

# Study of Hydrogen Supply System with Ammonia Fuel\*

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Carbon-free fuel is effective in preventing global warming. Hydrogen has no carbon and can be made also from nuclear energy or reproducible energies other than fossil fuels. However, hydrogen lacks portability because of its difficulty in liquefying, but ammonia can easily be liquefied at a room temperature and dissociated into high-content hydrogen and nitrogen using a suitable catalyst. An ammonia dissociation system for fuel cells is proposed in this paper. The residual ammonia by 13 ppm or more in the dissociated gas ( $H_2 + N_2$ ) causes a decrease in the output of fuel cells. To separate residual ammonia, it should be sent to an ammonia separator and then to an ammonia distiller. In the experiment, the authors examine the concentrations of ammonia after dissociation at various temperatures, pressures and space velocities. The ammonia separator uses the fact that ammonia dissolves well in water. Then the ammonia water is distilled in the distiller. Thereby, the authors have proposed an ammonia circulation system that is a clean energy system.

**Key Words:** Global Warming, Hydrogen, Ammonia, Alternate Fuel, Ammonia Dissociation, Fuel Cell

## 1. Introduction

Ammonia has many interesting characteristics as a hydrogen carrier for vehicles and portable energy devices, because it can be easily liquefied at a low pressure and theoretically dissociated to a mixture of high-content hydrogen and nitrogen. Ammonia also has an advantage in terms of global warming because it is a carbon-free fuel. Ammonia is a toxic gas that requires careful handling. However, it is easy to detect any leaks because of ammonia's unique irritating smell. Ammonia can also be the fuel with a high energy density by liquefaction. The fuel cost of ammonia is relatively close to that of petroleum. There is also a great wealth of experience available on the

handling of ammonia, as well as well-documented safety and medical procedures, mainly because of its use as a fertilizer<sup>(1)</sup>. The production, storage, and transportation of ammonia are well-understood procedures, benefitting from almost a century of experience and optimization. As a result, ammonia has excellent potential as an alternative fuel for fuel cells.

There are two methods for supplying hydrogen to different types of energy equipment such as fuel cells, combustion devices and engines. One is supplying directly from a high-pressure hydrogen bottle or a liquid hydrogen tank. The other is fuel reforming of methanol, gasoline, natural gas, ethanol or dimethyl ether. Ammonia is a reasonable fuel for a hydrogen carrier if it is dissociated on the catalyst such as nickel/alumina<sup>(1)</sup>. The nickel/alumina catalyst costs 1/1 000 compared with noble metal catalysts. The technology for LPG can be applied to a fuel tank, a vaporizer, and a fuel station. In addition, air conditioners will need no compressors using the latent heat of ammonia. In this paper, the authors describe the possibilities of ammonia as an alternative fuel for energy equipment and the proposal of a hydrogen generation system by ammonia dissociation.

## 2. Environmental Effects on Production of Ammonia

Ammonia is usually used as a fertilizer or chemical material, but seldom used as an automobile fuel. The

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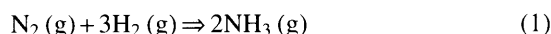
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transportation and storage systems of ammonia are examined in the World Energy Network (WE-NET)<sup>(2)</sup>. In these systems ammonia is synthesized from nitrogen and hydrogen obtained by electrolysis of water. Electrical power is produced in hydraulic power plants in foreign countries where there are rich hydraulic resources. Then, the ammonia is dissociated to hydrogen and nitrogen in demand sites.

Table 1<sup>(3)</sup> shows the properties of liquid fuels as hydrogen carriers for fuel cells. Ammonia has an achronatic property and an irritating smell. Ammonia has almost the same energy density as that of methanol. Ammonia contains 17.8 wt% of hydrogen and stores 30% more energy by liquid volume than liquid hydrogen. Ammonia is furthermore easily dissociated using 16% of the energy in the fuel and requires no energy for the final hydrogen purification stage.

Ammonia is usually manufactured from synthesis gas by the catalytic reaction of hydrogen with nitrogen. The modern production of ammonia relies on the Haber-Bosch process<sup>(4)</sup>, in which a stoichiometric mixture of nitrogen and hydrogen is reacted on a catalyst (a porous iron catalyst prepared by reducing magnetite,  $\text{Fe}_3\text{O}_4$ ) at high temperatures (300°C to 500°C) and high pressures (10 to 20 MPa). The reaction is as follows.



The circulation process is required because this process produces an ammonia gas yield of approximately 10 to 20%. The synthesis reaction between nitrogen and hydrogen to produce ammonia gas is exothermic, releasing 45.7 kJ/mol of energy at 298 K (25°C).

The practical ammonia synthesis can be split in two processes: a hydrogen and nitrogen production process and an ammonia synthesis process. The hydrogen may be produced mainly by natural gas reforming (steam or autothermal), coal gasification, water electrolysis, or steam-iron reaction. For example natural gas reforming is used as the process shown in Fig. 1. There are two methods to directly supply the hydrogen to a fuel cell, through ammonia synthesis and dissociation. The production of hydrogen is the major contributor to the energy consumption of ammonia synthesis. However, ammonia produced from water electrolysis for instance is more expensive than ammonia produced from natural gas.

According to the report of the International Fertilizer

Industry Association (IFA) in 2004<sup>(5)</sup>, the ammonia production capability is 159.1 million tons worldwide. In terms of cost, ammonia is 200 to 300 \$/ton while crude oil is 160 to 230 \$/ton. Therefore, both fuels have very similar costs. Also, according to the World Energy Network (WE-NET) in 1998<sup>(6)</sup>, the examined cost for transportation and storage of ammonia and hydrogen was 26.4 yen/kWh, almost equivalent to that of liquid hydrogen (25.5 yen/kWh).

Table 2<sup>(7)</sup> shows the cost comparison of liquid hydrogen, methanol and ammonia transportation systems, when hydrogen combustion turbine generates a power output of 1 000 MW. The cost of the ammonia transportation system is higher than that of methanol, since they are cost-calculated based on established technologies at present, so a new synthesis process and also a hydrogen separation process of ammonia must be developed.

### 3. Ammonia Properties

#### 3.1 Dissociation of ammonia

Ammonia is low cost and relatively easy to transport and store, compared with hydrogen. This makes it a potential candidate for use as a hydrogen carrier for fuel cell applications<sup>(1)</sup>. Ammonia,  $\text{NH}_3$ , can be dissociated into nitrogen and hydrogen via the reaction expressed in Eq. (2).

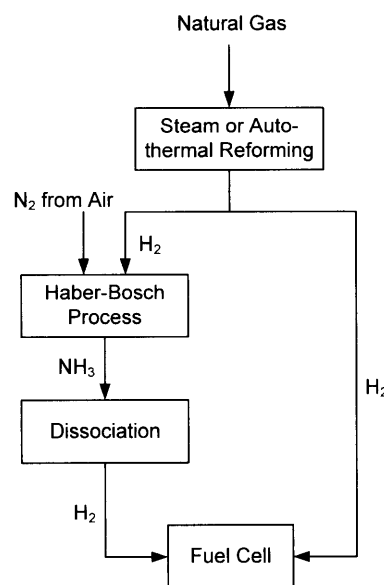


Fig. 1 Hydrogen supply directly and through ammonia to fuel cell

Table 1 Combustion properties of ammonia, hydrogen, octane, and methanol<sup>(3)</sup>

Combustion property	$\text{NH}_3$	$\text{H}_2$	$\text{C}_8\text{H}_{18}$	$\text{CH}_3\text{OH}$
Net heat of combustion (MJ/kg)	18.8	120.0	44.6	20.0
Flammability limits (% by volume)	15 to 28	4.7 to 75		6.7 to 36
Laminar burning velocity (m/s)	0.015	3.51	0.58	0.71
Spontaneous ignition temperature (°C)	651	571	230	470
Minimum ignition energy (mJ)	8.0	0.018	0.28	0.14

Table 2 Cost comparison of each transportation system<sup>(7)</sup>

Case	Liquid hydrogen	Methanol	Ammonia
Fuel generation cost on arrival basis (yen/MJ)	2.52	1.43	1.66
Hydrogen cost (yen/MJ)	3.85	2.39	3.75
Power generation cost (yen/kWh)	32.64	24.70	32.93
(transmission end power amount basis)		(30.83)*	

\* Parenthesized is the power generation cost including  $\text{CO}_2$  recovery and processing.

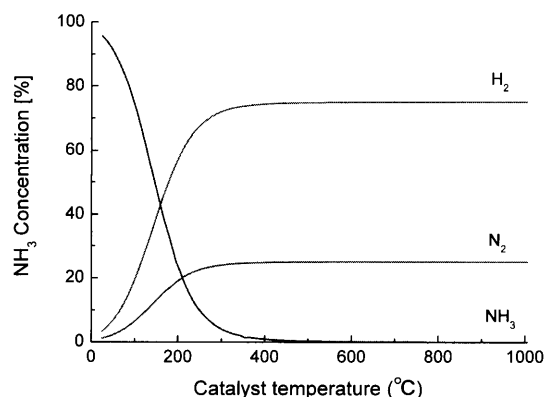


Fig. 2 Equilibrium calculation for ammonia at pressure of 100 kPa

The dissociation is an endothermic reaction, requiring 45.7 kJ/mol of energy at 298 K (25°C). The heating value on the right-hand side of the equation is 21.5 MJ/kg, which is 14.4% higher than that on the left-hand side by adding the dissociating energy (2.69 MJ/kg = 45.7 kJ/mol). The authors define “dissociated ammonia” as the mixture of hydrogen and nitrogen on the right-hand side of Eq. (2).

Figure 2 shows the equilibrium calculation using the chemical analysis software CHEMKIN III for ammonia. Thermodynamic analysis of equilibrium products and heat requirements is conducted for ammonia. The equilibrium calculation utilizes the CHEMKIN code for specified temperatures and pressures. Temperatures over 400°C are required for stable dissociation. The reaction rate is practically increased by operation at temperatures of 700°C or above<sup>(8)</sup>, although dissociation can occur at temperatures as low as 350°C<sup>(9)</sup>.

### 3.2 Combustion properties of ammonia

There are few data on ammonia combustion because ammonia is not usually considered as a fuel. Table 1 shows the combustion properties of hydrogen and ammonia. In the future, ammonia will be used with some difficulties as an automobile fuel. Whereas the laminar burning velocity of hydrogen is 3.51 m/sec, that of ammonia is 0.015 m/sec. Whereas the minimum ignition energy of hydrogen is 0.018 mJ, that of ammonia is 8.0 mJ. Hydrogen fuel causes easy flashback to intake manifolds because of its high propagation speed and its low minimum ignition energy. The end gas in the combustion chamber causes knocking for the short derivation time of hydrogen to spontaneous ignition. Furthermore, a numerical study<sup>(10)</sup> to investigate the characteristics of ammonia-air combustion in a spark ignition engine operation indicated that an ammonia-rich mixture produced low concentrations of nitric oxide under 200 ppm, presumably due to a lack of oxygen.

The fundamental data of the combustion properties of ammonia and dissociated ammonia with air are obtained using a slot burner and a spherical combustion bomb<sup>(11)</sup>.

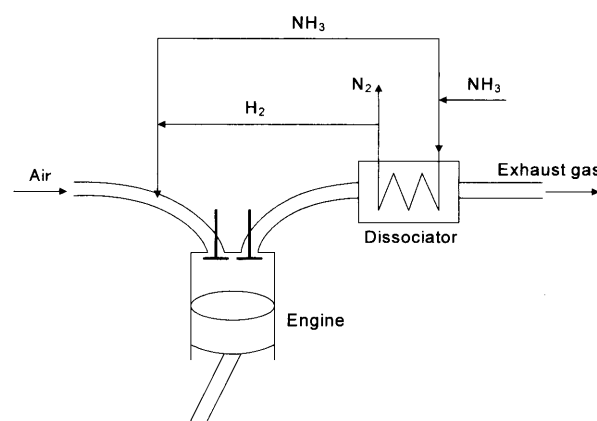


Fig. 3 Conceptual design of engine fueled with ammonia and hydrogen

In this paper, the authors also describe the possibility of reciprocating engines in which the chemical energy of ammonia is efficiently converted into power. It is demonstrated that the slow burning speed and the high required ignition energy are overcome by adding hydrogen from dissociated ammonia. It is clear that the partially dissociated ammonia engine system has the potential to be a promising ammonia-fueled system. Therefore, the authors propose a clean engine system using hydrogen from dissociated ammonia under a catalyst to improve the poor combustion properties of ammonia as shown in Fig. 3.

### 3.3 Ammonia dissociation

In the ammonia dissociation experiments<sup>(12)</sup>, ammonia was not dissociated at a temperature of 400°C at which ammonia can dissociate in the equilibrium calculation. Ammonia was almost completely dissociated to 75% hydrogen and 25% nitrogen at 700°C or higher at any pressure. However, a small amount of residual ammonia was found even at high temperatures of 700°C and 800°C. At higher temperatures and lower pressures, the residual ammonia decreased in concentration in the dissociator. The ammonia concentration was low in percent at 700°C and 800°C in the range of 600 to 3 000 (1/h). At a temperature of 700°C in the dissociator, however, the concentration of residual ammonia was over 4 000 ppm above a space velocity of 1 800 as shown in Fig. 4. On the other hand, the concentration at a temperature of 800°C was maintained under 300 ppm in the range of space velocities from 600 to 3 000. Therefore, the optimized conditions were as follows: the temperature in the dissociator was 800°C, the pressure in the dissociator was 100 kPa, and the space velocities were 600 to 3 000 (1/h).

### 3.4 Concept of fuel-cell system with ammonia dissociator

Figure 5 shows a conceptual diagram of the hydrogen supply system. The thermal efficiency in heat transfer is assumed to be 80%. The temperature of the liquid ammonia tank is assumed to be 20°C. The output of

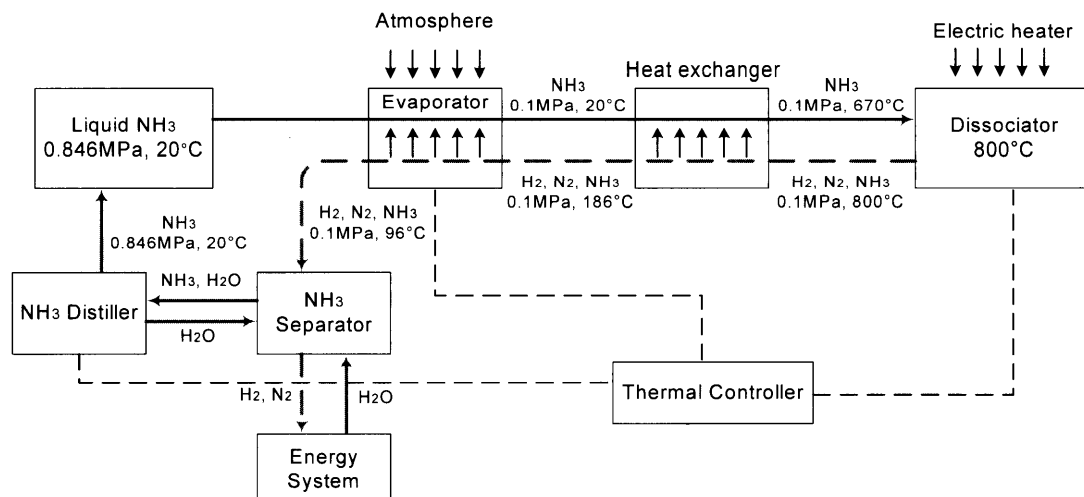


Fig. 5 Conceptual diagram of hydrogen supply system fueled with ammonia

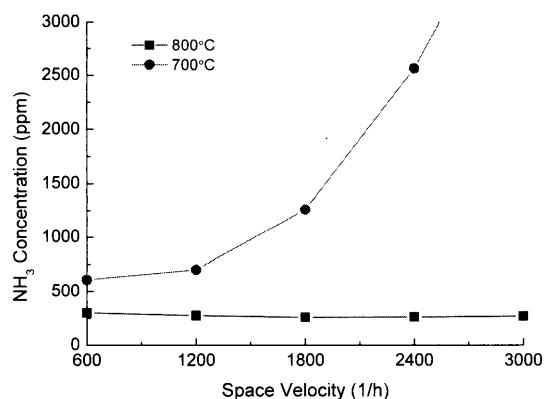


Fig. 4 Ammonia concentration in detail at pressure of 100 kPa

the system is assumed to be 10 kW for a small generation system. The flow rate of ammonia for the output power is  $0.472 \times 10^{-3}$  kg/sec. Liquid ammonia is vaporized in the evaporator using latent heat; 118.69 kJ/kg from the atmosphere. 56 W of heat can be obtained from the dissociated ammonia. The temperature in the dissociator is raised from 20 to 670°C in the heat exchanger after evaporation. There is 632 W of heat recovered from the dissociated gas. The ammonia gas is raised to the dissociation temperature, assumed to be 800°C from experiments. 158 W of heat is required from an electric heater for increasing the temperature from 670 to 800°C. The dissociation process requires 1.28 kW in the dissociator also from the electric heater. After dissociation, the temperature of the mixture of the dissociated gas; the hydrogen, the nitrogen and the residual ammonia, is lowered from 800 to 186°C in the heat exchanger by recovering 632 W of heat. The gas emitted from the heat exchanger is lowered from 186 to 96°C in the evaporator by recovering 70.1 W of latent heat. The system requires 1.44 kW of power only for heating and dissociation in the dissociator.

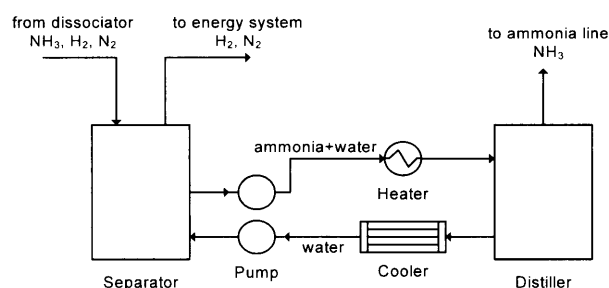


Fig. 6 Schematic diagram of ammonia circulation system

#### 4. Performance of Ammonia Separator and Distiller

##### 4.1 Concept of ammonia recirculation system

Ammonia is a toxic gas presenting danger to public health at high concentrations. The American Conference of Governmental Industrial Hygienists (ACGIH) has set the threshold limit value/time weighted average (TLV-TWA) to be less than 25 ppm<sup>(13)</sup>. The concentration of residual ammonia must also be reduced to the ppm level for use in proton exchange membrane fuel cells (PEMFCs), although alkaline fuel cells are not as sensitive to this. For PEMFC applications where low levels of ammonia impurity are required, a recent study recommends ammonia concentration of under 13 ppm impurity in the fuel<sup>(14)</sup>, because the output current of PEMFCs will be decreased. The residual ammonia from the dissociator should be further decreased, because it is on the order of 300 ppm<sup>(12)</sup> even under the optimized conditions for dissociating ammonia.

Hydrogen and nitrogen show a poor solubility in water. On the other hand, ammonia is highly soluble in water. These properties are used for the ammonia separation. Figure 6 shows the conceptual diagram of the ammonia recirculation system. In the separator, the residual ammonia is dissolved from the dissociated ammonia after the dissociator. When the water in the separator cannot strongly

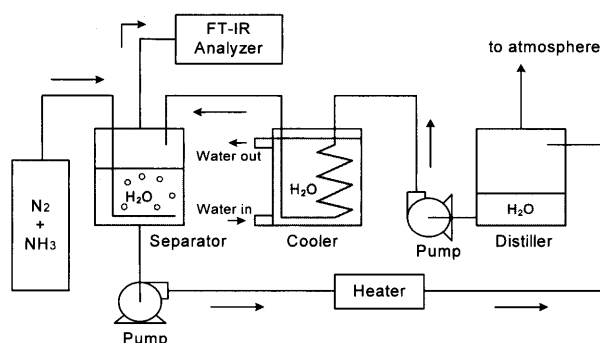


Fig. 7 Experimental apparatus for ammonia separation and distillation

dissolve ammonia, the water is circulated through the distiller. There, the ammonia in the water is extracted using the different boiling points of ammonia and water. Then, the water with a low concentration of ammonia is returned to the separator. In our previous paper<sup>(12)</sup>, 300 ppm of the residual ammonia from the dissociator can be reduced to about 0 ppm using the ammonia separator in which the refinement water temperature is 40°C or less, and the space velocity of the dissociated ammonia gas is 600 (1/h).

#### 4.2 Experimental apparatus and procedure for ammonia distillation

Figure 7 shows a schematic diagram of the experimental apparatus for ammonia separation and distillation. The apparatus consists of the separator with 4 liters of inside volume, the cooler, the heater and the distiller with 1.8 liters of inside volume. The nitrogen gas including 300 ppm of ammonia was used for the practice examination of ammonia separation and distillation.

The practice gas (nitrogen with 300 ppm of ammonia) set to a pressure of 100 kPa and a temperature of 25°C was introduced into the separator at a flow rate of 2 L/min. The practice gas after the separator was measured using a fourier transform infrared spectroscopy (FT-IR) analyzer (Horiba MEXA-4000FT-FC). The ammonia concentration of the gas was measured for 150 min continuously with or without the distiller operation.

The practice gas went through the ammonia separator containing 2 liters of purified water in the distiller operation. The ammonia water circulated around the system with a water flow rate of 50 mL/min and a circulation time of 40 min from the separator through the heater to the distiller as shown in Fig. 7. The water sent to the distiller by the pump was heated there to a temperature of 85°C. In the distiller, ammonia was extracted from the water using the different boiling points of water and ammonia. The water with a low concentration of ammonia (cooled to 25°C in the cooler) was returned to the separator.

#### 4.3 Results of ammonia distillation

Figure 8 shows the results with and without the distiller operation. When the experiment was carried out

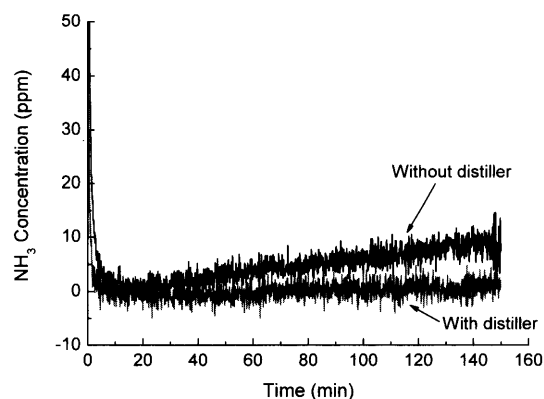


Fig. 8 Ammonia concentration after separator (25°C)

without the distiller, the ammonia concentration increased after 20 min because the ammonia concentration in the water increased for the resolution of ammonia into the water. However, in the distiller operation, the ammonia concentration did not increase for 150 min, so that the distiller system operated effectively.

### 5. Conclusions

In this study, the authors proposed an ammonia circulation system for hydrogen generation. The optimized dissociating conditions in the ammonia separator are elucidated to be a catalyst temperature of 800°C, a pressure of 100 kPa in the dissociator, and space velocities of 600 to 3 000 (1/h). However, for PEMFCs, the 300 ppm of the residual ammonia from the dissociator should be reduced to about 0 ppm using the ammonia separator at a refinement water temperature of 40°C or less. If the ammonia is extracted from the ammonia water, the circulation system for the hydrogen generation system fueled with ammonia can be constructed. This system recovers the waste heat and latent heat of ammonia in heat exchangers. Moreover, the system can be applied not only to combustion equipment, but also to various fields like portable generators or residential cogeneration systems. Ammonia will be an alternative fuel for energy systems in terms of environmental issues in the future.

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