably focused
30 infrared laser beam which is pulsed in the laser reactor A. Those selected organic molecules (about 1 part per 1000) which contain a deuterium atom will absorb the radiation and are preferentially decomposed and under proper conditions lead to the formation of a molecular specie containing the
35 deuterium atom (molecule (d)) and H₂ (for ethylene and propylene) or HCl (for vinyl chloride and dichloroethane). By way of example, after passing through laser reactor A the unreacted organic molecules (those without the deuterium atom) typically constitute about 99.9% of the output 12 and

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the molecule (D) and H_2 or HCl together typically constitute about 0.1% of the output 12.

5 The invented process results in the selected organic molecules being preferentially decomposed into stable molecular fragments and not reactive radicals. Therefore, no radical scavengers are needed to prevent the scrambling of identity between the isotopically selected irradiated molecules and non-isotope bearing molecules.

10 The output 12 from the laser reactor A is then passed into a separator B where the deuterium enriched molecules (D) are stripped from the unreacted selected organic molecules (without D) and H_2 or HCl . The enriched specie of molecules (D) will normally have about a 10% to 20% deuterium content. The separation can be easily accomplished in
15 separator B by known absorption techniques (e.g. with ammonia), by distillation or by other simple chemical separation methods, such as by using silver salts like silver nitrate to form complex salts which will bind the molecules and separate upon further heating. Also, known transition
20 metal such as palladium, nickel or ruthenium can be used in the separation process.

The enriched molecule (D) product 14 from separator B can then be burned in O_2 in a combustion unit C to form H_2O and CO_2 . The H_2O stream 15 so formed will typically
25 have about a 10% to 20% deuterium content.

If desired, the enriched water 15 can be used as a starting material for further enrichment as is now done in common practice. The enriched molecule (D) product can optionally be pyrolyzed over graphite at high temperatures
30 (e.g. about $1000^{\circ}C$ to $1200^{\circ}C$) in a furnace F to form hydrogen gas and carbon directly. The hydrogen gas 15' thus formed will typically have a 10% to 20% deuterium content and can be economically concentrated by cryogenic distillation to obtain substantially pure deuterium (i.e., 90 to 99.9%
35 purity).

The unreacted deuterium depleted organic molecule stream 16 can then be processed, treated and handled in the normal way as though the present process had not been utilized.

If desired, as an option, it is possible after a once-through operation to send the unreacted deuterium depleted ethylene and propylene molecules through a catalytic exchanger to restore the deuterium content by using an inexpensive source such as normal water or H₂.

For example, the unreacted, deuterium depleted ethylene and propylene molecules and H₂ leave separator B as stream 16 which is sent to a catalytic exchanger D into which ordinary or normal water 18 is brought in and exchanged catalytically the deuterium depleted stream 16 to produce the molecular compound with a natural abundance of deuterium. In such catalytic exchange treatments it is suggested that known countercurrent exchange techniques be employed for efficiency. Known catalysts for this purpose are acidified silica gel, silica-alumina gel, sulfuric acid or transitional metal ions in acid aqueous media. The water depleted of deuterium leaves the catalytic exchanger D as stream 20 and is not used again in the process.

The stream leaving the catalytic exchanger D is isotopically normal ethylene or propylene which is now available to be recycled as input 10' into the laser reactor A and the entire aforementioned cycle repeated to obtain the desired deuterium separation and enrichment.

While water has been described in the preferred recycle process as the source of replenishing the depleted deuterium, it should be understood that any other available sources (e.g. H₂) which contain at least a normal or natural abundance of deuterium can be used. The various percentages used herein, unless otherwise indicated, refer to mole percentages.

It should be understood that while the major amount of deuterium (e.g., 60% or more) is normally found in the organic molecule, a significant fraction (e.g., up to about 40%) of deuterium can be found in the H₂ and HCl products of the photolysis and therefore is also recovered in the process in order to maximize the enrichment.

The present invention provides an economical process for separating the deuterium isotope and providing an enriched deuterium supply for applications such as the

production of heavy water which is in great demand as a moderator for nuclear fission reactors. Also, the deuterium isotope is frequently used as a tracer element.

5 The preferred method shown in the drawing and described above is for purposes of illustration and should not be construed as limiting the present invention. It will be apparent to those skilled in the art that certain modifications can be made with respect to the above-described preferred method without departing from the overall scope
10 and spirit of the present invention. For example, other suitable and known catalysts and conventional separation techniques could be utilized in lieu of those specifically mentioned in the preferred method.

15 All the selected organic compounds discussed in the present application can be processed, using the present invention, on a once-through basis making the deuterium and/or heavy water a valuable by-product in any chemical plant that commercially produces such organic compounds. The economics of organic chemicals and the prices of heavy
20 water are such that the process can be advantageously practiced on both large scale and small scale chemical plants. When ethylene or propylene feed stocks are used one can employ techniques to restore the depleted deuterium and recycle the feed stocks.

CLAIMS

1. A method for separating and enriching deuterium containing molecules comprising the steps of: (a) providing a source of organic molecules containing deuterium atoms, said organic molecules selected from the group of compounds consisting of ethylene, vinyl chloride, dichloroethane and propylene; (b) exposing said organic molecules to the radiation of at least one infrared laser source which has been specifically tuned and focused to selectively decompose said organic molecules containing deuterium to form an enriched molecular specie containing deuterium; (c) separating said deuterium enriched molecular species from the undecomposed deuterium depleted molecules.

2. The method as claimed in Claim 1, wherein said deuterium enriched molecular specie is converted into water with an enriched deuterium content.

3. The method as claimed in Claim 1, wherein said deuterium enriched molecular specie is pyrolyzed to form hydrogen gas with an enriched deuterium content.

4. The method as claimed in Claim 1, wherein when ethylene or propylene is selected, said undecomposed deuterium depleted molecules are subsequently treated with a deuterium containing source to restore in the latter deuterium depleted molecules a supply of deuterium atoms.

5. The method as claimed in Claim 1 in which said laser is specifically tuned to provide pulsed frequencies in the range of about 900cm^{-1} to 2100cm^{-1} .

6. The method as claimed in Claim 2, wherein said deuterium enriched water contains about 10% to 20% deuterium.

7. The method as claimed in Claim 3, wherein said deuterium enriched hydrogen gas contains about 10% to 20% deuterium.

8. The method as claimed in Claim 4, wherein said deuterium restored molecules are recycled as the source of organic molecules containing deuterium atoms to be exposed to said infrared laser radiation for further selective decomposition and separation of deuterium containing molecules.

9. The method as claimed in Claim 5, wherein said infrared laser is a CO_2 or N_2O laser.

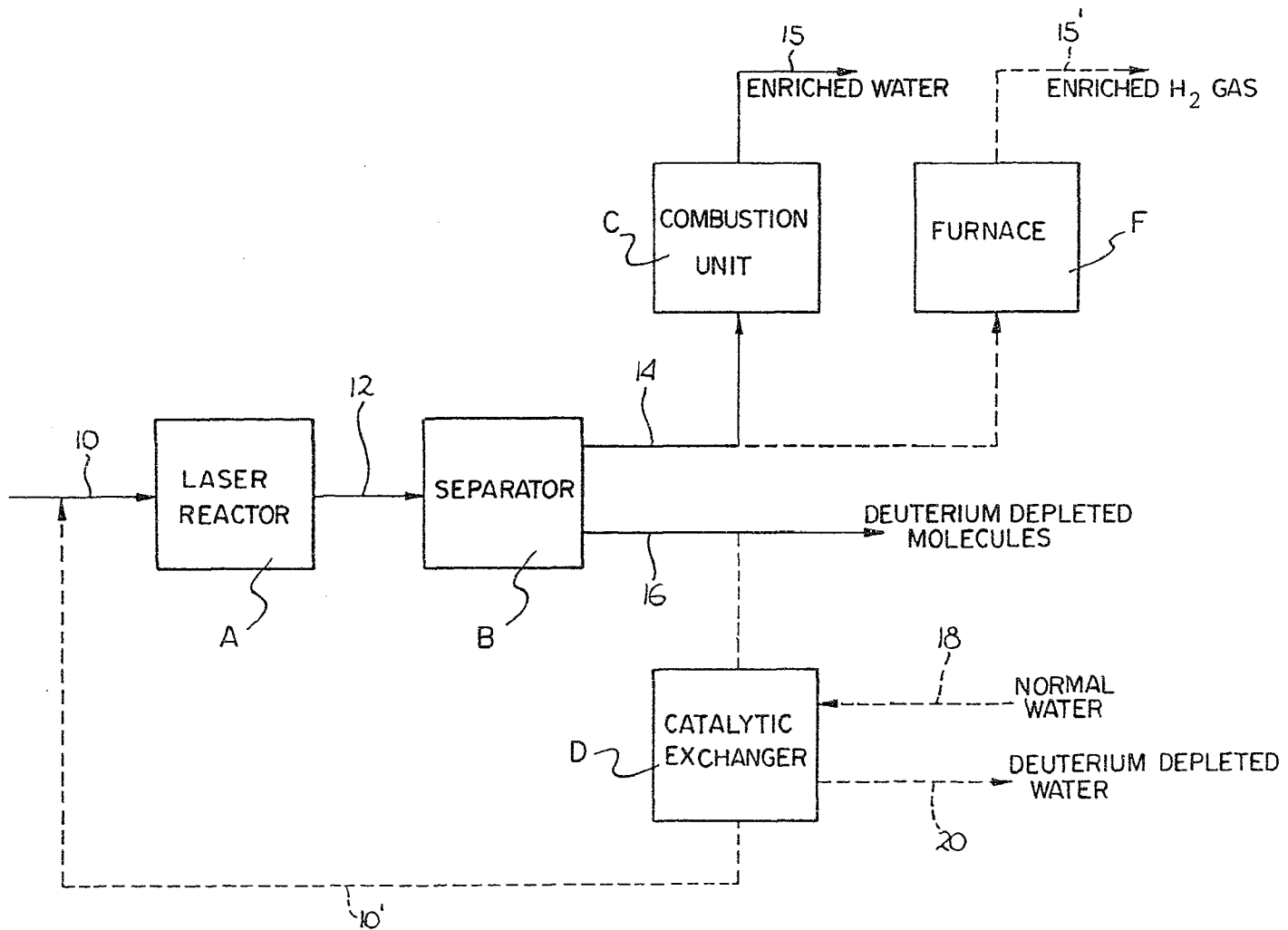
10. The method as claimed in Claim 5, wherein said infrared laser is a CO laser.

11. The method as claimed in Claim 4, wherein when ethylene or propylene is selected said decomposed deuterium depleted molecules are catalytically exchanged with water or H₂ to restore therein, a normal abundance of deuterium.

12. The method as claimed in Claim 5, wherein said infrared laser is a HBr laser.



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