FINAL TECHNICAL REPORT

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Title: Ammonia Combustion in Diesel Engines for Reducing Greenhouse Gas Emissions

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Signature of PI

Public Abstract

Combustion of ammonia alone does not produce carbon dioxide which is a very important greenhouse gas. Ammonia can also be produced from renewable sources such that it can be an attractive fuel to displace petroleum fuels. We have previously demonstrated that ammonia can be burned in a diesel engine as a result of an Iowa Energy Center-sponsored project. Research was further carried to develop an ammonia flow rate control mechanism and investigate the combustion efficiency and exhaust emissions in the present project. In our approach, vapor ammonia was introduced into the intake manifold and diesel fuel was directly injected into the cylinder to ignite the mixture. This "dual-fuel" approach was chosen because ammonia has a high resistance to autoignition. This approach was proven successful and only required minor modifications to the engine intake system.

Engine tests were performed on a multi-cylinder, turbocharged diesel engine manufactured by John Deere (Model 4045). An ammonia flow rate control mechanism was developed to obtain stable ammonia flow rate to achieve desirable engine torque. Results show that carbon dioxide can be greatly reduced if a high percentage of diesel fuel is replaced by ammonia while maintaining the same engine torque output. The present ammonia-diesel dual-fuel system also produces less NOx emissions than the original diesel system under most of the operating conditions while soot emissions vary depending on the operating conditions. Emissions of unburned hydrocarbon are generally higher than the original diesel system. On the other hand,

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the combustion efficiency of ammonia is approximately 95% and ammonia concentrations in the exhaust are on the order of thousand ppm under the conditions tested. The overall engine fuel efficiency is comparable to that of the original diesel system if a half of the diesel energy is replaced by ammonia. Further studies in improving the combustion efficiency and reducing ammonia emissions are recommended to develop optimal operating conditions to adopt ammonia in diesel engines.

Introduction

Combustion of ammonia alone does not produce carbon dioxide which is the most important greenhouse gas. Thus, using ammonia to replace diesel fuel is very attractive in reducing greenhouse gas emissions and alleviating global warming. This project is to study combustion and emissions characteristics of a diesel engine that burns ammonia and diesel fuel. The engine is a multi-cylinder, turbocharged diesel engine manufactured by John Deere (Model 4045) and is used in various tractor applications.

Because ammonia vaporizes at an ambient pressure lower than 5 bar and has a very high resistance to autoignition, we introduced ammonia in the engine intake to form a premixed mixture in the cylinder and use direct-injected diesel fuel to ignite the mixture. Note that ammonia has a high octane number (~130) and high autoignition temperature (~651 ℃, as compared to gasoline, 440 ℃ and diesel fuel, 225 ℃). As a result, combustion phasing is essentially controlled by the injection timing of diesel fuel. The present engine has been modified to adopt the ammonia induction system. Ammonia was injected at a location after turbocharger compressor and before the intake manifold. A high-pressure regulator was used to control ammonia flow rate from the high-pressure tank that contains liquid ammonia.

Dynamometer tests were performed to measure the engine power, fuel consumption, and exhaust emissions. Appropriate operating ranges were identified using various combinations of ammonia and diesel fuel. Ratios of energy substitution by ammonia for stable combustion without sacrificing engine performance were identified. Gaseous and particulate emissions as a function of ammonia-diesel ratios were measured.

Engine Test Facilities

Engine tests were performed at the Internal Combustion Engine Laboratory at Department of Mechanical Engineering, Iowa State University. The specifications and operating conditions of the engine used in this study are listed in Table 1.

Table 1 Engine Specifications

Engine Manufacturer	John Deere (JD)
Engine Model	4045TT068
Engine Serial Number	T04045T772802
Engine Type	In-line, 4-stroke
Bore and Stroke (mm)	106 x 127
Total engine displacement (L)	4.5
Firing Order	1-3-4-2
Compression Ratio	17.0:1
Piston Type	Bowl-in-piston
Valves per Cylinder Intake/Exhaust	1 / 1
Aspiration	Turbocharged
JD Turbo Part Number	RE59379
Injection System	Stanadyne DB4 Rotary Pump
JD Injection Pump Part Number	RE500617
Speed and Load	1000 rpm at 5 ~ 100%
Fuel	Ammonia, No. 2 Diesel fuel

In order to inject gaseous ammonia into the engine as a fuel, some modification was required to the original engine intake setup. A 1/4 in. FNPT pipe fitting was welded into the intake tube after the compressor before the intake manifold, as can be seen in Figure 1. A 3/8 in. outer-diameter (OD) 0.035 in. stainless steel (SS) tube was then run to the ammonia flow control system. Note that stainless steel is required for tubing due to the corrosive nature of ammonia.

Figure 1 – Ammonia intake location.
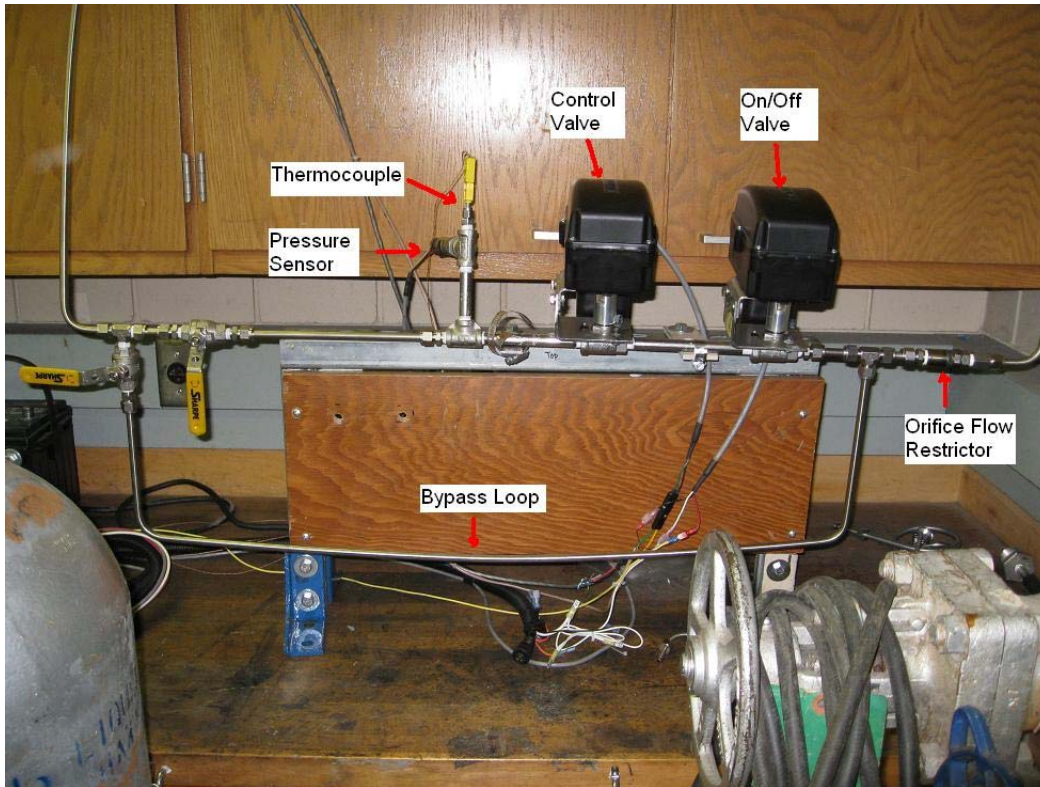
Ammonia Flow Control System

In order to effectively control the ammonia flow rate into the engine, a flow control system was developed using mechanical components and National Instruments LabVIEW 8.1. The control system connects liquid ammonia fuel tanks and engine intake port and regulates the ammonia flow rate.

As seen in Figure 2, three 150 lb. liquid storage ammonia tanks are connected together through a common manifold. Three tanks were used in order lessen the draw on each specific tank and to null the effect of changing tank pressure as ammonia was used. It was observed in early testing that as ammonia was used, it caused the tanks to chill from the vaporization of liquid to gas. This caused the tank pressure to drop sufficiently and, over time, significantly reduce flow. The chilling was also believed to cause liquid ammonia condensation upon the tank needle valves and over time cause erratic readings and insufficient flow. The three tanks were stored in an outside location for safety reasons and 3/8 in. OD 0.035 in. wall stainless steel tube connected the tank manifold to the ammonia flow control system.

Figure 2 – Ammonia storage tanks.

As seen in Figure 3, the tube from the tank manifold was connected to the flow control system. Upon initial connection ammonia flows through a tee which has ball valves on both outlets. These ball valves provide a bypass loop around the control system in order to vent the lines at shutdown. With the bypass loop closed ammonia is allowed to flow into the flow control system. This system utilizes a control ball valve, an on/off ball valve, and a replaceable orifice plate flow restrictor. The control valve is a variable position quarter-turn ball valve that utilizes a 12 V DC motor, controlled by software written in LabVIEW. The on/off ball valve is a two position (open/closed) 12V motorized valve that is also controlled by software in LabVIEW. Both the control valve and on/off valves were products sourced from Raven Industries. The orifice plate flow (Figure 4) restrictor provides back pressure to the flow control system, which allows better resolution with the control ball valve. The orifice plate flow restrictor was made from a TeeJet® Flow Restrictor, modified by welding a 3/8 in. NPT fitting on the outlet. The orifice plates were also sourced off-the-shelf from TeeJet®.

Figure 3 – Flow Control System.

Figure 4 – Orifice plate flow restrictor.

In addition to the flow control system, in Figure 3, there is also a pressure sensor from Raven Industries and a K-type thermocouple. Both are located before the control valve.

The LabVIEW software program developed for the flow control system contains a closed loop algorithm that controls the engine torque +/- 5 ft-lb through the opening/closing of the mechanical control valve. All control parameters are inputted by the user.

Engine Exhaust Emissions Measurement System

Both gaseous and particulate (soot) exhaust emissions were measured in order to determine the engine performance and the environmental acceptance of ammonia as a diesel fuel alternate. In particulate, ammonia concentrations in exhaust were also measured.

Engine Exhaust Emissions Measurement

Three gases are held world wide as the regulatory standards for diesel exhaust gas emissions measurement. These gases are carbon monoxide (CO), hydrocarbons (HC), and nitric oxides (NO_x). Two other gases are commonly measured and reported but are not regulated. These are carbon dioxide (CO_2) and oxygen (O_2).

The equipment used in this study to measure gaseous emissions concentration is a Horiba MEXA-7100DEGR gas analyzer. This analyzer is an industry standard emissions analyzer with high accuracy. The Horiba gas analyzer was used to measure CO, CO_2, O_2, and HC. This analyzer uses a flame ionized detector (FID) method to detect total HC content and is more responsive than other non-dispersive infrared (NDIR) methods. It was found through consultation with Horiba that ammonia present in the exhaust stream would poison the NO_x converter material used in the analyzer over the long term and affect short term dynamic measurement by introducing interference in the analyzer's converter and reactor. Therefore, the converter material was changed from COM-03 to COM-GC3, which uses glassy carbon materials that are resistant to ammonia poisoning.

A smoke meter, Model 415S, manufactured by AVL, was used to measure soot emissions. During the measurement, a sample of exhaust gas was drawn to the analyzer and soot concentrations are measured based on the blackness of the filter paper. The "filter smoke number" was reported.

Ammonia Concentration Measurement

In order to test ammonia concentration in the exhaust stream a modified version of EPA test procedure CTM-027 was used. The sample extraction equipment used was also derived from a

sampling train labeled as Method 17 as found in *EPA Quality Assurance Handbook for Air Pollution Measurement Systems,* Volume III – *Stationary Source Specific Methods*, Section 3.11, January, 1982 (EPA-600/4-77-027b) (EPA, CTM-027).

The sampling probe was located in the exhaust stream, as shown in Figure 5. The probe was constructed from a piece of 3/8 in. OD 0.035 in. wall stainless steel tubing with 1/8 in. holes drilled in a line every 1/2 in. for approximately 4 in. in total length. The same procedure was then used every 90 degree around the probe with a 1/4 in. offset. Using a compression fitting the probe was into a bung welded into the exhaust pipe horizontally. The probe was cut so that the probe tip was approximately 1/2 in. from the opposite side of the exhaust pipe. The tip of the probe was then crosscut with a 45 degree angle that would protrude perpendicular to the exhaust stream flow, as seen in Figure 6.
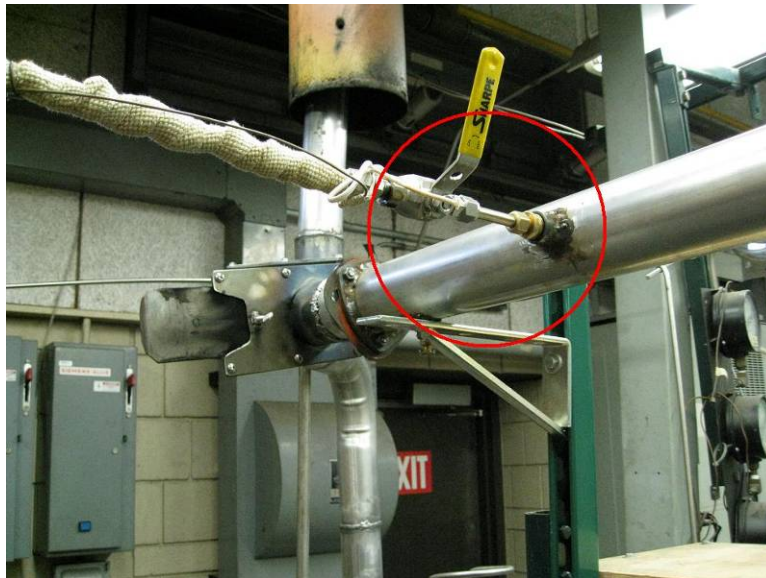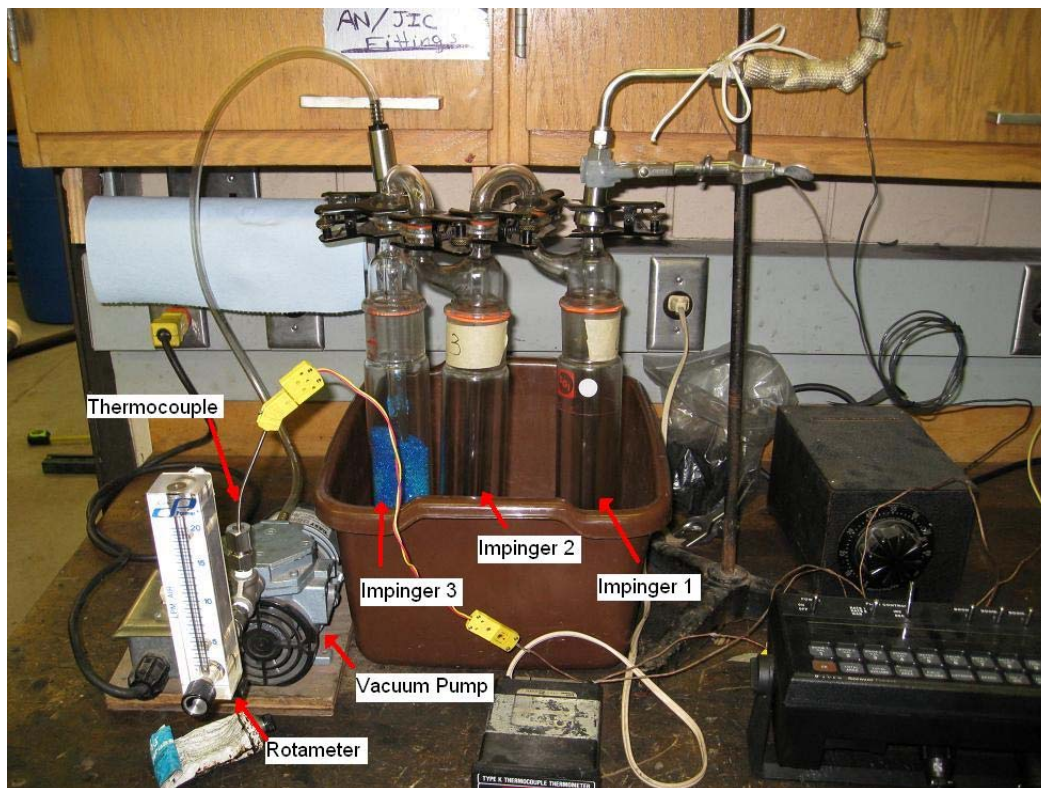

Figure 5 – Ammonia concentration sampling probe location.

Figure 6 – Sampling Probe.

The exhaust probe was then connected to the ammonia sampling train via a heated 3/8 in. OD 0.035 in. wall stainless steel tube, as shown in Figure 7. Early versions of the sampling train contained a particulate filter (Balston 58N with 100-12 Grade 404 Microfibre Filter Cartride) and none heated line. Early testing showed that ammonia concentration measurement is very sensitive to water condensation. In order to avoid this response, the sample line was heated and the particulate filter was removed.

Figure 7 – Ammonia concentration sampling train.

The sample train consists of three modified Greenburg-Smith impingers (no tapered tip) sitting in an ice water bath. The first two impingers contain 250 mL of 4 mL of H_2SO_4 diluted in 1 L de-ionized water (4 mL/L solution). The third impinger contains approximately 300 g of mesh 6-16 silica gel. The impinger train is then connected by 1/4 in. ID Tygon® tubing to a Gast Model MOA-P122-AA 4Z206 vacuum pump with a Cole Palmer rotameter attached to the outlet side. The rotameter is calibrated in units of 0-20 LPM Air. A K-type Omega thermocouple was located in a tee between the rotameter and vacuum pump.

In order to test the ammonia concentration in the exhaust stream, the engine was brought to steady state. The first two impingers were filled with fresh 250 mL of the 4 mL/L solution. The isolation ball valve and vacuum pump switch were turned on simultaneously. Each test had a 20 minute duration. Temperature measurements were recorded at 0, 10, and 20 minute intervals. A measurement of the flow rate going through the rotameter was recorded at 10 minutes.

After the test was completed each impinger was dumped into a 500 mL Nalgene sample bottle and labeled. Samples were then sent to a lab in order to be analyzed by the USEPA Method 350.1 for detecting Ammonia-N. This method uses alkaline phenol and hypo chlorite to react with ammonia to form indophenol blue. The blue color formed is then intensified by sodium nitroprusside and measured spectrophotometrically at 650-660 nm. The above procedures were completed using a SEAL AQ2 discrete analyzer with test and reagent parameters programmed for this application. Results were reported in mg Nitrogen found in the 250 mL solution for each impinger (mg N/250mL).

The method used to calculate ppmV of ammonia present in the exhaust stream is derived from the EPA calculation method (section 4.3 page A-8). Final ppmV NH_3 averages were then plotted for each testing scheme versus load as can be seen in the results section.

Results

Engine Power

Engine tests were performed to use ammonia to compensate diesel energy such that engine can reach it peak torque output at different levels of diesel fueling. In this test, diesel fuel flow rate was controlled so that the engine only produced a specific percentage of the peak torque. Then, the ammonia flow rate was adjusted until the engine generated the peak torque. The resulting engine power is shown in Figure 8a. The other set of operating conditions used only 5% energy from diesel fuel and variable ammonia flow rates to reach different levels of energy torque and power. In this approach, a small quantity of diesel fuel (i.e., 5% of total energy) was used to initiate the ammonia-air mixture, and the resulting power curve is shown in Figure 8b. As can be

seen in Figure 8, desirable engine power can be achieved and engine power is much more stable using the present ammonia flow rate control system compared to results of the previous year.
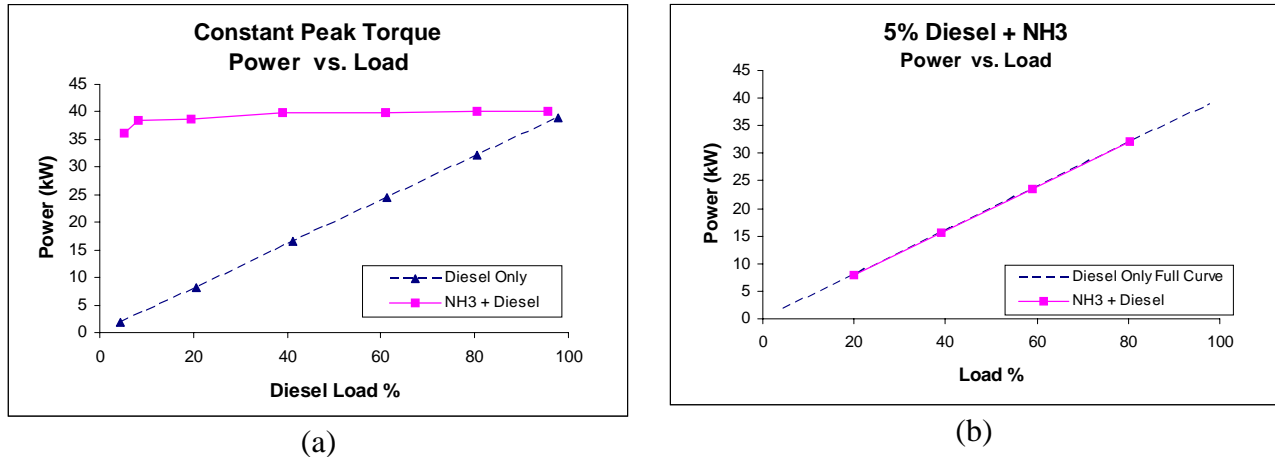
Figure 8 – Engine power using the dual-fuel system under (a) constant peak torque and (b) 5% diesel energy with variable ammonia energy.

Exhaust Emissions

Engine test results confirm that CO_2 emissions are greatly reduced when diesel fuel is partially replaced by ammonia while maintaining the same level of engine power, as shown in Figure 9. The reduction in CO_2 becomes more significant as the amount of ammonia replacing diesel fuel increases (Figure 9a). If only 5% of the total fuel energy is contributed by diesel fuel, CO_2 emissions are consistently at a low level, as seen in Figure 9b.
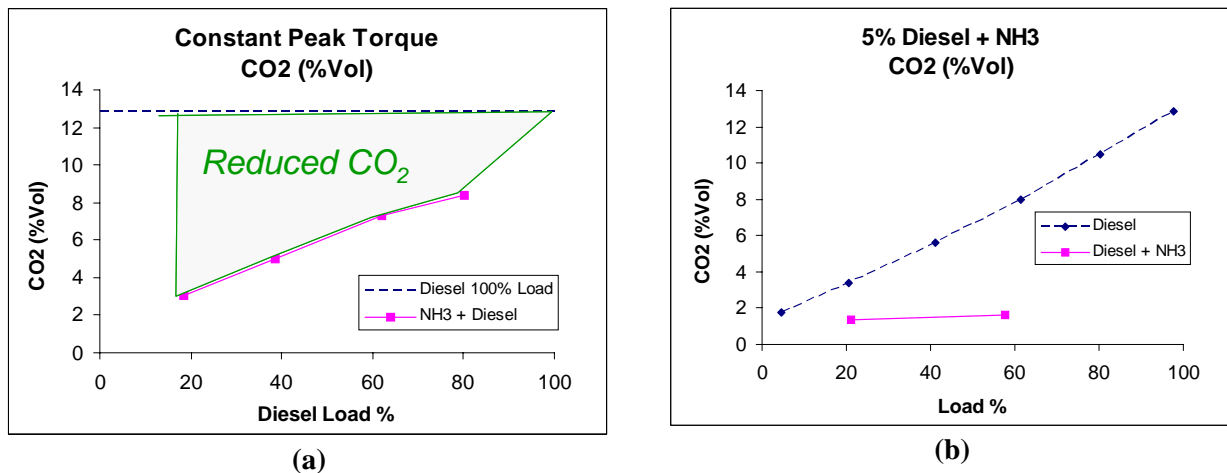
Figure 9 – CO_2 emissions under (a) constant peak torque and (b) 5% diesel energy conditions.

Emissions of nitric oxide (NO) could be a concern when ammonia is used due to the fuel-bound nitrogen. In fact, there are three factors that can influence the net exhaust NO emissions using ammonia in an engine. First, fuel-bound nitrogen in ammonia will contribute to the production of NO during combustion. Second, thermal NO can be reduced since combustion temperature is reduced due to the low flame temperature of ammonia-air flame. Third, ammonia can be a reduction agent for reducing NO to N_2 as shown in the modern diesel selective catalytic reduction (SCR) device. The above three factors compete with each other and determine the final NO emissions level.

Figure 10a shows that NO emissions are reduced if the energy substitution of NO does not exceed 20%, i.e., when the diesel load is more than 20%. As the amount of ammonia increases (i.e., moving toward lower diesel load points), NO emissions increase. Apparently the lower combustion temperature caused by ammonia combustion greatly reduces thermal NO production under such operating conditions. Furthermore, NO emissions are reduced significantly even under 5% energy substitution from ammonia. It is speculated that the effects of NO reduction by reacting with ammonia can also be significant under the conditions tested. On the other hand, if a large amount of ammonia is used, higher NO emissions are observed. Meanwhile, Figure 10b also shows that NO emissions are consistently lower using ammonia-diesel system than the pure diesel conditions.

(a)　　　　　　　　　　　　　　　(b)
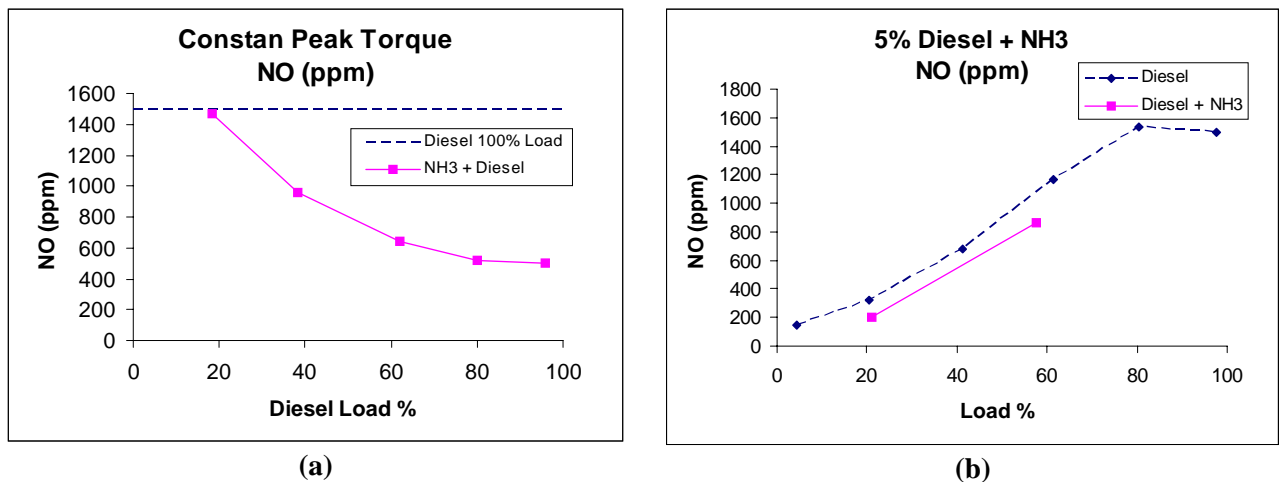
Figure 10 – NO emissions under (a) constant peak torque and (b) 5% diesel energy conditions.

Emissions of unburned hydrocarbon (HC) are found to increase when ammonia is used, as shown in Figure 11. Such increases are thought to be due to the lower combustion temperature in the system resulting in more incomplete combustion of diesel fuel.
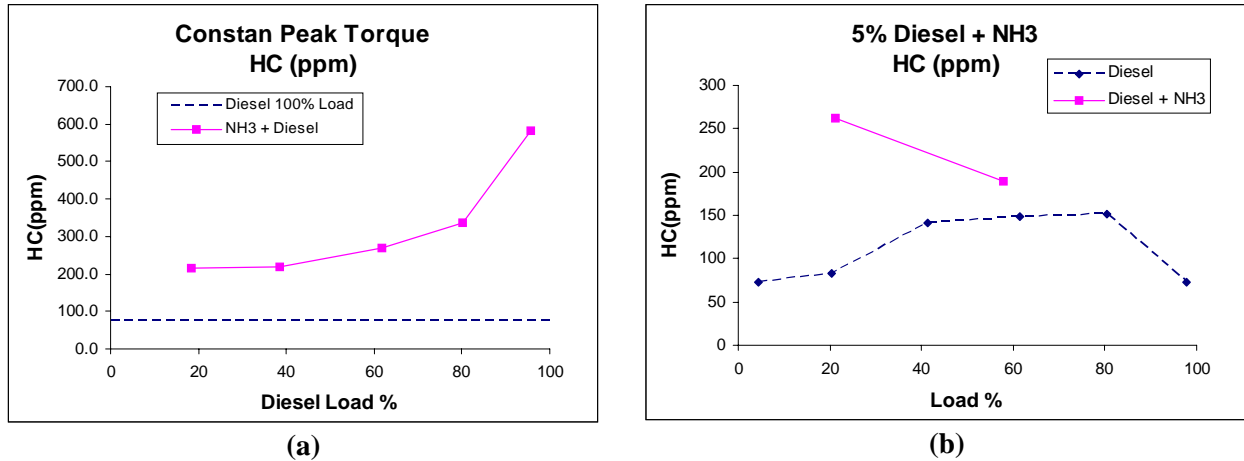

(a) **(b)**

Figure 11 – HC emissions under (a) constant peak torque and (b) 5% diesel energy conditions.
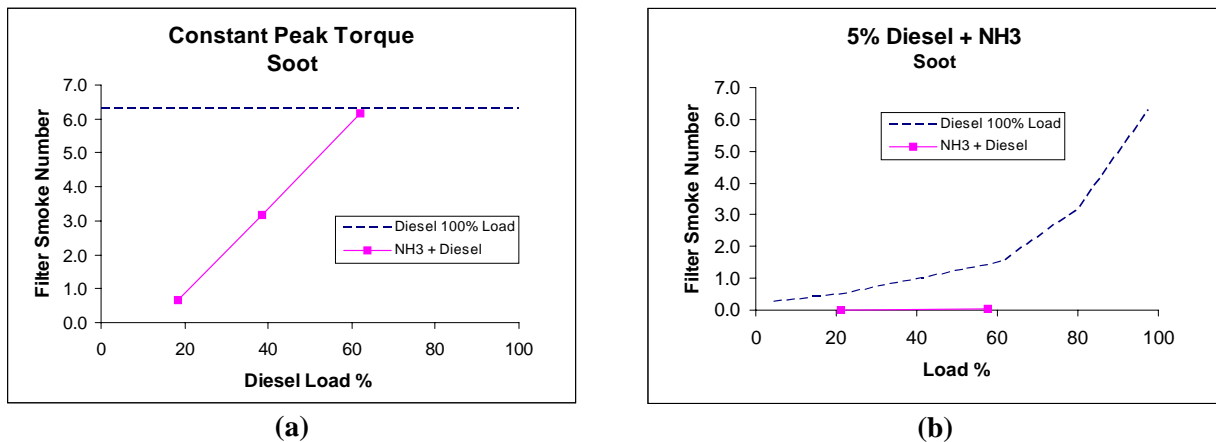

(a) **(b)**

Figure 12 – Soot emissions under (a) constant peak torque and (b) 5% diesel energy conditions.

Soot emissions, measured by filter smoke number (FSN), can be reduced for low diesel fueling rate under constant torque conditions, i.e., less than 60% of the total energy, as shown in Figure 12a. The reason is believed to due to the less amount of diesel fuel to make soot. When the diesel loading is more than 60% of the total energy, soot emissions using ammonia-diesel are higher than those using pure diesel due to the lower combustion temperature caused by ammonia combustion in the system. It is also of interest to note that there is a trade-off between NO and soot emissions with respect to the fuel mixture compositions (see the comparisons of Figure 10a and 12a). On the other hand, when only 5% of diesel energy is used (Figure 12b), soot emissions

are always lower than using pure diesel fuel due to the small quantity of diesel fuel to produce soot emissions.

Exhaust Ammonia Emissions

Ammonia concentrations in the exhaust are shown in Figure 13. Under constant engine torque conditions with various ammonia and diesel fueling rates (Figure 13a), as diesel loading increases, exhaust ammonia concentrations increase and then decrease with concentration varying between 3000 to 1000 ppm. At high diesel loading (i.e., low ammonia fueling), a higher diesel combustion temperature can help oxide ammonia more effectively resulting in low ammonia emissions. As diesel loading decreases, combustion temperature is reduced such that there is more incomplete combustion of ammonia. Additionally, as diesel fuel is reduced, combustion of ammonia will be more dependent on the flame propagation within the ammonia-air mixture. At very low diesel loading (i.e., high ammonia fueling), the premixed ammonia-air mixture is richer such that a better flame propagation can be sustained to consumed ammonia in another effective way. As a result, ammonia emissions can be reduced. However, exhaust ammonia is still at a high level since a significant amount of ammonia is used to replace diesel fuel under low diesel loading condition.

Figure 13b shows ammonia emissions under various engine load conditions with a constant diesel loading (i.e., 5%). It can be seen that the overall ammonia emissions level is relatively high, particularly under low engine loads. Under the conditions studied in Figure 13b, combustion of ammonia will rely on successful flame propagation within the ammonia-air mixture. At low engine loads (i.e., low ammonia fueling), the ammonia-air mixture is too lean to support effective flame propagation and combustion. As a result, high levels of ammonia are exhausted. Since a high concentration of ammonia in the exhaust is harmful, the strategy using minimum diesel fueling with variable ammonia flow rates will not be practical.
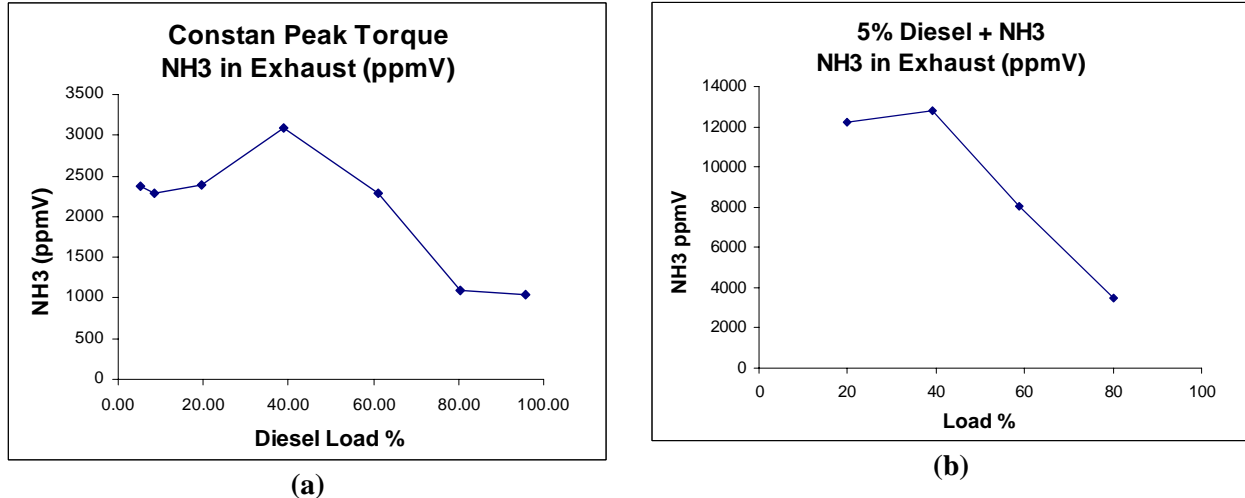
Figure 13 – Ammonia emissions under (a) constant peak torque and (b) 5% diesel energy conditions.

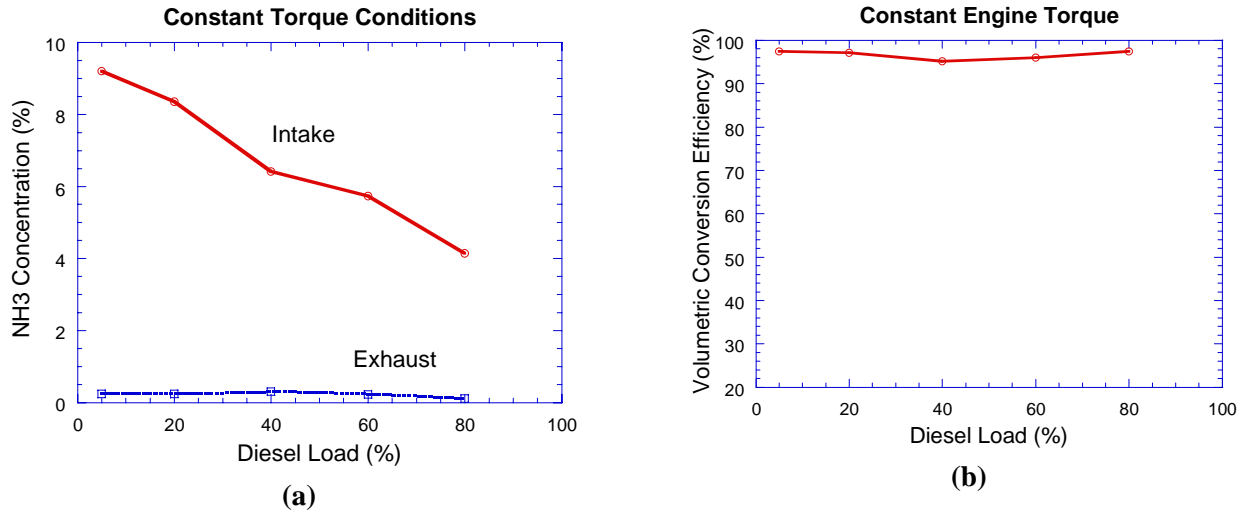*Ammonia Combustion Efficiency and Overall Engine Efficiency*

Ammonia concentrations in the intake manifold were calculated based on the flow rates and thermodynamic conditions of ammonia and air in the intake. Figure 14a shows the intake and exhaust ammonia concentrations for the constant engine torque conditions, which are of more interest. The intake ammonia ranges between 9% and 4% under the conditions studied. The volumetric conversion efficiency is defined as

$$\text{Volumetric Conversion Efficiency} = \frac{[NH_3]_{in} - [NH_3]_{ex}}{[NH_3]_{in}}$$

and the results are shown in Figure 14b. Despite the relatively high concentration of exhaust ammonia, the volumetric conversion efficiency is in the range of 95 to 97%. On the other hand, the mass conversion efficiency, also called combustion efficiency, is also calculated and defined as

$$\text{Mass Conversion Efficiency} = \frac{(m_{NH3})_{in} - (m_{NH3})_{ex}}{(m_{NH3})_{in}}$$

and the results are shown in Figure 15. The combustion efficiency of ammonia is in the range of 94 to 97%. At low diesel loads, although the exhaust ammonia is high (Figure 13a), combustion efficiency is high because the intake ammonia is relatively high.

(a)

(b)

Figure 14 – (a) Intake and exhaust ammonia concentration under constant peak torque. (b) Volumetric conversion efficiency of ammonia based on intake/exhaust concentrations.
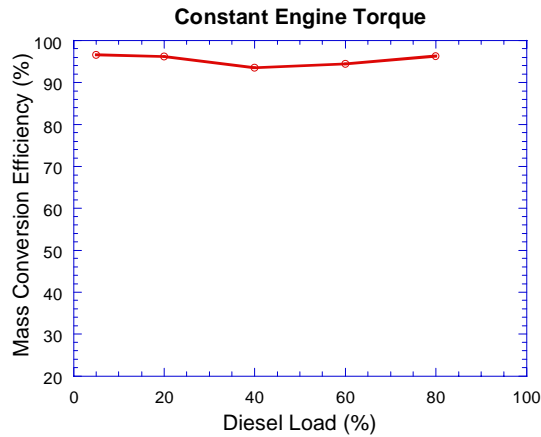
Figure 15 – Combustion efficiency of ammonia under constant peak torque conditions.

The overall thermal efficiency (η) of the engine was calculated based on the following definition,

$$\eta = \frac{\text{Engine power output}}{\text{Rate of fuel energy input}}$$

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and both ammonia and diesel fuel energy was considered. Both individual and overall thermal efficiencies were listed in Table 2. In general, diesel efficiency decreases as the fueling decreases, consistent with the common understanding of deteriorating part-load efficiency in an engine. The trend of the efficiency based on ammonia is not definitive due to the complex combustion modes in the present dual-fuel system. Note that the engine thermal efficiency does not follow the same trend as the combustion efficiency because the thermal efficiency is also related to the combustion phasing. Nonetheless, the overall engine thermal efficiency is highest when the diesel load is between 40 to 60%.

Table 2 Fuel efficiency of the operating conditions corresponding to Figure 8(a).

Diesel energy (%)	5	10	15	20	40	60	80
Ammonia energy (%)	95	90	85	80	60	40	20
Efficiency based on diesel fuel alone (%)	12.2	19.9	28.8	31.1	34.5	39.0	39.2
Efficiency based on NH_3 alone (%)	42.2	46.9	31.2	35.6	43.6	31.8	22.0
Overall fuel efficiency (%)	18.9	28.0	29.9	33.2	38.5	35.0	28.2

Summary

An ammonia flow rate control system was developed and implemented to give stable engine power output. Test results show that nitric oxide emissions using ammonia-diesel is generally lower than those using pure diesel fuel unless a significant amount of ammonia is used. In the present dual-fuel setup, emissions of unburned hydrocarbon are higher but soot emissions vary depending on the relative fueling rates of ammonia and diesel fuel. For a constant engine torque with variable ammonia and diesel fuel energy, ammonia concentrations in the engine exhaust are on the order of 1,000 to 3,000 ppm. If only 5% diesel energy is used, ammonia emissions are relatively high due to insufficient diesel combustion energy and poor flame propagation within the ammonia-air mixture.

For constant engine torque testing, the combustion efficiency of ammonia is approximately 95% under the conditions studied. Reasonable overall engine thermal efficiency can be achieved using

ammonia-diesel if the diesel loading is between 40 to 60%. In order to adopt ammonia in diesel engines, improvements in ammonia combustion efficiency is needed to reduce exhaust ammonia emissions. Further study is required to optimize overall efficiency at different engine loads and fuel ratios. Additionally, ammonia removal in the exhaust may also be required in practical applications.