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GAS PURIFICATION

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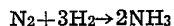
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This invention relates to the purification of gases and more particularly to the production of hydrogen and nitrogen substantially free of nitrogen oxide, for use in the production of synthetic ammonia or other uses requiring hydrogen-nitrogen gas substantially free of nitrogen oxide.

In the production of synthetic ammonia, various methods have been used for producing the nitrogen and hydrogen. In some cases, the hydrogen and nitrogen were produced separately as, for example, those processes where the hydrogen was produced from water gas or coke oven gas and the nitrogen produced from liquefaction of air or other means. The other type used has been a process in which the gases are produced together as, for example, from water gas and air. Most of these processes were followed by a liquefaction in which the gas was purified. These processes, however, are expensive as both investment and operative cost are high.

A less expensive process has been proposed in which the hydrogen is produced from natural gas and the nitrogen from combustion. This process has the disadvantage that sufficiently high concentrations of nitrogen oxide are present to cause substantial corrosion of the high compression apparatus. The removal of nitrogen oxide by absorption in liquid mediums has been considered but no efficient or satisfactory means has been developed.

In the production of synthetic ammonia, the cost of producing the factor gases, including initial plant investment, maintenance, and efficiency of production, is an extremely important item in determining the cost of the end product. Generally, the preparation of the hydrogen is the most costly feature of the whole process in which the union of the gases, which is exothermic, is represented by



Since 3 volumes of the costly hydrogen are required with one volume of nitrogen to yield the 2 volumes of ammonia, the production of the hydrogen requires prime consideration. It has been found that one of the most successful processes for the production of the hydrogen involves the catalytic cracking of hydrocarbon gases and vapors in a tubular furnace such as that set forth in my U. S. Patent Reissue 21,521. In a furnace of this type it is possible to react the hydrocarbon with steam under carefully controlled conditions to obtain a maximum yield of hydrogen without the formation of detrimental

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carbon due to the thermal decomposition of the hydrocarbon. The principal cause of carbon formation is the heating of at least a portion of the hydrocarbon to a thermal decomposition temperature prior to contacting the catalyst. Thus, an important feature of the present invention resides in passing a mixture of hydrocarbon and steam directly into a heated catalyst zone to avoid thermal decomposition and formation of detrimental carbon during production of the hydrogen.

In the production of nitrogen, it has long been realized that an economical method simply involved the combustion of natural gas. However, the principal disadvantage of this method is the high concentrations of nitrogen oxide present in the combustion product. The presence of nitrogen oxide in amount greater than two parts per million by volume in the combustion gas renders the gas unsuitable. Ordinarily, combustion gas will contain nitrogen oxide in amount of 250 parts per million or more. This amount must be reduced to less than two parts per million before it is suitable for passing into compressing apparatus without undue corrosion of the equipment. Consequently, steps must be taken to effect this reduction.

Since the step of producing hydrogen in accordance with this invention does not involve the formation of sufficient free carbon to react with the oxides of nitrogen to cause a substantial reduction thereof, the process must be conducted so that the hydrogen will accomplish this purpose by formation of nitrogen and water.

It is known that industrial gases containing 1 to 2 parts per million of nitrogen oxide have been reported free of nitrogen oxide by catalytic reaction with hydrogen. Although it is not clear as to whether such removal was obtained as reported or by adsorption by the solids used, it is recognized by those skilled in the art that the known reactions do not teach what will result when relatively large quantities of nitrogen oxide must be reduced to 1 to 2 parts per million. It is also known that high temperature of combustion yields nitrogen oxide, carbon monoxide and hydrogen concentrations in the same gas; further, that a number of efforts to eliminate the oxides, both catalytic and adsorptive have resulted at best in poor partial elimination. Accordingly, it cannot be reasoned, a priori, what would be the result from knowledge that industrial gases containing a few parts (1-2 P. P. M.) have been purified. It is an additional feature of this invention that the source of nitrogen may

be obtained from air with the oxygen removed by combustion during which step considerable quantities of oxides of nitrogen are formed. These products of combustion mixed with the stream comprising hydrogen, carbon monoxide and steam from the cracking step may be formed simultaneously with the cracking step and in the presence thereof in which case the cracking function and the combustion function are carried out within a single furnace. In the case where the combustion function is carried out apart from the cracking function an excess of oxygen up to about 6% is employed for efficiency purposes. The products of combustion from this gas contain considerable quantities of nitrogen oxides, that is, they may be present in amount of 250 parts per million or more. It is likewise a feature of this invention that the combustion products be passed into the hydrogen stream during or after the catalytic cracking of the hydrocarbon to form the hydrogen and carbon monoxide. Thus the reduction of oxides of nitrogen may take place while in contact with the cracking catalyst or while in contact with the conversion catalyst depending upon at what point along the path the combustion products are mixed with the hydrogen containing gas. Moreover, the combustion products may be mixed in part or in toto along the path of the hydrogen so long as they subsequently contact catalyst to convert the nitrogen oxides.

In addition, and extremely important, is the flexibility of the present process in handling sulfur containing material. For example, sulfur containing hydrocarbons or sulfur containing combustion products may be efficiently utilized in the presence of catalysts poisoned at usual operating temperatures. Furthermore, higher temperatures favorable to improved cracking efficiency in the presence of sulfur compounds may be obtained by the heat of combustion when the cracking function and combustion function are carried out simultaneously in the presence of each other. Under conditions where higher temperatures are not employed and where cracking efficiencies would be reduced due to the presence of sulfur compounds, sulfur containing combustion products may be introduced or formed at a point downstream from the cracking catalyst and the mixture thus formed subsequently passed into contact with conversion catalyst resistant to sulfur poisoning. In addition, steam is added to the hydrogen-nitrogen mixture prior to contacting the conversion catalyst to facilitate the first of the two interrelated functions of the converter: First, to perform the normal function of conversion of the carbon monoxide and steam to carbon dioxide and hydrogen upon contact with the conversion catalyst; Second, to convert any nitrogen oxide to nitrogen by reaction with the hydrogen simultaneously with the conversion of the carbon monoxide to carbon dioxide by means of the steam in the presence of the conversion catalyst.

For certain uses, the conversion step may be eliminated utilizing the cracking catalytic step for conversion of the nitrogen oxide to nitrogen by reaction with the hydrogen. As an example of such use, the hydrogen-nitrogen gas so produced may be employed directly or in combination with other gases to produce a satisfactory fuel gas and cooling may be obtained by water or other suitable means.

Accordingly, it is the principal object of this invention to provide an efficient process for the pro-

duction of a gas substantially free of oxides of nitrogen and comprising hydrogen and nitrogen for any use where the presence of oxides of nitrogen would be detrimental. Other objects of the invention will be apparent as set forth herein.

Now in accordance with the present invention, these objects are accomplished by a combination of the following steps: maintaining a mixture of gaseous hydrocarbon and steam at a temperature below the thermal decomposition temperature of the hydrocarbon; passing the mixture into contact with cracking catalyst to obtain a hydrogen-carbon monoxide mixture substantially free of detrimental carbon; intermixing the hydrogen-carbon monoxide mixture with combustion products during or after catalytic cracking to convert nitrogen oxide in the combustion products to nitrogen by reaction with the hydrogen to thereby obtain hydrogen and nitrogen substantially free of nitrogen oxide; and cooling the resulting mixture.

The nature and purpose of the invention have been indicated in general. A more detailed description follows in which the examples are illustrative of the method of carrying out the process.

Example 1

An admixture of nitrogen and hydrogen substantially free of nitrogen oxide was produced in the following manner. Hydrogen gas produced by cracking hydrocarbon gas in a furnace such as is described in my U. S. Reissue Patent No. 21,521, and nitrogen produced by burning hydrocarbon gas with air in a suitable furnace such as a marine boiler and containing an undesirably high percentage of nitrogen oxide were admixed and passed over a suitable catalyst such as iron oxide containing chromium oxide. The hydrogen taken from the cracking furnace at approximately 850° C. was admixed with the nitrogen, which was at approximately 350° C. and at a pressure of about 1 lb. and an excess of steam over that required for reaction. The mixing took place at the entrance of a converter containing a bed of the catalyst. The admixture was passed through the catalyst bed at a space velocity of 1500 and a temperature of 400° C. The admixture upon exit contained less than 2 parts per million nitrogen oxide and was suitable for immediate use in ammonia synthesis.

Example 2

A mixture of nitrogen and hydrogen substantially free of nitrogen oxide was produced in the following manner. Hydrogen gas was produced by cracking hydrocarbon gas in a furnace such as is described in my U. S. Reissue Patent No. 21,521. Nitrogen gas was obtained from the flue gas of the same furnace. This flue gas was cooled down to about room temperature and was then compressed by a low pressure compressor. The compressed gas at a pressure of about 10 lbs. was again heated and mixed with the hydrogen gas and steam and passed through a CO converter. The CO converter removed about 95% of the carbon monoxide present and reduced the nitrogen oxide content to about 1 part per million.

The mixture of gaseous hydrocarbon and steam should be maintained at a temperature below the thermal decomposition temperature of the hydrocarbon prior to contacting the cracking catalyst. It has been found when using a furnace of the type referred to in the examples that a temperature between about 200° and 400° C. is satisfac-

tory even for liquid hydrocarbons in the vapor phase and that this temperature will prevent the formation of detrimental carbon. The mixture is then immediately passed into contact with a cracking catalyst having a maximum temperature zone between about 750° and 1300° C. For normally gaseous hydrocarbons the lower range of catalyst temperature may be used; however, for hydrocarbons and particularly normally liquid hydrocarbons containing appreciable amounts of sulfur the upper range of catalyst temperature is preferred to effect improved cracking efficiency.

The combustion gas is gas rich in nitrogen and may contain some oxygen although the amount of oxygen should be kept as low as possible and yet permit good combustion efficiency. It has been found that satisfactory results are obtained when there is not more than about 6% and preferably from 0 to 4% of oxygen in the resulting nitrogen containing gas. The nitrogen containing gas may be produced in separate apparatus or it may be produced in the cracking furnace. In either event, it is intermixed with the hydrogen-carbon monoxide mixture produced as a result of the cracking step of the process. A preferred point of introducing the nitrogen containing gas, when produced in separate apparatus, is at the entrance to the converter at which point excess steam is also added to cool the entire mixture. The combustion gas is preferably obtained by burning natural gas in air. Since natural gas or other gas substantially comprising methane is preferred as the source of hydrocarbon for the cracking step, it is likewise preferred as the source of hydrocarbon for the combustion step and may constitute the flue gas utilized in the cracking step. However, other gaseous hydrocarbons may be used as a source for the hydrocarbon and the nitrogen including normally liquid hydrocarbons such as those containing more than two carbon atoms per molecule.

The optimum temperature for efficient conversion of carbon monoxide and nitrogen oxide is about 350° to 450° C. for which the space velocity should be preferably below 3000. Steam should be supplied in substantial amounts for the purpose of cooling gases to produce said temperature and to provide excess steam required for the conversion. This excess should be substantial, preferably from about 600% to about 1200% of the amount required for conversion of the carbon monoxide.

Wherever the specification refers to removal of nitrogen oxide from the factor gases, it need not mean the complete removal of the nitrogen oxide. In the manufacture of nitrogen from flue gas, for example, the content of nitrogen oxide may be 250 parts per million or more, and this is reduced by the present process to about 1 part per million or less. A content of less than 2 parts per million of nitrogen oxide can be considered removal of nitrogen oxide for purposes of substantial corrosion of the compressing apparatus.

Similarly, the reference to the removal of carbon monoxide does not necessarily mean the complete removal of the carbon monoxide but only a very substantial reduction in carbon monoxide content. Reductions in the nature of 80 to 95% of the carbon monoxide content may be considered to be removal of the carbon monoxide.

The preferred cracking catalyst for use with this invention is a nickel catalyst containing more than 10% nickel by weight. Suitable catalysts of this type include nickel-zirconium silicate-magnesia, nickel-aluminum oxide-magnesia,

nickel-zirconium silicate, nickel-aluminum oxide, nickel-diaspore, nickel-magnesia, nickel-pumice, nickel-titanium oxide, etc. These catalysts may be made by any of the methods of the prior art and are desirably given a preliminary tempering treatment with heat prior to use.

The preferred conversion catalyst for use with this invention is a chrome oxide-iron oxide catalyst. Other suitable conversion catalysts include iron oxide and the promoted iron oxide catalysts in general.

The advantages of the process of this invention are multifold. The cracking step is conducted without formation of detrimental carbon which would impair the yield of hydrogen and necessitate periodic removal of carbon and even new catalyst. The cracking step may be conducted with a wide range of hydrocarbons including sulfur containing hydrocarbons. The combustion products may be passed in part or in toto into the hydrogen stream during or after the cracking step thereby affording a very flexible and extremely efficient process. The nitrogen oxide and the carbon monoxide are substantially removed in the process, and the nitrogen oxide is reduced by a medium already in the system, namely, the hydrogen. The process provides for a mixture of hydrogen and nitrogen economically produced and suitable for ammonia synthesis operations, other operations, or direct use requiring gases substantially free of nitrogen oxide.

The term "space velocity" as used in the specification and claims is defined as the volume of steam-hydrocarbon mixture per volume of catalyst per hour.

This application is a continuation-in-part of my application Serial No. 467,823 filed December 4, 1942, now abandoned which in turn is a continuation-in-part of my application Serial No. 370,747 filed December 19, 1940 which is now U. S. Patent No. 2,381,696.

What I claim and desire to protect by Letters Patent is:

1. In the process of producing hydrogen and nitrogen by the dissociation of hydrocarbon gases and vapors, the improvement which comprises in combination maintaining a mixture of gaseous hydrocarbon and steam at a temperature below the thermal decomposition temperature of the hydrocarbon; passing the mixture into contact with nickel catalyst at a temperature above the thermal decomposition temperature of the hydrocarbon in the presence of nickel catalyst to obtain a hydrogen-carbon monoxide mixture substantially free of detrimental carbon; intermixing the hydrogen-carbon monoxide mixture with hydrocarbon combustion products containing nitrogen oxide to convert the nitrogen oxide to nitrogen by reaction with hydrogen in the presence of iron catalyst to thereby obtain a mixture comprising hydrogen and nitrogen substantially free of nitrogen oxide; and cooling the mixture thus formed.

2. In the process of producing hydrogen and nitrogen by the dissociation of hydrocarbon gases and vapors, the improvement which comprises in combination maintaining a mixture of gaseous hydrocarbon and steam at a temperature below the thermal decomposition temperature of the hydrocarbon; passing the mixture into contact with nickel cracking catalyst at a temperature above the thermal decomposition temperature of the hydrocarbon in the presence of nickel catalyst to obtain a hydrogen-carbon monoxide mixture substantially free of detrimental car-

bon; intermixing the hydrogen-carbon monoxide mixture with hydrocarbon combustion products containing nitrogen oxide in the presence of the cracking catalyst to convert the nitrogen oxide to nitrogen by reaction with hydrogen to thereby obtain a mixture comprising hydrogen and nitrogen substantially free of nitrogen oxide; and cooling the mixture thus formed.

3. In the process of producing hydrogen and nitrogen by the dissociation of hydrocarbon gases and vapors, the improvement which comprises in combination maintaining a mixture of gaseous hydrocarbon and steam at a temperature below the thermal decomposition temperature of the hydrocarbon; passing the mixture into contact with nickel cracking catalyst at a temperature above the thermal decomposition temperature of the hydrocarbon in the presence of nickel catalyst to obtain a hydrogen-carbon monoxide mixture substantially free of detrimental carbon; intermixing the hydrogen-carbon monoxide mixture with hydrocarbon combustion products containing nitrogen oxide in the presence of the cracking catalyst to convert nitrogen oxide to nitrogen by reaction with hydrogen; cooling the mixture thus formed; and passing the cooled mixture into contact with iron conversion catalyst to convert any remaining nitrogen oxide to nitrogen by reaction with hydrogen to thereby obtain a mixture comprising hydrogen and nitrogen substantially free of nitrogen oxide.

4. In the process of producing hydrogen and nitrogen by the dissociation of hydrocarbon gases and vapors, the improvement which comprises in combination maintaining a mixture of gaseous hydrocarbon and steam at a temperature below the thermal decomposition temperature of the hydrocarbon; passing the mixture into contact with nickel cracking catalyst at a temperature above the thermal decomposition temperature of the hydrocarbon in the presence of nickel catalyst to obtain a hydrogen-carbon monoxide mixture substantially free of detrimental carbon; intermixing the hydrogen-carbon monoxide mixture with hydrocarbon combustion products containing nitrogen oxide in the presence of the cracking catalyst to convert nitrogen oxide to nitrogen by reaction with hydrogen; cooling the mixture thus formed; and passing the cooled mixture and additional combustion products containing nitrogen oxide into contact with iron conversion catalyst to convert nitrogen oxide to nitrogen by reaction with hydrogen to thereby obtain a mixture comprising hydrogen and nitrogen substantially free of nitrogen oxide.

5. In the process of producing hydrogen and nitrogen by the dissociation of hydrocarbon gases and vapors, the improvement which comprises in combination maintaining a mixture of gaseous hydrocarbon and steam at a temperature below the thermal decomposition temperature of the hydrocarbon; passing the mixture into contact with nickel cracking catalyst at a temperature above the thermal decomposition temperature of the hydrocarbon in the presence of nickel catalyst to obtain a hydrogen-carbon monoxide mixture substantially free of detrimental carbon; intermixing the hydrogen-carbon monoxide mixture with hydrocarbon combustion products containing nitrogen oxide; cooling the mixture thus formed with steam; and passing the cooled mixture into contact with iron conversion catalyst to convert the carbon monoxide to carbon dioxide and to convert nitrogen oxide to nitrogen by reaction with the hydrogen to thereby ob-

tain a mixture comprising hydrogen and nitrogen substantially free of nitrogen oxide.

6. In the process of producing hydrogen and nitrogen by the dissociation of hydrocarbon gases and vapors, the improvement which comprises in combination maintaining a mixture of gaseous hydrocarbon and steam at a temperature below the thermal decomposition temperature of the hydrocarbon; passing the mixture into contact with nickel cracking catalyst at a temperature above the thermal decomposition temperature of the hydrocarbon to obtain a hydrogen-carbon monoxide mixture substantially free of detrimental carbon; intermixing the hydrogen-carbon monoxide mixture with hydrocarbon combustion products, said combustion products containing nitrogen and more than two parts per million by volume of nitrogen oxide; cooling the mixture thus formed with excess steam; and passing the cooled mixture into contact with iron conversion catalyst to convert the carbon monoxide to carbon dioxide and to convert the nitrogen oxide to nitrogen by reaction with the hydrogen to thereby obtain a mixture comprising hydrogen and nitrogen substantially free of nitrogen oxide.

7. In the process of producing hydrogen and nitrogen by the dissociation of hydrocarbon gases and vapors, the improvement which comprises in combination maintaining a mixture of gaseous hydrocarbon and steam at a temperature below the thermal decomposition temperature of the hydrocarbon; passing the mixture into contact with nickel cracking catalyst at a temperature above the thermal decomposition temperature of the hydrocarbon to obtain a hydrogen-carbon monoxide mixture substantially free of detrimental carbon; intermixing the hydrogen-carbon monoxide mixture with hydrocarbon combustion products, said combustion products containing nitrogen and more than two parts per million by volume of nitrogen oxide; cooling the mixture thus formed with excess steam; and passing the cooled mixture into contact with iron conversion catalyst having a maximum temperature zone between about 350° and 450° C. to convert the carbon monoxide to carbon dioxide and to convert the nitrogen oxide to nitrogen by reaction with the hydrogen to thereby obtain a mixture comprising hydrogen and nitrogen substantially free of nitrogen oxide.

8. In the process of producing hydrogen and nitrogen by the dissociation of hydrocarbon gases and vapors, the improvement which comprises in combination maintaining a mixture of gaseous hydrocarbon and steam at a temperature below the thermal decomposition temperature of the hydrocarbon; passing the mixture into contact with nickel cracking catalyst at a temperature above the thermal decomposition temperature of the hydrocarbon to obtain a hydrogen-carbon monoxide mixture substantially free of detrimental carbon; intermixing the hydrogen-carbon monoxide mixture with hydrocarbon combustion products, said combustion products containing nitrogen and more than two parts per million by volume of nitrogen oxide; cooling the mixture thus formed with excess steam to a temperature between about 350° and 450° C.; and passing the cooled mixture into contact with iron conversion catalyst to convert the carbon monoxide to carbon dioxide and to convert the nitrogen oxide to nitrogen by reaction with the hydrogen to thereby obtain hydrogen and nitrogen substantially free of nitrogen oxide.

9. In the process of producing hydrogen and nitrogen by the dissociation of hydrocarbon gases and vapors, the improvement which comprises in combination maintaining a mixture of gaseous hydrocarbon and steam at a temperature below the thermal decomposition temperature of the hydrocarbon; passing the mixture into contact with nickel cracking catalyst at a temperature above the thermal decomposition temperature of the hydrocarbon to obtain a hydrogen-carbon monoxide mixture substantially free of detrimental carbon; intermixing the hydrogen-carbon monoxide mixture with hydrocarbon combustion products, said combustion products containing nitrogen and more than two parts per million by volume of nitrogen oxide and containing from 0 to not more than 6% of oxygen; cooling the mixture thus formed with excess steam to a temperature between about 350° and 450° C.; and passing the cooled mixture into contact with iron conversion catalyst to convert the carbon monoxide to carbon dioxide and to convert the nitrogen oxide to nitrogen by reaction with the hydrogen to thereby obtain a mixture comprising hydrogen and nitrogen substantially free of nitrogen oxide.

10. In the process of producing hydrogen and nitrogen by the dissociation of hydrocarbon gases and vapors, the improvement which comprises in combination maintaining a mixture of gaseous hydrocarbon and steam at a temperature below the thermal decomposition temperature of the hydrocarbon; passing the mixture into contact with nickel cracking catalyst at a temperature above the thermal decomposition temperature of the hydrocarbon to obtain a hydrogen-carbon monoxide mixture substantially free of detrimental carbon; intermixing the hydrogen-carbon monoxide mixture with hydrocarbon combustion products, said combustion products containing nitrogen and more than two parts per million by volume of nitrogen oxide; cooling the mixture thus formed with excess steam to a temperature between about 350° and 450° C., said excess steam being present in amount from about 600 to 1200% of the amount required for conversion of the carbon monoxide; and passing the cooled mixture into contact with iron conversion catalyst to convert the carbon monoxide to carbon dioxide and to convert the nitrogen oxide to nitrogen by reaction with the hydrogen to thereby obtain a mixture comprising hydrogen and nitrogen substantially free of nitrogen oxide.

11. In the process of producing hydrogen and nitrogen by the dissociation of hydrocarbon gases and vapors, the improvement which comprises in combination maintaining a mixture of gaseous hydrocarbon and steam at a temperature below the thermal decomposition temperature of the hydrocarbon; passing the mixture into contact with nickel cracking catalyst at a temperature above the thermal decomposition temperature of the hydrocarbon to obtain a hydrogen-carbon monoxide mixture substantially free of detri-

mental carbon; intermixing the hydrogen-carbon monoxide mixture with hydrocarbon combustion products, said combustion products containing nitrogen and more than two parts per million by volume of nitrogen oxide; cooling the mixture thus formed with excess steam to a temperature between about 350° and 450° C., said excess steam being present in amount from about 600 to 1200% of the amount required for conversion of the carbon monoxide; and passing the cooled mixture into contact with iron conversion catalyst at a space velocity not more than 3000 and at a temperature between 350° and 450° C. to convert the carbon monoxide to carbon dioxide and to convert the nitrogen oxide to nitrogen by reaction with the hydrogen to thereby obtain a mixture comprising hydrogen and nitrogen substantially free of nitrogen oxide.

12. In the process of producing hydrogen and nitrogen by the dissociation of hydrocarbon gases and vapors, the improvement which comprises in combination maintaining a mixture of gaseous hydrocarbon and steam at a temperature between about 200° and 400° C.; passing the mixture into contact with nickel cracking catalyst having a maximum temperature zone between about 750° and 1300° C.; intermixing the hydrogen-carbon monoxide mixture with hydrocarbon combustion products, said combustion products containing nitrogen and more than two parts per million by volume of nitrogen oxide; cooling the mixture thus formed with excess steam to a temperature between about 350° and 450° C., said excess steam being present in amount from about 600 to 1200% of the amount required for conversion of the carbon monoxide; and passing the cooled mixture into contact with iron conversion catalyst at a space velocity not more than 3000 and at a temperature between 350° and 450° C. to convert the carbon monoxide to carbon dioxide and to convert the nitrogen oxide to nitrogen by reaction with the hydrogen to thereby obtain a mixture comprising hydrogen and nitrogen substantially free of nitrogen oxide.

JAMES H. SHAPLEIGH.

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