

2016 Project Abstract

For the Period Ending June 30, 2019

PROJECT TITLE: Hydrogen Fuel from Wind-Produced Renewable Ammonia
PROJECT MANAGER: William Northrop
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FUNDING SOURCE: Environment and Natural Resources Trust Fund
LEGAL CITATION: M.L. 2016, Chp. 186, Sec. 2, Subd. 07c

APPROPRIATION AMOUNT: \$250,000
AMOUNT SPENT: \$250,000
AMOUNT REMAINING: \$ 0

Sound bite of Project Outcomes and Results

This project proved that anhydrous ammonia can be used efficiently as a fuel in diesel engines at a replacement rate of 50%. Ammonia contains no carbon molecules. Therefore, its combustion emits no carbon emissions when produced renewably from wind or solar power, reducing the carbon intensity of agriculture in Minnesota.

Overall Project Outcome and Results

Combustion of anhydrous ammonia in engines reduces carbon dioxide and soot emissions because it is a carbon-free molecule. Ammonia has not been considered a suitable replacement for petroleum fuels in engines due to its low flame speed and poor combustion efficiency, resulting in unburned ammonia emissions and low efficiency. Hydrogen supplementation enhances ammonia combustion. Hydrogen can be produced from ammonia by dissociating it over a catalyst using waste engine heat. This project practically demonstrated a novel chemical reactor and engine control strategy for efficient ammonia combustion in diesel engines. A reactor was designed and tested which utilized engine waste heat to produce hydrogen from an ammonia fuel stream. Diesel fuel was replaced at a rate of 50% on a fuel energy basis in laboratory engine tests. Reactor size limited ammonia replacement to 50%, but higher amounts are envisioned in future designs. The fueling system was also demonstrated on a 1994 Deere 6400 at the West Central Research and Outreach Center (WCROC) in Morris, MN. Engine behavior and emissions were found to be similar across laboratory and field test engines. Hydrogen produced led to more complete ammonia combustion and increased engine efficiency under heavy engine loading. Engine soot particle emissions were shown to decrease, but nitrogen oxides (NOx) emissions increased as a result of ammonia fueling. In future work, integration of mature aftertreatment technologies such as selective catalytic reduction will be developed to reduce NOx emissions from similar ammonia systems. This project improves on the work of other groups by allowing up to 50% ammonia replacement in practical diesel engines with low levels of ammonia emissions. Given the potential for renewable ammonia production using solar and wind power in Minnesota, use in diesel equipment could reduce the carbon intensity of agriculture and save fuel costs for farmers.

Project Results Use and Dissemination

Research results from the project were published at the American Society of Mechanical Engineers Fall Technical Conference in Chicago, IL in October of 2019 (attached). Additional research results are being prepared for submission to a peer-reviewed journal (draft attached for reference). The tractor demonstration was publicized by a number of news outlets including a piece on Minnesota Public Radio on June 19, 2019 (<https://www.mprnews.org/story/2019/06/19/can-fertilizer-fuel-greener-tractors>). Results from the research has also been used in project proposals to the US Department of Energy and other federal/stated entities.



Environment and Natural Resources Trust Fund (ENRTF) M.L. 2016 Final Report

Date of Report: March 25, 2021

Final Report

Date of Work Plan Approval: June 7, 2016

PROJECT TITLE: Hydrogen Fuel from Wind-Produced Renewable Ammonia

Project Manager: William Northrop

Organization: University of Minnesota

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Location: Minneapolis (Hennepin County), Morris (Stevens County)

Total ENRTF Project Budget:

ENRTF Appropriation: \$250,000

Amount Spent: \$250,000

Balance: \$0

Legal Citation: M.L. 2016, Chp. 186, Sec. 2, Subd. 07c

Appropriation Language:

\$250,000 the second year is from the trust fund to the Board of Regents of the University of Minnesota to develop a technical solution for converting wind-produced ammonia to hydrogen through catalytic decomposition, for use in reducing emissions from diesel engines and powering fuel cell vehicles. This appropriation is subject to Minnesota Statutes, section 116P.10. This appropriation is available until June 30, 2019, by which time the project must be completed and final products delivered.

I. PROJECT TITLE: Hydrogen Fuel from Wind-Produced Renewable Ammonia

II. PROJECT STATEMENT:

Over 16.5M metric tons of anhydrous ammonia is transported in the US each year, 80% of which is used in the production of fertilizer for agriculture. This project builds on past and pending ENRTF investments in renewable ammonia production and utilization from wind. Expanding carbon-free ammonia production opens the possibility for its use as a clean replacement fuel for diesel engines used in ammonia transport and for agricultural equipment as its combustion results in no carbon dioxide emissions. Renewable ammonia also has long-term potential to enable efficient hydrogen (H₂) production for fuel cell-powered vehicles. ***This project will develop a novel technical solution to converting ammonia to hydrogen through catalytic decomposition for use in dual-fuel diesel engine applications.*** Ammonia moves within the US using diesel engine-powered barges, trains, and pipelines which could be fueled, in part, by ammonia using the developed technology. On farm diesel equipment like tractors and irrigators could also be partially fueled by ammonia.

Our proposed concept uses a catalytic reactor, thermally integrated into the exhaust manifold of a diesel engine to decompose ammonia into H₂, thus converting it into a useable fuel for dual-fuel diesel engine operation. The goals of the project are to:

- 1) Replace up to 50% of total fuel energy with renewable ammonia in a laboratory diesel engine using a thermally integrated catalytic ammonia decomposition system.
- 2) Reduce soot emissions from the laboratory US EPA Tier 2 certified diesel engine using the dual fuel system to 0.15 g/kW-hr over an eight-mode off-highway test cycle. This emissions level marks a 50% reduction in emissions from the original certified value.
- 3) Demonstrate ammonia decomposition system in a diesel tractor by installing it and using it on-farm over a three-month period.

Funding this project will have two key impacts on the environment in Minnesota and nationally:

- Existing diesel engines used in ammonia transport or agriculture can significantly reduce engine soot, meeting US EPA Tier 4 regulatory standards without expensive aftertreatment catalysts that add significant cost for small businesses.
- Renewable ammonia derived from wind will lead to significant benefits in net-CO₂ emissions from diesel engines. Our team has already demonstrated that ammonia can be economically produced from wind and has applied the technology to fertilizer production in Minnesota. Furthermore, primarily ammonia-powered diesel engines will reduce the carbon intensity of commercial agriculture and positively impact the lifecycle CO₂ emissions of biofuels like corn-based ethanol.

All design and development work of the diesel engine system will be performed at the University of Minnesota (UMN) TE Murphy Engine Research Laboratory where specialized dynamometer facilities and emissions measurement instruments will be used to develop and characterize the dual fuel system. A field-ready prototype of the system will be demonstrated at the UMN's West Central Research and Outreach Center (WCROC) in the third year of the project. In the demonstration, a diesel engine in an existing tractor at the WCROC will be retrofitted with the dual fuel system and auxiliary ammonia tank. The developed catalytic decomposition system will have a significant impact in Minnesota by raising the profile of ammonia used as a fuel. The project will generate data useful in future studies to encourage the use of ammonia as an energy carrier for zero-emissions hydrogen fuel cell-powered passenger cars in the state.

III. OVERALL PROJECT STATUS UPDATES:

Project Status as of January 1, 2017: The thermally integrated ammonia decomposition system is designed and ready for fabrication. The project is on target for fabricating the system and installing it on the test engine located at the Thomas E. Murphy Engine Research Laboratory in the spring of 2017 as scheduled.

Project Status as of July 1, 2017: The thermally integrated reactor has been fabricated and is installed on the test engine. The system was designed with guidance from a computer simulation and solid modeling. The reactor is ready for testing to achieve 50% fuel energy replacement in an 8-mode test during Activity 2. Thus far, the project is on target to achieve the projected milestones. The entire team met to decide on the application for installation of the system on a tractor at the WCROC and a vehicle was chosen.

Project Status as of January 1, 2018: The reactor is still installed on the engine and is awaiting testing. Activity 1 has been completed and Activity 2 is approximately 4 months behind schedule. The system is expected to be tested at the UMN-MERL in March of 2018, which will not impact the overall schedule. Delays in the project are due to safety and lab systems required to be installed in the MERL facility to allow ammonia testing.

Project Status as of July 1, 2018: The exhaust manifold reactor was tested on the dynamometer engine and a full characterization was completed. The diesel engine was operated over a range of engine load with and without ammonia. Up to 50% ammonia by energy was achieved per the project target. However, the reactor resulted in excessive pressure drop, which restricted the maximum load. A new reactor was designed that will be located after the turbocharger and incorporates parallel flow paths, resulting in 1/16 the pressure drop as the first reactor. A delay in the on-farm tractor demonstration has been incurred due to the unforeseen reactor redesign.

Amendment Request (08/20/2018): This amendment request is being made to: 1) Extend the project completion date to June 30, 2019; and 2) to allow the purchase of a piece of capital equipment through re-adjustment of the project budget. A project duration extension is requested because a design revision of the original ammonia decomposition reactor is required. Budget: Reduce instrumentation service budget to \$998 from \$5000 because instrumentation calibration and service was not necessary above the spent amount. Eliminate \$5,000 diesel mechanic service for tractor because tractor service is no longer required to install the dual-fuel ammonia system. Increase Activity 3 salary budget by \$5,002 to allow for graduate student to work on project from Jan 1 through June 29. Increase Activity 2 non-capital budget to \$10,000 from \$5,000 to allow funds for second version of reactor to be fabricated. Request capital budget for \$6,650 to purchase specialty tank and valving for tractor demonstration. Reduce travel costs for Activity 3 from \$1000 to %500 because installation and demonstration of dual fuel tractor will be accomplished mostly at the MERL facility.

Project Status as of January 1, 2019: The original ammonia decomposition reactor re-design was completed, and hardware was fabricated for laboratory testing. The high exhaust pressure drop issue that limited engine load found in first iteration was eliminated and engine operating range was extended to all speeds and loads from dynamometer testing. Reactor was tested on dynamometer engine with diesel replacement of 5% to 50% tested. Emissions data was collected and quantified. The second iteration reactor is currently being installed on the WCROC tractor in order to accomplish outcomes in Activity 3. Project is on schedule to complete project by amended completion date June 30, 2019.

Overall Project Outcomes and Results: Combustion of anhydrous ammonia in engines reduces carbon dioxide and soot emissions because it is a carbon-free molecule. Ammonia has not been considered a suitable replacement for petroleum fuels in engines due to its low flame speed and poor combustion efficiency, resulting in unburned ammonia emissions and low efficiency. Hydrogen supplementation enhances ammonia combustion. Hydrogen can be produced from ammonia by dissociating it over a catalyst using waste engine heat. This project practically demonstrated a novel chemical reactor and engine control strategy for efficient ammonia combustion in diesel engines. A reactor was designed and tested which utilized engine waste heat to produce hydrogen from an ammonia fuel stream. Diesel fuel was replaced at a rate of 50% on a fuel energy basis in laboratory engine tests. Reactor size limited ammonia replacement to 50%, but higher amounts are envisioned in future designs. The fueling system was also demonstrated on a 1994 Deere 6400 at the West Central Research and Outreach Center (WCROC) in Morris, MN. Engine behavior and emissions were found to be similar across laboratory and field test engines. Hydrogen produced led to more complete ammonia combustion

and increased engine efficiency under heavy engine loading. Engine soot particle emissions were shown to decrease, but nitrogen oxides (NOx) emissions increased as a result of ammonia fueling. In future work, integration of mature aftertreatment technologies such as selective catalytic reduction will be developed to reduce NOx emissions from similar ammonia systems. This project improves on the work of other groups by allowing up to 50% ammonia replacement in practical diesel engines with low levels of ammonia emissions. Given the potential for renewable ammonia production using solar and wind power in Minnesota, use in diesel equipment could reduce the carbon intensity of agriculture and save fuel costs for farmers.

Amendment Request (03/25/2021): This amendment request is being made to revise budget categories to reflect actual project spending. The following changes are requested: 1) Reduce the personnel budget to \$51,182 by reducing the PI salary in the third year of the project. This was done to allow higher spending on other budget items to complete the project. 2) Increase Equipment/Tools/Supplies to \$12,447 to allow more items for the tractor demonstration to be purchased. 3) Increase Capital Expenditures to \$7,750 due to a higher cost for the ammonia tank from the supplier. 4) Reduce Activity 3 travel to \$214 because most travel was done earlier in the project as part of Activities 1 and 2.

Amendment Approved by LCCMR 3/31/2021

IV. PROJECT ACTIVITIES AND OUTCOMES:

ACTIVITY 1: Design and Install Catalytic Ammonia Decomposition System on Laboratory Diesel Engine

Description: In part of this activity, the project team will work with Johnson Matthey (JM), an industry partner on the project to identify promising catalyst formulations for ammonia decomposition. Project staff will work with JM to identify two candidate materials for evaluation in the laboratory engine experiments. These catalysts will be chosen based on previous work and can be optimized in a follow-on project after the proof-of-concept demonstration is completed.

The reactor design to be used in the engine dual fuel (ammonia/diesel) system will also be designed and a prototype will be constructed during Activity 1. The reactor will be built into a custom exhaust manifold such that heat is transferred directly from the exhaust gases from the engine before the turbocharger to the catalytic decomposition reactor. Heat exchange will be optimized in the design process through finite element analysis (FEA) using commercially available codes. An ammonia flow control system will also be designed such that the proper amount is injected as a function of engine load and speed. The control system will have its own on-board microprocessor in a laboratory breadboard with the knowledge that it will be later field ruggedized for the on-farm demonstration. A design review will be held at the completion of the design that will include project personnel as well as outside advisors before the prototype reactor is fabricated.

The reactor will be installed on an available John Deere 4045 Tier 2 diesel engine located at the MERL facility. This engine will be modified appropriately to accept the dual fuel system. The engine will be operated at one speed and load point to determine that performance and safety measures are acceptable before laboratory validation testing is completed in Activity 2. A complete safety review will be also conducted for using ammonia in the MERL as part of Activity 1. This safety review will encompass the transport, storage and use of the ammonia fuel for both the laboratory-testing period and the field demonstration study.

Summary Budget Information for Activity 1:

ENRTF Budget: \$ 82,654
Amount Spent: \$ 82,654
Balance: \$ 0

Outcome	Completion Date
1. Design review complete for dual fuel system, ready for fabrication.	January 1, 2017
2. Developed ammonia system installed on laboratory test engine and is operational at one engine speed and load.	October 1, 2018

Activity 1 Status as of January 1, 2017: The design of the ammonia decomposition system was completed and reviewed by the PI. The conceived design consists of a replacement exhaust manifold for a John Deere 4045 diesel engine already installed and working in the MERL. A catalytic reactor will be installed inside the custom manifold that has a metal catalyst substrate inside and heat exchange fins on the exterior of the tube. Waste engine heat will be transferred through the fins into the catalyst substrate to provide energy for the ammonia decomposition reactor. The metal substrate will be provided by Metal Substrates Inc. (TX) and the catalyst material will be provided by Johnson Matthey LLC (UK). Computer analysis has been completed to determine suitable control strategy for the reactor when operating with the engine. An ammonia delivery system was installed at the MERL and will be used for the laboratory testing to be completed in the later part of Activity 1 and in Activity 2.

Activity 1 Status as of July 1, 2017: Based on the design specifications mentioned in the previous update, the catalytic reactor and custom manifold have been built and assembled as shown in Figure A2 in the appendix document accompanying this Work Plan. The final design was the culmination of an iterative process where a selection of reactor concepts was evaluated based on performance and manufacturability. The catalyst substrate was ordered and received from Metal Substrates, and coated by Johnson Matthey using 4.72% wt. Ruthenium on Alumina catalyst. An extensive literature review was completed to confirm this metal as ideal for ammonia decomposition reactions. A computer simulation of the engine and reactor together was created to further refine the design and confirm the system's expected performance. The reactor is installed on the test engine and will be tested at one speed and load to finish Activity 1 milestones, in Sept. of 2017.

Activity 1 Status as of January 1, 2018: This task has been completed.

Activity 1 Status as of July 1, 2018: A design iteration of the ammonia decomposition reactor was required based on the laboratory data collected in this project period. A new reactor was designed that will be installed after the turbocharger on the engine, unlike the previous design that was installed as a replacement to the exhaust manifold prior to the turbocharger. The new design was easier to install as it took the place of the muffler in the actual application and has significantly less pressure drop than the previous design, an issue that necessitated the re-design. The reactor will be completed in September of 2018.

Activity 1 Status as of January 1, 2019: Reactor redesign was completed, and replacement reactor was fabricated. The reactor was installed on the test engine and successfully tested using the eight-mode EPA test cycle. This task is now complete.

Final Report Summary: The initial reactor design for the ammonia system consisted of four series catalyst modules which each contained two sections separated by a solid metal wall. The exhaust side oxidizes unburned fuel in the exhaust and directs heat energy into the second section. The second section absorbed waste heat and increased the ammonia fuel temperature. Once sufficiently warm, ammonia breaks into hydrogen and nitrogen. By design, the hydrogen production of the reactor never approaches 100% and is expected to yield 20%-50% H₂ at rated conditions. Preliminary testing of the first reactor revealed a fatal design flaw. Exhaust backpressure was increased using the reactor design such that engine operability range was crippled. Redesign was required midway through the project. The final reactor design rearranged the initial design so that the restrictive exhaust-side catalyst sections were in a parallel configuration instead of series. Under ideal circumstances, this reduced the flow restriction pressure drop of the exhaust flow by 16 times the original value. A second reactor was constructed as designed and tested successfully on both laboratory and field engines. Exhaust restriction was reduced substantially, such that all engine operating modes were easily achieved for lab and field engines.

ACTIVITY 2: Experimentally Validate Ammonia Decomposition Dual Fuel System

Description: In this activity, the prototype system installed during Activity 1 will be thoroughly tested at the MERL dynamometer facility. An eight-mode test cycle adapted from the US EPA regulations for off-highway engines will be used in the first round of testing with the dual fuel ammonia decomposition system. Instruments

to be used include a Fourier Transform Infrared analyzer bench and MicroSoot photo-acoustic soot mass analyzer. These instruments are available at the MERL for use on the project and are ideally suited for evaluating the dual-fuel system's performance. It is likely that the prototype system will require design iteration during Activity 2 to optimize its performance. Outcomes of Activity 2 will include achieving project goals of 50% diesel fuel replacement with ammonia and reduced engine-out soot emissions to 0.15 g/kW-hr. The performance and emissions of the system will also be evaluated.

After the performance evaluation, a ruggedized version of the dual fuel system will be fabricated. This system will use a weatherproof controller box and sensors. The system will also be mechanically configured to match the tractor chosen at the WCROC. An ammonia sensor will be installed as part of the system to determine slip levels through the decomposition system and engine. If high levels of ammonia are present in the exhaust, an ammonia oxidation catalyst may be required. The outcome of this task will be a system ready for installation on the tractor at the WCROC facility in Activity 3.

Summary Budget Information for Activity 2:

ENRTF Budget: \$ 95,753
Amount Spent: \$ 95,753
Balance: \$ 0

Outcome	Completion Date
<i>1. Dual fuel system can achieve 50% diesel energy replacement with ammonia over US-EPA eight-mode test cycle.</i>	October 31, 2018
<i>2. Engine tests and refinement complete, dual fuel system achieves 0.15 g/kW-hr soot emissions target over eight-mode test.</i>	October 31, 2018
<i>3. Ruggedized demonstration prototype constructed and ready for installation on tractor.</i>	October 31, 2018

Activity 2 Status as of January 1, 2017: No progress has been made on this activity prior to this date.

Activity 2 Status as of July 1, 2017: The dual fuel system has been installed on the test engine and is ready to begin the eight-mode EPA test cycle. Also per the research addendum, the team is on target to complete several rounds of testing to achieve this deadline and will publish the results in the peer-reviewed literature.

Activity 2 Status as of January 1, 2018: The dual fuel system has been delayed because the ammonia fuel infrastructure required to operate the system has taken longer than expected. Ammonia requires additional safety precautions for use in the laboratory than other fuels. The system and plumbing are expected to be installed in the MERL by March of 2018 and testing will begin shortly thereafter. To speed up and maintain overall project timing, the demonstration tractor installation and laboratory testing tasks will occur simultaneously.

Activity 2 Status as of July 1, 2018: The Activity 2 tasks for the first reactor have been completed with exception to the third outcome. The engine met the 0.15 g/kW-hr soot target at the tested conditions above 10% diesel fuel replacement and the reactor/engine system was able to achieve 50% diesel energy replacement at selected engine operating conditions. The second version of the reactor will also be tested in the same manner in the fall of 2018 before being installed on the tractor.

Activity 2 Status as of January 1, 2019: The Activity 2 tasks for the second reactor have been completed. The John Deere diesel engine was operated on the dynamometer over the full 8 mode test with good results. Similar diesel replacement ratios were found, but without penalty of high pressure drop through the reactor. High speed modes do not meet 0.15 g/kW-hr soot target due to effect of ammonia fumigation on engine combustion efficiency. Low speed modes do meet 0.15 g/kW-hr soot target. Since the demonstration tractor engine operates with higher exhaust temperatures, emissions data will be taken from the integrated system to determine whether similar performance to the dynamometer experiments are obtained. Soot emissions are

expected to be lower on the demonstration engine. The reactor is now being installed on the tractor in accordance with activity 3 tasks.

Final Report Summary: The initial reactor design was tested and found capable of 50% replacement rate, but not capable of 8-mode test due to exhaust flow restriction by exhaust-side catalyst. The reactor was consequently disassembled and redesigned to eliminate pressure restriction. The second design was demonstrated on laboratory engine and met both the 50% replacement goal and was capable of 8-mode engine operability. Greater than 50% is physically possible but decreases ammonia combustion efficiency due to low hydrogen yield at the high reactor throughput required. Laboratory engine tests did not meet the soot target due to shift in combustion mode when introducing ammonia fuel. The field tractor and engine showed compliance with 0.15 g/kw-hr limit across the 8-mode test, with high-speed low load conditions yielding highest soot output of 0.25-0.45 g/kw-hr at 30% fuel replacement rate. The field tractor was successfully demonstrated using final reactor in field without issue, highlighting the rugged and transient-capable design of the fueling system.

ACTIVITY 3: Install Ammonia Decomposition system on tractor at WCROC and perform on-farm demonstration
Description: In this activity, the developed catalytic ammonia decomposition system, or a copy of the laboratory system, will be installed on a John Deere tractor at the WCROC. The installation will be complete by the end of the summer of 2018 and will be ready for use during the harvest season. The goal of the demonstration phase of the project is to prove that the ammonia system is robust and safe for operational use on-farm and that the system can achieve 50% diesel replacement by energy. During this activity, system data will be logged and transmitted to MERL researchers for understanding in-use performance and emissions. The data will also be used to diagnose potential system malfunctions. Compiled data from the six-month demonstration period will be organized and published to complete the project. WCROC researchers will also compare fuel costs between using on-site generated renewable ammonia and the diesel fuel it displaced using the developed system.

Summary Budget Information for Activity 3:

ENRTF Budget: \$ 71,592
Amount Spent: \$ 71,592
Balance: \$ 0

Outcome	Completion Date
1. Ammonia dual fuel system is installed on tractor and can be used operationally for the harvest in fall of 2018.	October 31, 2018
2. On-farm demonstration proves that diesel fuel can be replaced at over 50% by energy using ammonia dual fuel system.	May 21, 2019
3. Energy savings and soot emissions benefits area quantified and published for Sept-Feb period.	May 21, 2019

Activity 3 Status as of January 1, 2017: No progress has been made on this activity prior to this date.

Activity 3 Status as of July 1, 2017: The Research team, consisting of MERL and WCROC staff, met to discuss and coordinate the plan for executing Activity 3 on August 3, 2017. The farm tractor for this activity has been identified and will be delivered to the MERL team at their lab in January of 2018. A photograph of the tractor is shown in Figure A2 in the appendix attached to this Work Plan. Once delivered, the ruggedized ammonia fueling system will be installed and tested before sending the tractor and system back to WCROC for use during the summer of 2018.

Activity 3 Status as of January 1, 2018: Further meetings have occurred between the MERL staff and the WCROC staff since the summer. Since engine testing activities have been delayed by 3 months, the tractor to be converted will be delivered in March of 2018. It is expected that after delivery to UMN, the tractor will require 3-5 months for the conversion process and demonstration in the summer of 2018 will occur as planned.

Activity 3 Status as of July 1, 2018: The tractor to be used for demonstration of the dual fuel ammonia system was delivered to the TE Murphy Engine Research Laboratory during this project period and a power take-off (PTO) dynamometer was acquired to perform performance testing on the engine in the tractor. A National Instruments control system was developed to control the dual-fuel system on the tractor. The tractor was also used to package the new reactor concept using mockups and computer 3-D models.

Activity 3 Status as of January 1, 2019: Towards project outcome 1, the ammonia decomposition reactor is currently being installed on the tractor for demonstration. Outcomes 2 and 3 are on schedule to be completed before July 1, 2019. A National Instruments LABVIEW control program is currently in development to control ammonia fumigation based on intake manifold boost pressure. Low and high flow ammonia cut-offs and tractor cab emergency-stop equipment has also been specified and is will be installed on the tractor to ensure safe operation. A system for preheating liquid ammonia from a tank mounted on the front of the tractor was designed.

Final Report Summary: This project developed and constructed an ammonia decomposition reactor and system for a practical on-farm demonstration. The system was quantified from 0% to 50% diesel replacement rate using laboratory engine to confirm operative success on field tractor before installation. The reactor was installed on a field tractor at the TE Murphy Engine Research Laboratory before the on-field demonstration. The tractor was demonstrated and tested from 0% to 50% fuel replacement rate at UMN MERL before shipping tractor to Morris for demonstration at the WCROC. A microcontroller -based real-time flow control system was developed for demonstration of tractor under transient real-world conditions on a farm field. The tractor was successfully demonstrated using chisel plows and road box grader on multiple occasions. The demonstration tractor is currently still operable at WCROC.

V. DISSEMINATION:

Description: Results regarding the ammonia decomposition dual fuel system will be disseminated through journal papers in scientific publications and through presentations at conferences. The Program Manager will also work with the WCROC to schedule tours and activities during the demonstration phase of the project (Activity 3).

Status as of January 1, 2017: No progress has been made on this activity prior to this date. On February 22nd, the PI will present the results of the ammonia decomposition system design at the University of Minnesota Sustainable Ammonia Technology Showcase in St. Paul.

Status as of July 1, 2017: No further progress has been made on this activity since February 22nd, 2017. Once required eight-mode testing is complete, per Activity 2, results will be collected and published in a scientific journal. Dan Gundersen of Minnesota Public Radio contacted the PI and expressed interest in broadcasting a story about the project once the demonstration phase is underway.

Status as of January 1, 2018: At this point in the project, no publications or data have been presented to the public since the engine testing has not been completed. The graduate student on the project attended and met with participants at the ammonia fuel conference held in Minneapolis in November of 2017. The graduate student also presented a work-in-progress poster at the 2017 American Society of Mechanical Engineers (ASME) Internal Combustion Engines Division conference in Seattle, WA in October of 2017 that included a section on the ammonia reforming activities underway.

Status as of July 1, 2018: A journal paper based on the data collected from the first ammonia reactor dynamometer study is in submission to Energy and Fuels. The project team also gave a poster presentation and demonstration to attendees of the ARPA-E REFUEL program review on July 18, 2018. The REFUEL program is focused on ammonia production and use for energy.

Status as of January 1, 2019:

Journal entry to Energy and Fuels was delayed because the second iteration of the reactor needed to be completed. More complete data from second iteration reactor design was collected and This entry will focus mainly on the emissions of the ammonia dual-fueled system. A conference paper for American Society of Mechanical Engineers (ASME) Internal Combustion Engines Division Fall Technical Conference, ICEF 2019, will also be submitted based on energy recovery analysis of the tractor with installed reactor. Emissions data will also be included in this work as a secondary focus.

Final Report Summary: The following were major dissemination activities by the project team over the duration of the program and beyond:

- 2/22/17: PI William Northrop presents design and summary of ammonia decomposition system for use in project to Ammonia Technology Showcase. (St. Paul, MN)
- 10/28/17: Work in Progress poster presented at ASME Internal Combustion Engine Fall Technical Conference in Seattle, WA. Reactor was redesigned and final reactor design is featured on the poster.
- 7/18/18: Second poster presentation at ARPA-E REFUEL meeting showing final reactor design along with preliminary analysis of emissions and engine performance data.
- 6/19/19: PI Northrop was interviewed on MPR News <https://www.mprnews.org/story/2019/06/19/can-fertilizer-fuel-greener-tractors> for a story on the ammonia-fueled tractor.
- 10/22/19: Presentation and subsequent publication of ASME technical paper ICEF2019-7241 at 2019 ASME Internal Combustion Engine Fall technical conference. The publication quantifies and analyzes the emissions and engine performance metrics of the project field tractor equipped for ammonia-diesel dual fuel. Replacement rates of up to 42% were measured in this study, and both emissions and efficiency were measured to increase under heavy engine loading.
- 2/2/21: Planned submission of research work conducted on laboratory engine system to the Journal Energy Conversion and Management.

VI. PROJECT BUDGET SUMMARY:**A. ENRTF Budget Overview:**

Budget Category	\$ Amount	Overview Explanation
Personnel:	\$ 202,591	1 project manager at 3% FTE (\$13,896); 1 Co-PI researcher at 6% FTE (\$16,056), 1 research scientist at 25% FTE (\$50,220); 1 undergraduate student researcher at 4% FTE (\$2,508); one WCROC Technician at 50% FTE (\$13,581); and 1 graduate research assistant at 50% FTE \$115,240
Professional/Technical/Service Contracts:	\$998	Emissions instrument calibration at MERL \$998. Contractor selection to be made using university procedures.
Equipment/Tools/Supplies:	\$ 37,447	Laboratory system plumbing, electrical supplies, consumables, test cell parts and other consumables (est. \$10,000). Parts for engine decomposition system(s) including metal parts, fittings, control hardware, wiring, and catalysts (est. \$10,000). Tractor and engine parts and

		consumables for WCROC facility experiments (\$15,000)
Capital Expenses:	\$7,750	60-gallon anhydrous ammonia storage tank and support for tractor demonstration
Travel Expenses in MN:	\$1,213	Mileage and travel expenses for field site visits and meetings at Morris, MN. Travel costs for system installation and commissioning in second summer of project.
TOTAL ENRTF BUDGET:		\$ 250,000

Explanation of Use of Classified Staff: NA

Explanation of Capital Expenditures Greater Than \$5,000: A capital request for the ammonia tank used in on-farm demonstration will cost more than \$5,000. A certified and safe tank with valving is necessary for operation at the WCROC facility. Ammonia use on any farm requires meeting proper regulations and safety precautions.

Number of Full-time Equivalents (FTE) Directly Funded with this ENRTF Appropriation: 1.45

Number of Full-time Equivalents (FTE) Estimated to Be Funded through Contracts with this ENRTF Appropriation: 0.20

B. Other Funds:

Source of Funds	\$ Amount Proposed	\$ Amount Spent	Use of Other Funds
Non-state			
Johnson Matthey Inc.	\$25,000	\$ 25,000	Some materials may be available before July 1, 2017 Although not offered as cost share, engineering services and catalytic material support will be provided by JM. Materials will be supplied to UMN through University Material Transfer Agreement signed by both parties.
State			
Regents of the University of Minnesota	\$102,344	\$ 46,765	The foregone federally negotiated ICR funding constitutes the University's cost share to the project. The cost share is determined using the federal IDC rate of 52% with appropriate exclusions for equipment and academic year tuition and benefits.
TOTAL OTHER FUNDS:	\$127,344	\$ 71,765	

VII. PROJECT STRATEGY:

A. Project Partners:

This project involves collaboration between two colleges a UMN, the College of Science and Engineering and the College of Food, Agricultural and Natural Resource Sciences (CFANS). The CSE project team is at the MERL

within the Department of Mechanical Engineering. The recently commissioned MERL is ideally equipped for the research project as it contains four engine test cells equipped with engines, dynamometers and advanced emissions measurement systems. The laboratory also contains all the necessary software for designing and modeling the prototype system.

The CFANS project team is located at the WCROC is an agricultural experiment station in Morris, MN. It consists of approximately 1,100 acres of crop and pasture lands, horticulture gardens, dairy and swine production facilities, and several renewable energy systems. The Renewable Energy Program has five research scientists / engineers and has a five-year strategy to reduce fossil energy consumption in production agricultural through the adoption of renewable and efficient energy systems. The UMN WCROC built and now operates a Renewable H2 and ammonia Pilot Plant powered with a co-located utility-scale 1.65 MW wind turbine. The WCROC also has agreed to retrofit an existing diesel engine-powered tractor with the developed ammonia dual fuel system.

Johnson Matthey (JM) is a global manufacturer of sustainable technologies including catalytic materials for a large number of industrial sectors including petrochemical and automotive areas. JM has a corporate focus on clean air, clean energy and low carbon technologies and are experts in the application and recycling of precious metals. JM will provide in-kind engineering assistance and catalytic materials for the ammonia decomposition systems to be developed in this project.

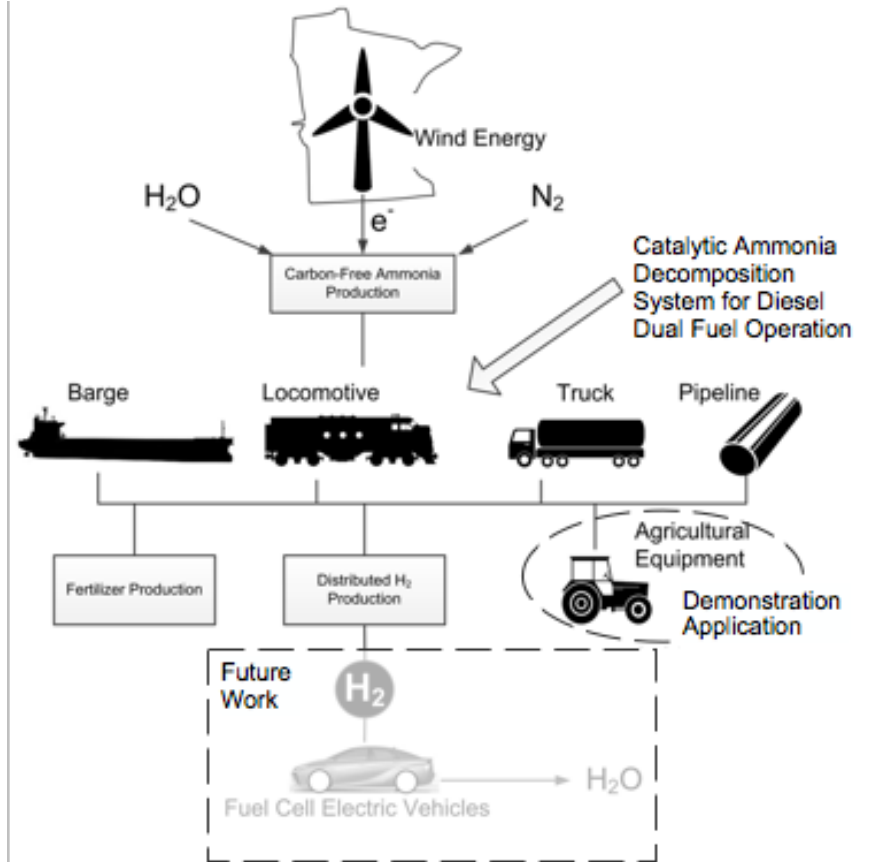
B. Project Impact and Long-term Strategy:

The main goal of this project is to show that ammonia can be effectively used as a replacement for diesel fuel in off-highway equipment. The project team will accomplish this by proving a new technology that will allow ammonia to burn better by partially decomposing it to hydrogen. One long term goal of the project is to develop a commercially viable dual fuel system for diesel engines used in transporting ammonia (e.g., rail and barge) and for on-farm applications. Another goal of the project is to raise public awareness of ammonia as a carbon-free fuel in the Minnesota and the nation. Extensions of this project could use similar catalytic decomposition technology to convert ammonia to compressed gaseous hydrogen for fueling fuel cell vehicles.

C. Funding History:

Funding Source and Use of Funds	Funding Timeframe	\$ Amount
<p>The U of MN Renewable Hydrogen Pilot Plant was funded partially through an \$800k 2006 ENRTF project. The University and the State provided an additional \$2.95 million to complete the hydrogen pilot plant and add the ammonia production process. Research funded by U of MN MnDRIVE (\$500K) and U of MN IREE (\$400K) is in progress to evaluate novel production methods for renewable nitrogen (ammonia) fertilizer. A 2015 ENRTF project (101E - \$1 million) is also pending legislative approval to further expand renewable nitrogen fertilizer research at the University. This proposal will evaluate the use of ammonia as a fuel. Both fuel and fertilizer production will use ammonia generated using wind power at the U of MN pilot plant.</p>	<p>The funds have been secured</p>	<p>\$5,650,000</p>

IX. VISUAL COMPONENT:



X. RESEARCH ADDENDUM: Peer review of addendum was completed

XI. REPORTING REQUIREMENTS:

Periodic work plan status update reports will be submitted no later than January 1, 2017,-2018 and 2019, and July 1 2017, 2018. A final report and associated products will be submitted between December 31 and February 15, 2019 May 31 and June 29, 2019.

**Environment and Natural Resources Trust Fund
Final - M.L. 2016 Project Budget**

Project Title: Hydrogen Fuel from Wind-Produced Renewable Ammonia

Legal Citation: M.L. 2016, Chp. 186, Sec. 2, Subd. 07c

Project Manager: Will Northrop

Organization: University of Minnesota

M.L. 2016 ENRTF Appropriation: \$ 250,000

Project Length and Completion Date: 3 Years, June 30, 2019

Date of Report: 3/25/2021



ENVIRONMENT AND NATURAL RESOURCES TRUST FUND BUDGET	Activity 1 Budget	Amount Spent	Activity 1 Balance	Activity 2 Budget	Amount Spent	Activity 2 Balance	Revised Activity 3 Budget 03/31/2021	Amount Spent	Activity 3 Balance	TOTAL BUDGET	TOTAL BALANCE
BUDGET ITEM	Design and Install Catalytic Ammonia Decomposition System on Laboratory Diesel Engine			Experimentally Validate Ammonia Decomposition Dual Fuel System			Install Ammonia Decomposition system on tractor at WCROC and perform on-farm demonstration				
Personnel (Wages and Benefits) - Overall	\$62,154	\$62,154	\$0	\$89,255	\$89,255	\$0	\$51,182	\$51,182	\$0	\$202,592	\$0
Prof. Will Northrop, Project Manager (75% salary, 25% benefits); 3% FTE for 2.5 2.0 years (\$12,247)											
Michael Reese, Key Personnel (75% salary, 25% benefits); 6% FTE for 1.5 years (\$16,056)											
Research Technician at WCROC,(75% salary, 25% benefits), 50% FTE for 1.5 years (\$13,581)											
Darrick Zarling, Research Scientist (75% salary, 25% benefits); 25% FTE for 2.5 years (\$50,220)											
1 Undergraduate Research Assistant (100% salary); 4% FTE for 2.5 years (\$2,508)											
1 Graduate Research Assistant (60% salary, 40% benefits); 50% FTE for 2.5 years (\$111,238)											
Professional/Technical/Service Contracts											
Diesel engine mechanic for rebuilding, configuring and installing system on tractor engine at WCROC facility. To be competitively selected following University of Minnesota							\$0	\$0	\$0	\$0	\$0
Emissions instrument calibration at MERL for FTIR analyzer and micro-soot analyzer. To be competitively selected following University of Minnesota procedures.				\$998	\$998	\$0				\$998	\$0
Equipment/Tools/Supplies											
Laboratory system plumbing, electrical supplies, consumables, test cell parts and other consumables. Parts for engine ammonia decomposition system(s) including metal parts, fittings, control hardware, wiring, and catalysts. Parts for ruggedized system including a new reactor and	\$20,000	\$20,000	\$0	\$5,000	\$5,000	\$0	\$12,447	\$12,447	\$0	\$37,447	\$0
Capital Expenditures Over \$5,000											
60-gallon anhydrous ammonia storage tank and support for tractor demonstration							\$7,750	\$7,750	\$0	\$7,750	\$0
Travel expenses in Minnesota											
Mileage and travel expenses for field site visits and meetings at Morris, MN. Lodging and expenses for a 1-month student visit for system installation and commissioning in second summer of project	\$500	\$500	\$0	\$500	\$500	\$0	\$214	\$214	\$0	\$1,214	\$0
COLUMN TOTAL	\$82,654	\$82,654	\$0	\$95,753	\$95,753	\$0	\$71,593	\$71,593	\$0	\$250,000	\$0

THERMOCHEMICAL AND SENSIBLE ENERGY RECUPERATION USING THERMALLY-INTEGRATED REACTOR AND DIESEL-AMMONIA DUAL FUELING STRATEGY

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Department of Mechanical Engineering
Minneapolis, MN 55455

ABSTRACT

Anhydrous ammonia produced using wind power on farms can be a renewable alternative to conventional fertilizers and to fossil fuels used in engine-powered equipment. Although it has been shown that ammonia can be used in dual fuel modes in diesel engines, its inherently low flame speed results in poor combustion efficiency and thus reduces allowable diesel fuel replacement ratios. In this work, a novel method using a thermochemical recuperation (TCR) reactor system to partially decompose ammonia into hydrogen and nitrogen over a catalyst was demonstrated in diesel engine powered tractor. In the experiments, a John Deere 6400 agricultural tractor powered by a non-EPA tier-certified 4045TL diesel engine was operated in dual-fuel mode using anhydrous ammonia as the secondary fuel. Liquid ammonia from a tank was vaporized and heated using a series of heat exchangers and partially decomposed to hydrogen gas before being fumigated into the intake manifold. The catalytic TCR reactor utilized both exhaust waste heat and unburned hydrocarbon heating value to drive the ammonia decomposition process. Engine emissions and performance data were collected across a standard 8-mode test. The engine was operated using diesel only and in dual fuel mode with up to 42% replacement of diesel with ammonia on a lower heating value basis. Engine loading was accomplished using a power takeoff (PTO) dynamometer. Measured brake thermal efficiency was improved by up to 5.0% using thermochemical recuperation, and brake specific CO₂ emissions were reduced by up to 44% over diesel-only rates.

Keywords: Ammonia, Dual-Fuel, Thermochemical Recuperation

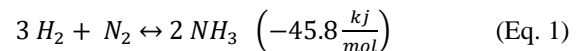
NOMENCLATURE

AFR	Air-Fuel Ratio
BTE	Brake Thermal Efficiency
CDC	Conventional Diesel Combustion
CE	Combustion Efficiency

CPSI	Cells Per Square Inch
FEF	Fumigant Energy Fraction
FTIR	Fourier Transform Infrared Spectrometer
IMEP	Indicated Mean Effective Pressure
LGA	Laser Gas Analyzer
PTO	Power Take-off
NO_x	Oxides of Nitrogen
SCR	Selective Catalytic Reduction
TCR	Thermochemical Recuperation

1. INTRODUCTION

Anhydrous ammonia is produced industrially for use as agricultural fertilizer and as a chemical synthesis feedstock. Consisting of hydrogen and nitrogen, ammonia is produced using the Haber-Bosch reaction (Eq. 1) at temperatures of 400 °C and pressures of 200 bar.



Hydrogen for the process is commonly provided by steam reforming natural gas which emits carbon dioxide as a byproduct. Alternatively, hydrogen can be produced renewably using water electrolysis and electric power from solar or wind sources. Small pilot-scale operations have demonstrated the feasibility of renewable ammonia production in this manner [1]. In addition to providing a useful fertilizer from wind power, small pilot plants offer an alternative use for excess electrical power by storing it chemically in the ammonia produced. Excess ammonia production could be reused for its energy content later, by either converting back to hydrogen for fuel cell use, or through direct combustion in vehicles and electric generators.

As a fuel, ammonia is energy dense and flammable, but exhibits poor flame speed and is highly resistant to ignition due to high molecular stability. Its adiabatic flame temperature is 1800 °C, [2] which is lower than most common fuels and retards flame propagation during combustion. Despite this, ammonia has still been previously investigated as a fuel due to its mature

industrial production network and the lack of carbon emissions when burned.

Spark-ignition strategies for ammonia combustion in engines have been extensively studied. For example, some previous work has shown success with ammonia-hydrogen combustion where hydrogen is used to enhance the ammonia flame propagation [3–6]. While the studied engines did not produce noticeable ammonia emissions, oxides of nitrogen (NO_x) production was increased when using the ammonia fuel. Grannell et al. showed that for spark ignition engines, up to 70% of gasoline could be replaced with ammonia if the engine load was kept high [7]. Combustion was found to be unstable with any ammonia fueling at indicated mean effective pressures (IMEP) below 4 bar and at replacement rates beyond 70% for higher IMEP. Haputhanthri studied the capacity for gasoline and alcohol fuels as ammonia emulsions [8]. Dual-fuel combustion was achieved at replacement rates of 61.8 grams of ammonia dissolved within one liter of gasoline or ethanol, solving the issue of carrying separate ammonia fuel. Most similar to the work done here is the work presented by Reiter and Kong [9,10]. An off-highway diesel engine was fumigated with anhydrous ammonia achieving diesel replacement rates over 80 percent. However, exhaust ammonia emissions were greater than 1000 ppm even at low replacement rates, which was due to ammonia's poor flame speed and low reactivity.

One alternative to direct ammonia combustion is to dissociate the fuel into hydrogen and nitrogen catalytically using the reverse Haber-Bosch reaction (Eq. 1). Hydrogen has inherently high adiabatic flame temperature, two orders of magnitude higher than that of ammonia. When burned together with ammonia, hydrogen increases laminar flame speed by a factor of 10 at as low as 30% hydrogen fuel fraction. [11,12] Previous studies [3,13–19] have shown that with the use of a proper catalyst, ammonia can be easily cracked to hydrogen and nitrogen using exhaust-relevant temperatures of 300-600 °C. If exhaust waste heat is used to feed dissociation, it follows that partial conversion of ammonia to hydrogen before combustion will improve both engine thermal and combustion efficiency. To perform this conversion onboard an engine, a compact ammonia reformer is needed.

Compact reforming for engines has been studied and experimentally demonstrated by several groups [20–26]. One challenge for practical implementation of compact reforming systems is effectively integrating heat and energy streams to yield improvements in overall system thermal efficiency. Ammonia requires significantly lower activation temperatures relative to hydrocarbon reforming. Due to this, engine waste heat can be used to produce hydrogen from ammonia and increase ammonia combustion efficiency. Diesel engine brake thermal efficiency is generally between 30 to 40% [27], meaning 60 to 70% of fuel energy is wasted through exhaust and heat transfer processes. More common waste energy recovery systems include turbocharging and thermoelectric generators [28], though the latter suffers from poor thermal efficiency. Using exhaust energy to increase the chemical energy of the fuel is a process known as thermochemical recuperation (TCR). TCR for

engines generally involves an endothermic fuel reformation process such as steam reforming or decomposition. The reformed fuel contains greater heating value than the original and can deliver this captured energy back into the thermodynamic cycle. This both lowers rejected heat and net input fuel energy, raising overall thermal efficiency.

The objective of this study was to examine the sensible and chemical energy recovery of a diesel engine equipped to run dual-fuel using anhydrous ammonia in a practical engine system on a vehicle. Ammonia fumigant was partially dissociated catalytically using reclaimed engine waste heat to produce hydrogen. This work examines the energy flows through the system and demonstrates the feasibility of such systems for practical implementation in off-highway diesel-powered equipment.

2. EXPERIMENTAL METHODS

A catalytic reactor was designed to partially dissociate fumigated ammonia into hydrogen as depicted in Figure 1. A schematic of the overall system is given in Figure 2. The reactor was installed in place of the stock exhaust muffler directly downstream from the turbocharger as shown in the system installation photo in Figure 2. Sensible heat from the exhaust as well as chemical energy from unburned fuel in the exhaust provided energy at temperatures appropriate for converting ammonia into hydrogen and nitrogen according to Eq. 1. Additional sensible energy was provided to the ammonia fumigant from engine waste heat streams using a liquid ammonia evaporator and an ammonia-exhaust heat exchanger. The heat exchangers were used to vaporize liquid ammonia and preheat it to exhaust temperatures before introduction to the reactor.

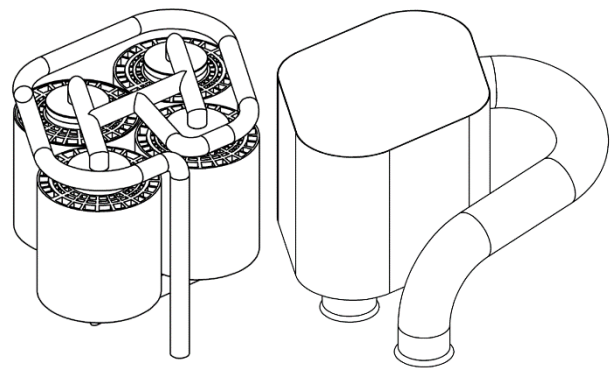


FIGURE 1: INTERIOR ARRANGEMENT OF FOUR CYLINDRICAL CATALYST SECTIONS IN THE TCR REACTOR. EXHAUST ENTERS THROUGH THE FACE FLANGE AND EXITS THROUGH THE CURVED PIPE ON THE RIGHT.

The reactor used in this study consisted of four catalytic assemblies containing an outer oxidation catalyst bound to an inner ammonia decomposition catalyst and separated by a common wall. The monoliths were constructed from FeCrAl metal foil with 300 cells per square inch (CPSI) for oxidation and 600 CPSI for decomposition. The monoliths were wash-coated

with an ammonia decomposition catalyst 4.72% Ru/Al₂O₃ while the outer monoliths were wash-coated with a proprietary rhodium-containing catalyst R44. Both wash-coated catalysts were provided by Johnson Matthey. The sections were welded together such that both exhaust and ammonia flow through parallel sections and in counter-flow to each other to achieve higher rates of heat exchange. A small loop of tubing for ammonia was installed within the exit flow of the exhaust stream to promote further pre-heating before entering the decomposition catalysts. The assembly was insulated externally using rock-wool batts to retain heat and prevent damage to the tractor or engine.

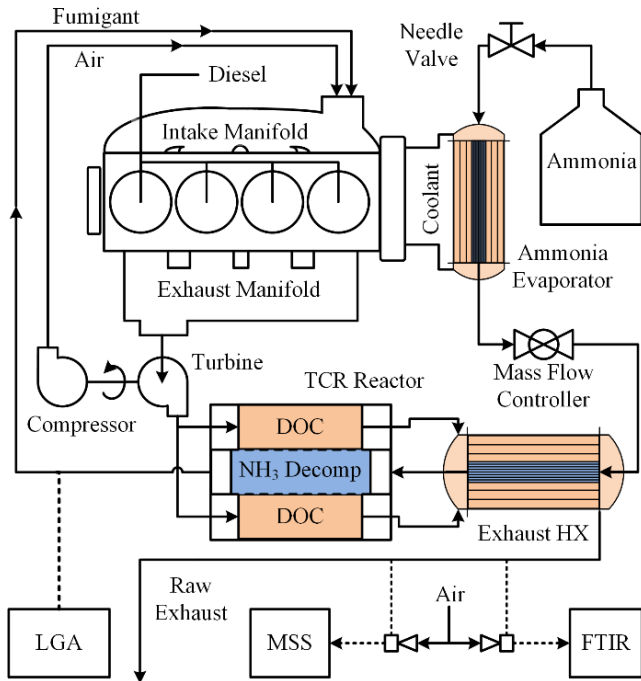


FIGURE 2: SCHEMATIC FOR THE AMMONIA TCR SYSTEM USED IN THIS STUDY. HEAT RECOVERY DEVICES SHOWN IN SEQUENTIAL THERMAL RECOVERY PATH FOR AMMONIA FUEL. DASHED LINES DEPICT SAMPLE PATHS FOR GAS AND PARTICULATE ANALYSIS.

A second custom exhaust heat exchanger assembly was inserted downstream from the reactor to preheat the ammonia as seen in the photo in figure 3. The assembly consisted of two shell and flat-tube EGR coolers assembled in parallel with exhaust in the tubes and ammonia in the shell. The heat exchanger was constructed entirely of 304 stainless steel and is shown in detail in figure 4. The parallel arrangement and open area of the tubes results in negligible flow restriction on the exhaust stream. Exhaust gases again flow in counter-flow to maximize ammonia outlet temperature and thermal recovery.

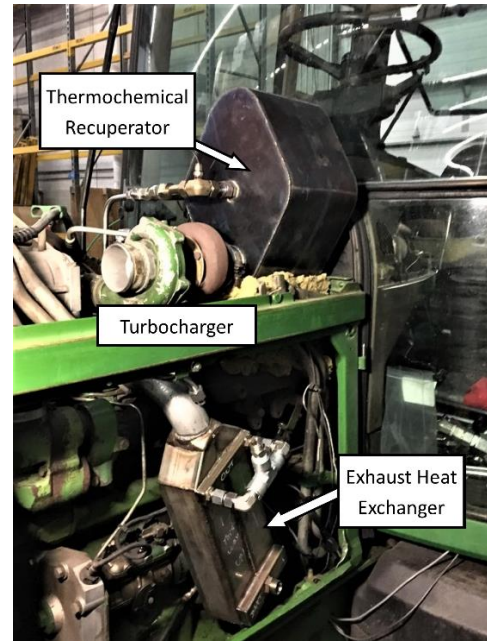


FIGURE 3: TCR REACTOR AND EXHAUST HEAT EXCHANGER SHOWN INSTALLED ON JOHN DEERE 6400 TRACTOR. TURBOCHARGER, REACTOR AND EXHAUST HEAT EXCHANGER ARE LABELED.

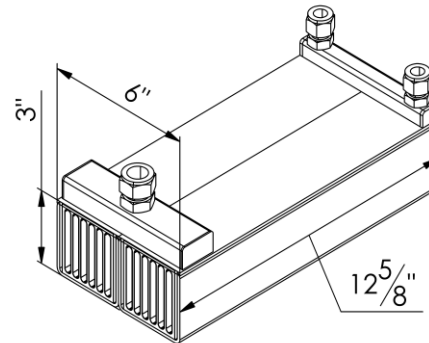


FIGURE 4: DIMENSIONED DRAWING OF THE SECONDARY HEAT EXCHANGE ASSEMBLY. INTERNAL SHELL BAFFLES PREVENT AMMONIA FROM SHORT-CIRCUIT FLOW AND IMPROVE HEAT TRANSFER.

To produce the ammonia vapor needed for this study, liquid withdrawal was necessary. In earlier work, high gas withdrawal rates caused rapid cooling of laboratory cylinders due to ammonia's latent heat of vaporization. This decreased cylinder vapor pressure below that needed for high volume withdrawal. A custom ammonia evaporator was designed such that ammonia's latent heat could be derived from engine coolant. A needle valve was used to throttle the ammonia into the heat exchanger. The resulting drop in pressure caused the ammonia to rapidly cool on the heated fins, producing warmed vapor from engine waste heat. Vapor pressure within the cylinder continues to push ammonia into the system until equalized with the evaporator pressure, or the cylinder is emptied. Coolant flows in a co-flow arrangement with ammonia and is pulled from the engine oil cooler outlet to provide increased temperatures over the engine water jacket.

A 1994 model year John Deere 6400 tractor with JD4045TL engine was used for this study. Engine specifications are listed in Table 1. No emissions aftertreatment was implemented in the tractor's stock configuration. To load the engine, a dynamometer was attached to the tractor's power take-off (PTO) shaft. The PTO shaft rotates in a direct ratio of 1:2.15 with the engine and load torque is controlled at the dynamometer. The PTO dynamometer is a model NEB-600 friction brake device manufactured by AW dynamometers. Engine speed was manually controlled by cab operator using a locking engine throttle hand lever. Load was controlled by hydraulic resistance at the dynamometer and set manually by a separate operator.

Table 1: Engine Specifications

Manufacturer/Model	John Deere 4045TL
Engine Type	4-Stroke DI Diesel
Cylinders	4, in-line
Displacement (L)	4.5
Bore x Stroke (mm)	106 x 127
Compression Ratio	17.0:1
Maximum Power (kW at RPM)	75 at 2200
Aspiration	Turbocharged
Injection System	Inline Distributed Governor
Emissions Certification	Not Certified

The ISO 8178 C1 off-road 8-mode test was used to examine the energy recovery and TCR reactor across all operating conditions. For this engine, the modes and their corresponding loads and speeds are reported in Table 2. Due to low exhaust temperature, mode 8 was not tested using fumigation. This standard provides a weighting factor to assess general emissions from an off-road vehicle, and by extension will provide insight into benefits provided by the dual-fuel strategy and thermal recovery. In addition to the eight modes, each mode was tested with four fumigation rates. The rates of fumigation were decided on a diesel-replacement basis. The fraction of chemical energy provided to the engine when evaluated on a lower heating value basis is known as the fumigant energy fraction (FEF). The values of FEF targeted in this study were 10%, 20%, 30%, and conventional diesel combustion with no fumigation as a baseline (i.e.; 0% FEF). Ammonia fueling was controlled using a Sierra Instruments C100M mass flow controller. Ammonia FEF targets were determined by percentage of conventional diesel fuel consumption, and measured FEF minimally varied from targeted values. Diesel fuel consumption was measured using two Brooks Instruments Oval gear meters attached to the inlet and return from the fuel pump. The net consumption was found by the difference of the two meters over time. The engine controlled fueling using a mechanical governor which maintains constant engine speed for a given throttle position. The governor automatically decreased diesel fueling after introducing fumigant into the intake stream.

Table 2: 8-Mode Test Parameters

Mode	Speed [RPM]	Load [N-m]
1	2200	275
2		210
3		140
4		65
5	1500	310
6		230
7		155
8	1000	0

Temperature was measured using type-K thermocouples installed only at the outlet of each recovery device. Energy recovery rates were calculated using CoolProp, [29] an open-source thermodynamic properties software. Thermochemical recovery was calculated using gas species concentrations measured directly from the thermochemical reactor outlet. Heat exchanger efficiencies were calculated using the ratio of realized heat exchanged over the maximum possible heat exchanged. A Raman-laser gas analyzer by Air Recovery, Inc was used to directly measure the hydrogen and nitrogen components of the fumigant. The remaining fraction was assumed to be ammonia, as no other stable species may be produced from the pure ammonia reactant. Reactor conversion efficiency and reforming efficiency are given in equations 2 and 3, respectively and broadly describe the thermochemical recovery process. Conversion efficiency is the ratio of reacted ammonia to the maximum possible reacted amount. Reforming efficiency describes the ratio of lower heating values of the all fuels in the outlet stream over the fuels in the inlet stream. For ammonia, when the outlet stream is completely converted to hydrogen and nitrogen, the maximum theoretical reforming efficiency is 114.5%. Chemical energy recovery is calculated using the product of reforming efficiency, ammonia mass flow, and lower heating value.

$$\eta_c = \frac{\dot{m}_{NH_3,in} - \dot{m}_{NH_3,out}}{\dot{m}_{NH_3,in}} \quad (\text{Eq. 2})$$

$$\eta_r = \frac{\sum(\dot{m}_{out} * LHV_{out})}{\sum(\dot{m}_{in} * LHV_{in})} \quad (\text{Eq. 3})$$

Gaseous and particulate emissions were measured using an AVL Fourier Transform Infrared Spectrometer (FTIR) and AVL MicroSoot sensor, respectively. Both devices sampled from exhaust downstream from all attached recovery devices. Gaseous emissions are thus reported after residence on the oxidation catalyst. Gaseous emissions were diluted 20:1 to prevent over-ranging of ammonia in the FTIR. Soot emissions samples were diluted 5:1 using the dilution system supplied with the MSS instrument. Engine intake air mass flow and total exhaust mass flow rates were calculated using exhaust O₂ concentrations and fuel flow measurements.

3. RESULTS AND DISCUSSION

3.1 Sensible and Latent Heat Recovery

Heat was recovered using the three separate heat exchange devices employed in this system as depicted in figure 2. Of the three, the ammonia vaporizer showed the greatest rates of recovery across all ammonia flows. Figure 5 shows the total sensible and latent recovery by the evaporator versus ammonia flow, and the corresponding heat exchange efficiency. Ammonia vaporization required significant energy over the flow range due to its latent heat. Vaporization took place at the temperature of the liquid tank or lower, due to the downstream pressure in the evaporator being at or below the tank vapor pressure. This generated a consistent temperature differential which enhanced heat transfer rates inside the evaporator. For this reason and due to high boiling heat exchange coefficients, the heat exchange efficiency was consistently above 97% for all tested modes, and ammonia outlet temperatures within 10 °C of the coolant outlet temperatures.

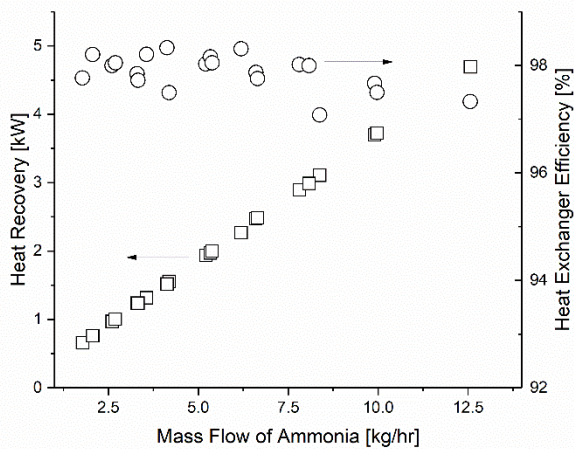


FIGURE 5: HEAT RECOVERY RATE AND HEAT EXCHANGER EFFICIENCY FOR THE AMMONIA VAPORIZER.

The ammonia-exhaust heat exchanger had heat transfer rates and efficiencies that were lower than the evaporator. Recovered energy increased with increasing ammonia flow, as internal convection coefficients of the ammonia increased. Heat exchanger efficiency decreased with increased flow, causing outlet ammonia temperatures to decrease. Figure 6 shows the recovery rate and efficiency of the ammonia-exhaust heat exchanger. The purpose of the device was not to create maximum heat recovery, but to serve as a secondary ammonia pre-heating system to assist catalytic decomposition over the catalyst. The achieved heat exchange efficiencies of 40-60% were acceptable for this reason, as any heat recovered in the device was not needed from within the TCR reactor.

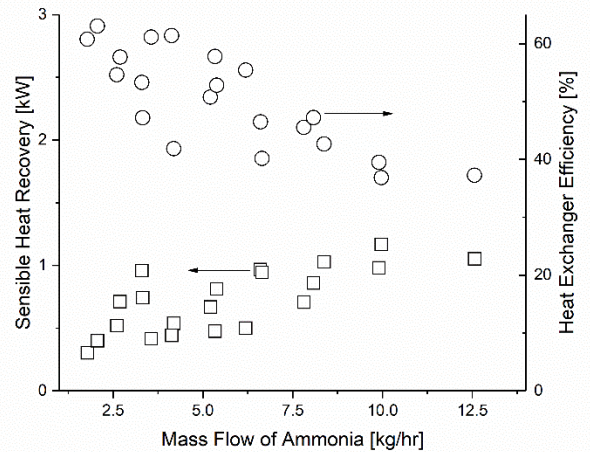


FIGURE 6: HEAT RECOVERY RATE AND HEAT EXCHANGER EFFICIENCY FOR THE AMMONIA-EXHAUST HEAT EXCHANGER

The sensible recovery within the TCR reactor is plotted in figure 7 along with heat exchange efficiency. The heat exchange efficiency appears to plateau near 60% efficiency with increasing ammonia flow. Increased ammonia flow is accompanied by increased engine fueling rates, power output, and exhaust temperatures. Increasing ammonia and exhaust flow enhanced convective heat transfer, but the short residence time at high flows counteracted this. The data indicate that for this reactor, decreased residence time may overwhelm higher heat transfer rate at ammonia flows greater than 12.5 kilograms per hour. Heat recovery trends non-linearly upward, as heat transfer rates are enhanced by the increased temperature difference at higher fueling rates.

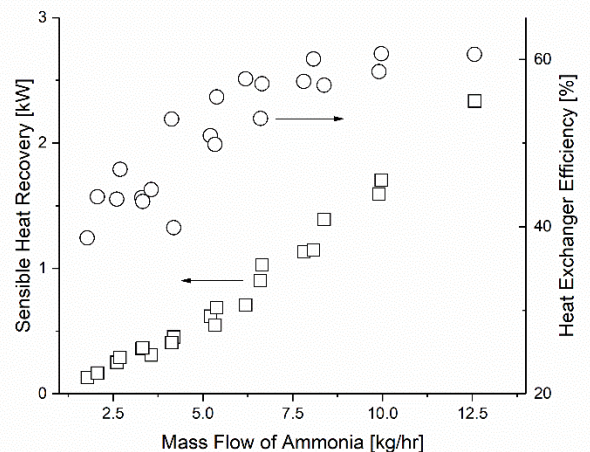


FIGURE 7: HEAT RECOVERY RATE AND HEAT EXCHANGER EFFICIENCY FOR THE TCR REACTOR.

3.2 Thermochemical Recuperation

Figure 8 shows both the exhaust-side reactor inlet temperatures and energy recuperation as a function of mode and FEF. Exhaust inlet temperatures were found to scale with engine load, with similar outlet temperatures for mode pairs 1 and 5, 3 and 6, and 4 and 7. As load increased, combustion became less lean and combustion temperatures increased. Higher combustion temperatures led to the increased exhaust temperatures seen the experimental measurements. Increased fumigation also increased exhaust temperature across every mode due to the reclaimed sensible energy from the fumigant. Fumigation resulting in lowered air-fuel ratio (AFR) or decreased thermal efficiency of the combustion cycle would also result in higher exhaust temperatures. Higher initial intake charge temperatures produced higher peak in-cylinder temperatures which increased the exhaust temperature.

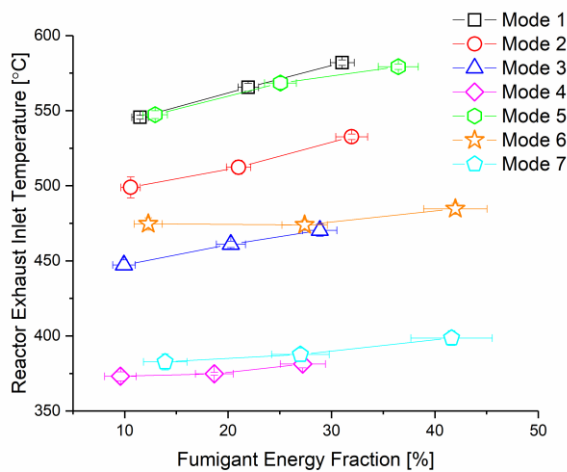


FIGURE 8: EXHAUST TEMPERATURES MEASURED AT THE INLET TO THE TCR REACTOR AS A FUNCTION OF FEF FOR ALL MODES.

Thermochemical heat recovery rate was calculated as the net increase in lower heating value of the fumigant fuel as it passed through the reactor. Figure 9 shows the chemical heat recovery rate by the TCR reactor as a function of mode and FEF. With the exception of mode 1, trends show linear behavior with increasing FEF. Flat or decreasing recovery with increasing FEF is seen in modes 2-4, 6, and 7. This indicates thermally limited kinetics for which additional fumigation does not yield additional hydrogen production. Higher ammonia flow rates increase heat exchange coefficients within the reactor, but also decrease residence times and increase the rate at which sensible energy is removed from the reactor. Depending on the inlet ammonia temperature, the decomposition catalyst may decrease in temperature. This decreases catalyst activity and hydrogen yield. For mode 5, high exhaust temperatures and lower ammonia flows allowed for increasing recovery as fumigation increased. Conversion efficiency was high at low FEF and high temperature. The

reaction caused a rapid decrease in ammonia mole fraction, causing conversion rates to decrease by the catalyst exit. Increased fumigation decreased conversion efficiency but produced more hydrogen by mass from the fumigant stream.

Total recovered energy scaled with the rate of production of hydrogen, and thus higher flows increased recovered energy. Low recovery was calculated for modes 4 and 7, which also showed the lowest measured exhaust temperatures. These temperatures are near the minimum required for catalytic ammonia decomposition activity, suggesting that any further decrease would cause the reaction to cease. The catalyst temperature was also dependent on the monolith geometry and heat transfer effects. While this TCR reactor is limited at temperatures below 350 °C, activity at lower temperatures is possible with improvements to the reactor's thermal design.

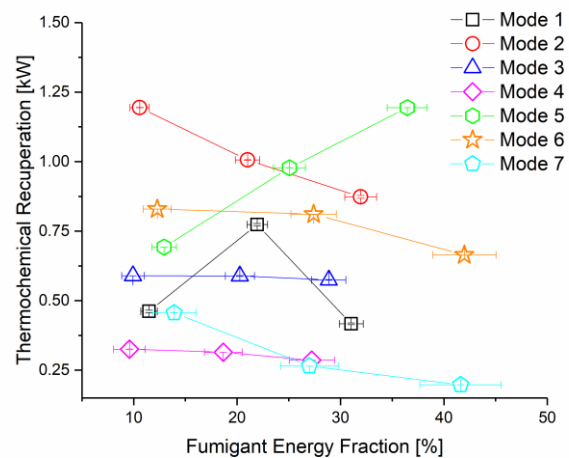


FIGURE 9: THERMOCHEMICAL RECUPERATION RATE AS A FUNCTION OF FEF FOR ALL MODES.

The chemical energy recovered by the TCR reactor decreased the total heating value input needed to produce a given engine power output. This corresponded to an increase in engine brake thermal efficiency, which is plotted as a function of mode and FEF in figure 10. Modes 1, 2, 5-7 showed increased BTE with increased ammonia fumigation indicating net thermochemical recuperation was achieved. Decreases in brake thermal efficiency noted in modes 3 and 4 were caused by poor conversion efficiency through the decomposition catalyst accompanied by decreased combustion efficiency. Unburned ammonia emissions represent lost heating value which exceeds the additional energy provided by TCR. Mode 1 and 5 show a maximum benefit to BTE at 10% replacement. This was due to low flow causing high conversion efficiency in the reactor and leading to high chemical energy recovery with lower flow rates of ammonia. Unburned ammonia emissions also decreased with high conversion as some ammonia was converted to hydrogen before the combustion event. Intake hydrogen molar concentration was calculated based on the conversion efficiency and reformat mass flow rate. The hydrogen concentrations are

reported in figure 11 and showed the same trends as the thermochemical recuperation rate.

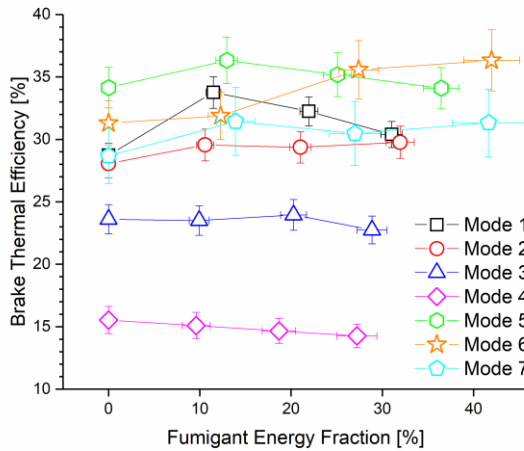


FIGURE 10: BRAKE THERMAL EFFICIENCY VS. FEF FOR ALL MODES.

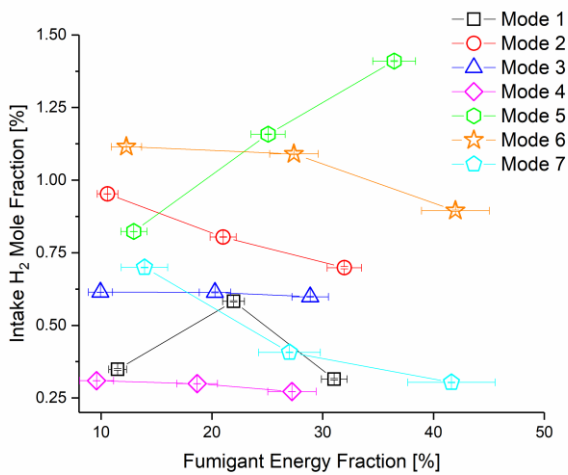


FIGURE 11: INTAKE CHARGE H₂ MOLAR CONCENTRATION AS A FUNCTION OF FEF FOR ALL MODES.

A first law analysis was performed for the TCR system. The results are depicted in the two Sankey diagrams shown in figures 12 and 13. The figures show the 0% and 30% FEF cases, respectively for mode 5. Using the ammonia TCR system, 30% FEF resulted in a net measured BTE increase from 33.4% to 34.1%. Total recovered energy rate was calculated to be 7.8 kW which resulted in a fuel energy decrease of 3.1 kW. Thermal energy recovered by the TCR system was recycled into the engine thermodynamic cycle but did not reduce fuel energy input as chemically recovered energy did. However, the increased thermal energy served to increase in-cylinder combustion temperatures by heating the intake charge. This resulted in faster combustion kinetics for diesel and ammonia and increased combustion efficiency. Higher combustion temperatures also produced higher NO_x levels through the thermal mechanism.

While thermal and combustion efficiencies both showed a measured increase, they were only realized with a marked increase in harmful emissions. In modern engines, the energy expended on aftertreatment for this additional NO_x may negate the benefit of the efficiency gains.

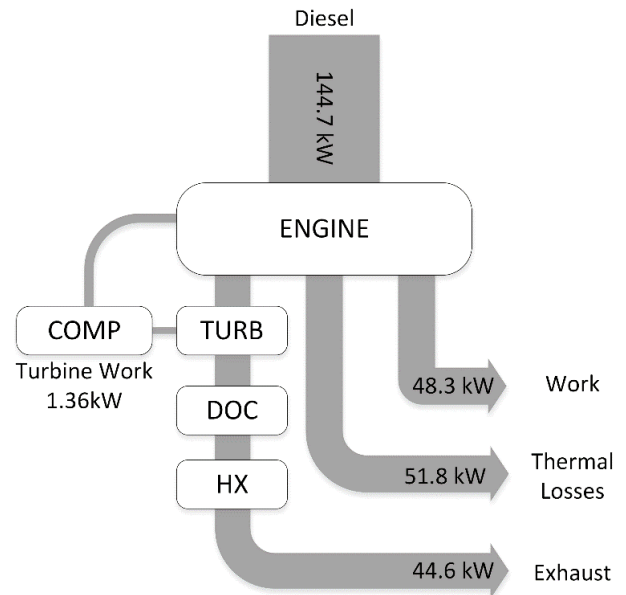


FIGURE 12: SANKEY DIAGRAM FOR MODE 5 CDC.

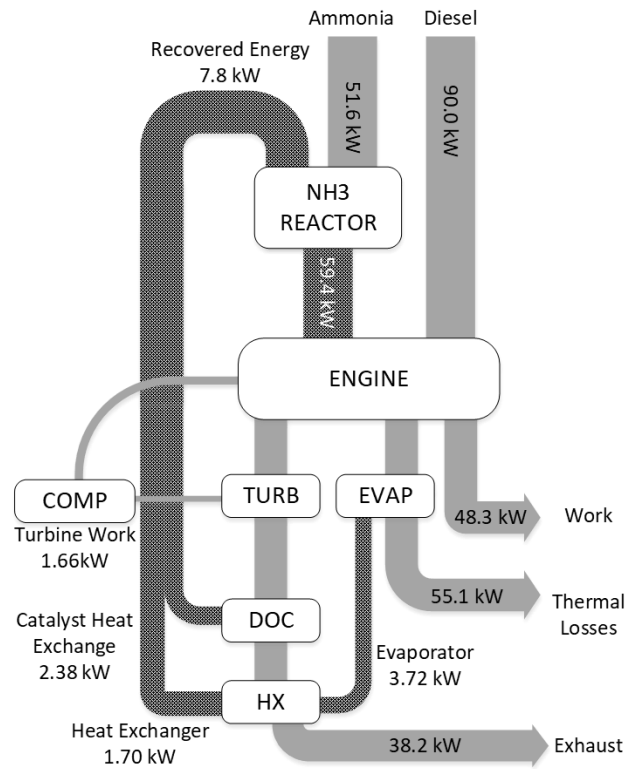


FIGURE 13: SANKEY DIAGRAM FOR MODE 5 WITH 30% AMMONIA REPLACEMENT.

3.3 Emissions Analysis

Ammonia contains no carbon; therefore, engine CO₂ emissions decreased linearly with increasing FEF as depicted in figure 14. CO₂ emissions also decreased on a brake-specific basis due to increasing engine efficiency for modes 1, 2, 6, and 7. Despite this, modes where efficiency decreased due to fumigation still show CO₂ emissions benefit when ammonia replaces diesel fuel.

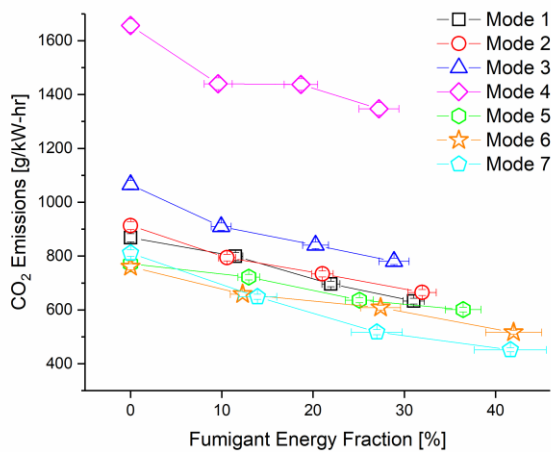


FIGURE 14: BRAKE SPECIFIC CO₂ EMISSIONS VS. FEF FOR ALL MODES.

Figure 15 shows the trends for brake specific soot emissions as a function of mode and FEF. The EPA Tier-4 final limit is shown as a horizontal black bar and is adjusted by a factor of 0.5 to account for the soluble organic fraction of particulate matter [30,31]. Soot emissions increased strongly ammonia fumigation for some modes, with only mode 6 and 7 showing a decrease by 30% FEF. Mode 1, 2, and 5 show decreases from baseline before increasing by 30% FEF. Increasing soot trends can be explained by the ammonia's effect on the intake charge.

When ammonia was fumigated into the intake stream, the intake manifold pressure increased slightly. The increased pressure upstream of the compressor would cause decreased air mass flow rate. This, in turn, decreased the mole fraction of oxygen in the charge and also decreased the AFR slightly. When diesel was injected into the intake charge near top dead center, the fuel burned diffusively. The local equivalence ratio of the diffusion flame was increased with increased ammonia fuel present in the intake charge. However, since ammonia combustion cannot directly produce soot, emissions were reduced with increasing FEF due to the displacement of diesel fuel with ammonia.

Decreasing soot emissions at intermediate FEF levels were caused by displacement of carbon in the diesel fuel, but also the increase in BTE with these levels of fumigation. The hydrogen

fraction of the fumigant fuel would enhance flame propagation in the case of intermediate FEF levels and could serve to promote both turbulent mixing increase diesel combustion kinetics. The former of which would lower local equivalence ratio in the diesel flame, whereas the latter could serve to either promote or retard soot production depending on the timing of the hydrogen-ammonia combustion relative to the diesel combustion.

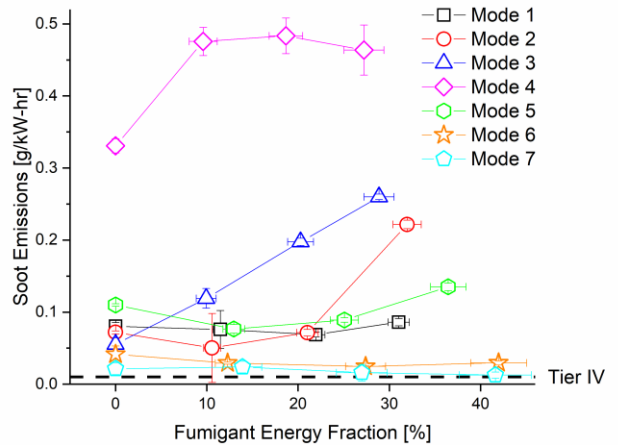


FIGURE 15: BRAKE SPECIFIC SOOT EMISSIONS AS A FUNCTION OF FEF FOR ALL MODES. TIER FOUR LIMIT SHOWN AS DASHED LINE

Ammonia combustion is known to increase engine NO_x emissions due to fuel-bound nitrogen atoms. This production phenomenon is called fuel-NO_x and was shown to occur in all measurements in this study. Shown in figure 16, all seven modes show increasing NO_x emissions with FEF and all tested points exceed the even the initial EPA tier-1 emissions standards. This was expected as the experimental engine predates the tier-1 standard. However, excluding modes 3 and 4, most modes remained near their diesel-only baseline values. This is due to the high ammonia dissociation through the reformer at high engine load that reduced the concentration of ammonia in the intake charge. NO_x emissions increased with fumigation for modes 3 and 4 due to the poor conversion of ammonia within the TCR reactor. Fumigated fuel consisted of unconverted ammonia, which burns inefficiently without hydrogen to promote flame propagation. Lean conditions prevented fuel-NO_x from oxidizing other fuel, and it is exhausted from the cylinder unreduced. Rhodium-based catalysts have been long-known to selectively oxidize ammonia to NO_x under lean conditions such as diesel exhaust. [32] Due to similar catalyst formulation, the diesel oxidation catalyst within the TCR reactor was also expected to convert some unburned ammonia to additional NO_x. This conversion further increased the measured emissions.

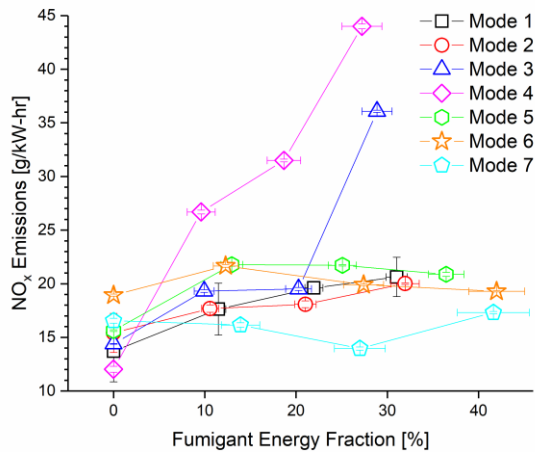


FIGURE 16: BRAKE SPECIFIC NO_x EMISSIONS FEF FOR ALL MODES.

Ammonia slip through the system was measured and is reported in figure 17. Increased fumigation resulted in increased levels of ammonia exhaust emissions, with the lowest brake specific emissions resulting from the modes with highest TCR activity. Ammonia's poor flame propagation was enhanced by the presence of hydrogen, higher temperatures, and richer combustion. It serves to reason in this case that higher ammonia emissions were likely a stronger function of lower hydrogen concentration in the intake manifold, as increasing fumigation would increase intake charge temperature and increase premixed charge equivalence ratio. The TCR reactor used a diesel oxidation catalyst which oxidized unburned ammonia. Higher temperatures enhanced the rate of ammonia oxidation. Exhaust temperatures were shown to increase with engine load, as was engine brake thermal efficiency. For this reason, brake specific ammonia emissions are highest for modes with low efficiency and low exhaust temperature. Modes 3 and 4 are high speed and low load conditions which are unlikely long-term operating points for an agricultural tractor. For a dynamic fueling system installed on such a vehicle, high specific ammonia emissions could be eliminated by fueling these modes with diesel only.

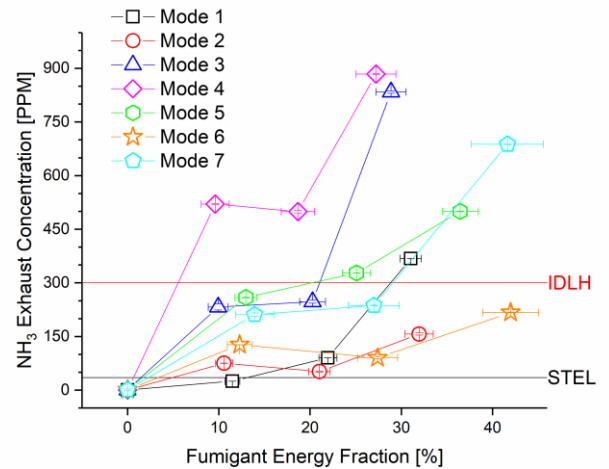


FIGURE 17: PPM NH₃ EMISSIONS FEF FOR ALL MODES. NIOSH IMMEDIATE DANGER TO LIFE AND HEALTH LEVEL AND SHORT TERM (15 MINUTE) EXPOSURE LEVELS ARE SHOWN AS HORIZONTAL BARS. [33]

4. CONCLUSION

In this work, an ammonia-diesel dual fuel TCR reactor system was demonstrated on a tractor. The tractor was operated over a standard 8-mode test and fueled with ammonia at FEF of 10-30%. The system demonstrated both thermal and chemical recuperation using an ammonia decomposition reactor and produced hydrogen fuel from the ammonia. Brake thermal efficiency was improved for most modes due to reclaimed energy in hydrogen production and more efficient ammonia combustion due to the effect of hydrogen flame-speed enhancement.

First-law analysis showed that both chemical and thermal energy was reclaimed effectively by the TCR system. Benefits to engine efficiency were realized though recovery of waste thermal and chemical energy. Thermal energy was shown to be recycled into the engine intake charge through fumigant, though the direct effect on combustion remains unclear. Conversion efficiency of the ammonia TCR reactor was below 50% for all 30% FEF cases, indicating the need for more efficient heat transfer or larger reactor volume to accommodate further recuperation.

Emissions from the engine under CDC and ammonia fumigation were measured. CO₂ emissions were shown to decrease due to the replacement of hydrocarbon fuel with carbon-free ammonia. Soot emissions showed an increasing trend with fumigation, as did both NO_x and ammonia emissions. Low temperature exhaust at low-load conditions decreased the conversion efficiency of ammonia and increased the brake specific emissions of ammonia and NO_x. High brake-specific ammonia and NO_x emissions at these conditions can be eliminated if fumigation is used selectively. Fumigating only at medium and high loads would both increase TCR rates per unit ammonia consumed, and lower average emissions by avoiding

high-emission conditions entirely. In the case that NO_x formation and ammonia slip were still excessive, use of selective catalytic reduction either within the TCR reactor or downstream on the exhaust side would eliminate both the ammonia and NO_x simultaneously. By using only unburned ammonia in the exhaust stream, this passive process would decrease both emissions without increasing ammonia consumption.

These findings indicated feasibility for both ammonia-diesel dual-fuel engines and TCR systems for commercial vehicles. Energy recuperation increased brake thermal efficiency for most modes, but low total ammonia conversion suggests much greater capacity for recuperation. Increased recuperation would be realized by more efficient heat exchange, which allows the TCR reaction to proceed at higher temperatures and faster rates. Higher catalyst loading or more active catalyst formulations would also produce greater conversion rates. Future work will explore these designs to improve both efficiency and emissions of ammonia TCR systems.

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