# Soot Characterization in Ammonia-Diesel Dual Fuel Engines


Mohammed Zaher, Amin Yousefi, Mehran Dadsetan, Brian Liko, Simon Lafrance, Hongsheng Guo, Murray Thomson.

جامعة الملك عبدالله للعلوم والتقنية King Abdullah University of Science and Technology — Clean Combustion Research Center

UNIVERSITY OF TORONTO FACULTY OF APPLIED SCIENCE & ENGINEERING

Canada NRC-CNRC


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## How Would Ammonia Impact Marine Emissions?

- Shipping vessels contribute to 2.2% of the global $CO_2$ emissions in 2015, this percentage is expected to increase by up to 250% due to growth in global trading [1].

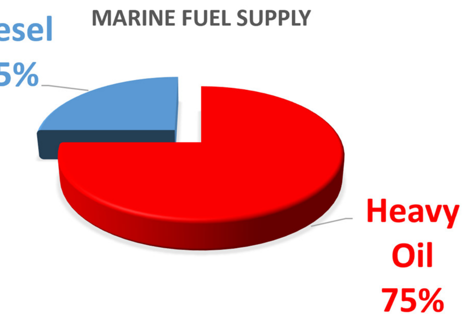



Fig.(1) – Current Marine Fuel Mix

- Ammonia $NH_3$ is a carbon-free fuel that can decarbonize marine engines by replacing heavy oil if mixed with diesel for ignition [2].

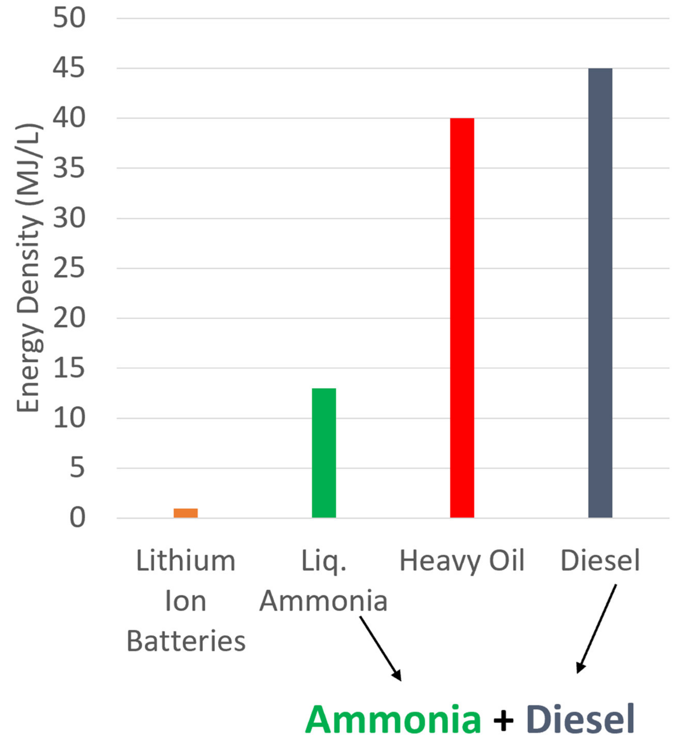



Fig.(2) – Comparison of Energy Densities of Marine Vessels Power and Fuels

- Soot formation is inhibited by adding $NH_3$ to an ethylene $C_2H_4$ flame for a fixed carbon flow [3].

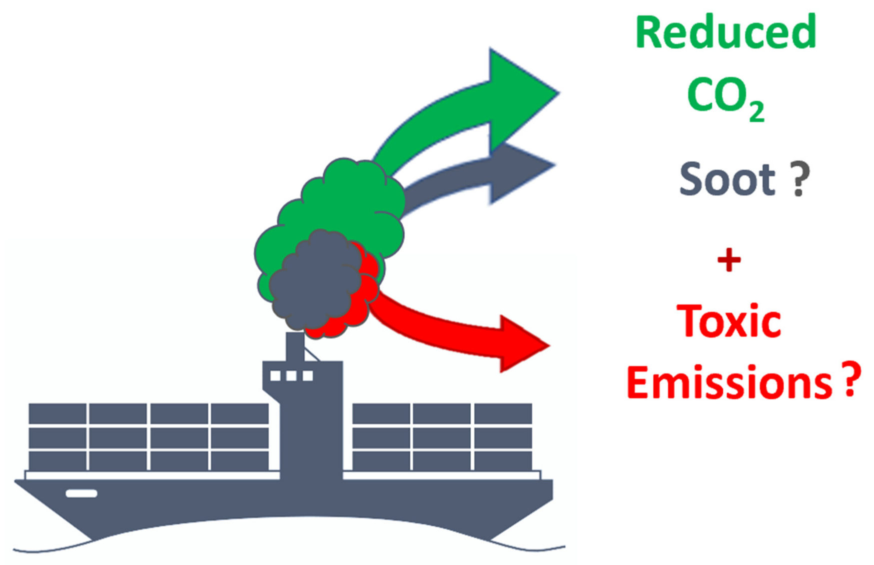



Fig.(3) – Possible Marine Emissions

## Experimental Testing of $NH_3$-Diesel Dual-fuel Engine Exhaust GHG and Soot Emissions

### Experimental Setup

To investigate the engine GHG emissions:

- **Exhaust gas compositions ($NH_3$, CO, $CO_2$, UHC, NO, $NO_2$, and $N_2O$)** were measured **using Fourier Transform Infra-red (FTIR) multi gas analyzer.**

To study the engine soot characteristics, exhaust soot was collected using an isokinetic sampling setup for ex-situ testing of:

- **Brake specific soot emissions** of the engine using **gravimetric analysis.**
- **Average primary particle diameter** using **analysis of TEM images** of soot samples.
- **Soot nanostructure** using **Raman Spectroscopy and X-ray Photoelectron Spectroscopy (XPS)**.
- Soot surface **nitrogen content** and bonding using **XPS.**

Table (1) – Engine Specifications

| | |
|---|---|
| **Engine model** | Caterpillar 3401 |
| **Number of cylinders** | 1 |
| **Bore × Stroke (mm × mm)** | 137.2 × 165.1 |
| **Conn. rod length (mm)** | 261.62 |
| **Compression ratio** | 16.25 |
| **Displacement (L)** | 2.44 |
| **Intake valve opening (IVO)** | -358.3 ºATDC |
| **Intake valve closing (IVC)** | -169.7 ºATDC |
| **Exhaust valve opening (EVO)** | 145.3 ºATDC |
| **Exhaust valve closing (EVC)** | 348.3 ºATDC |

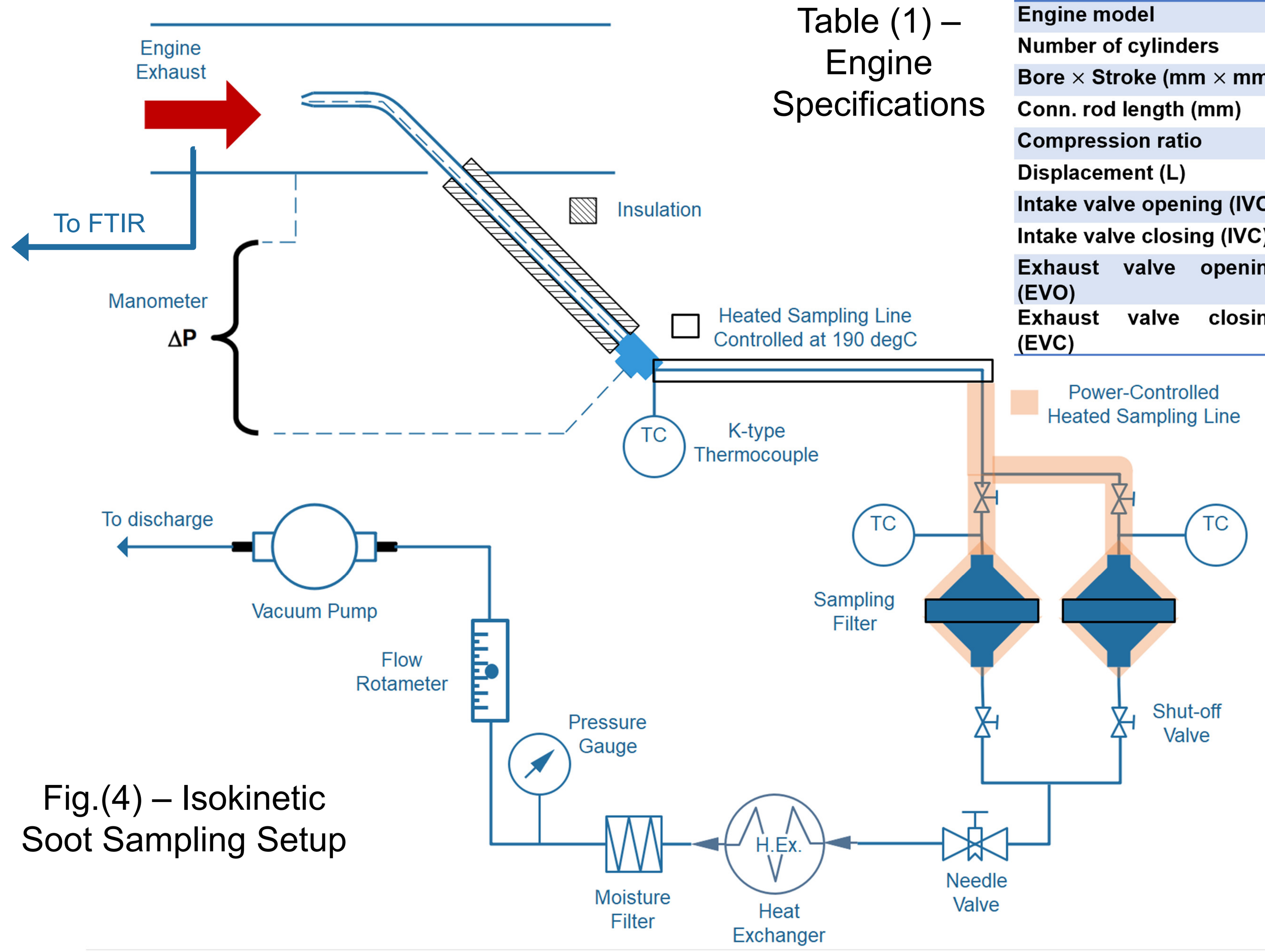



Fig.(4) – Isokinetic Soot Sampling Setup

### Engine Testing Conditions

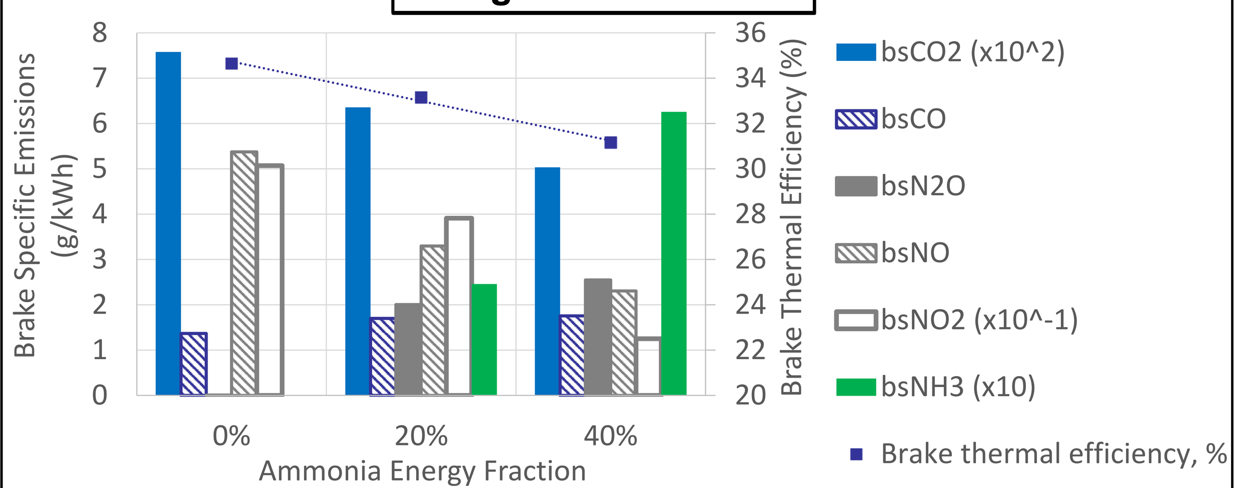
- Under constant load, engine speed, and SODI:

| Test point # | $NH_3$ energy fraction (%) | SODI (ºATDC) | EODI (ºATDC) | Diesel (kg/h) | $NH_3$ (kg/h) | Air (kg/h) |
|---|---|---|---|---|---|---|
| 1 | 0 | -13 | -1.49 | 1.81 | 0 | 68.31 |
| 2 | 20 | -13 | -2.33 | 1.52 | 0.86 | 66.71 |
| 3 | 40 | -13 | -3.73 | 1.21 | 1.88 | 65.18 |

Table (2) – Engine Test Parameters

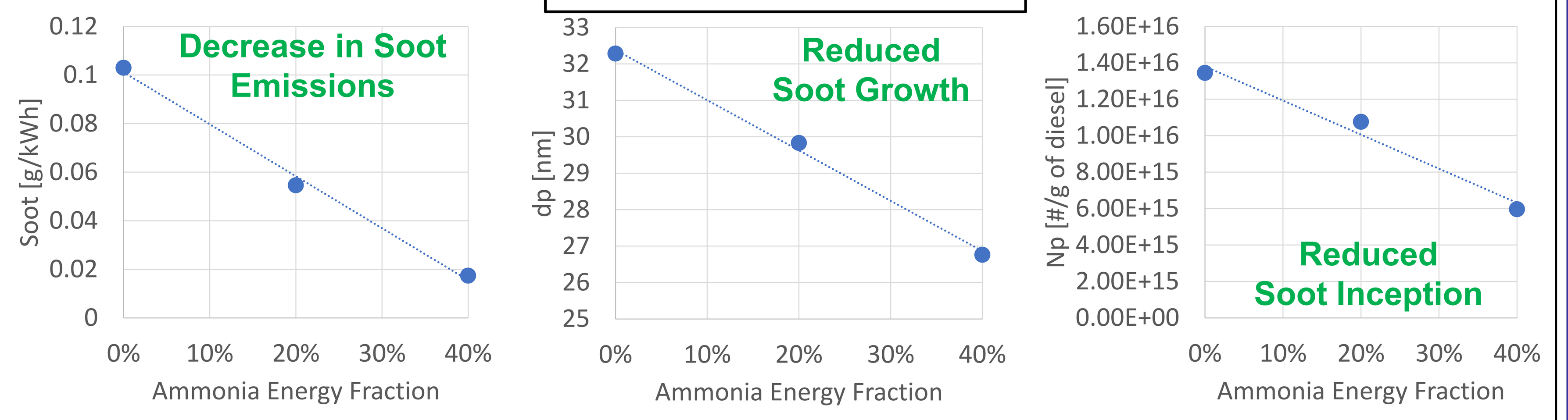
## Impact of Ammonia on Engine Emissions and Exhaust Soot Morphology, Nanostructure, and Composition

### Engine Emissions



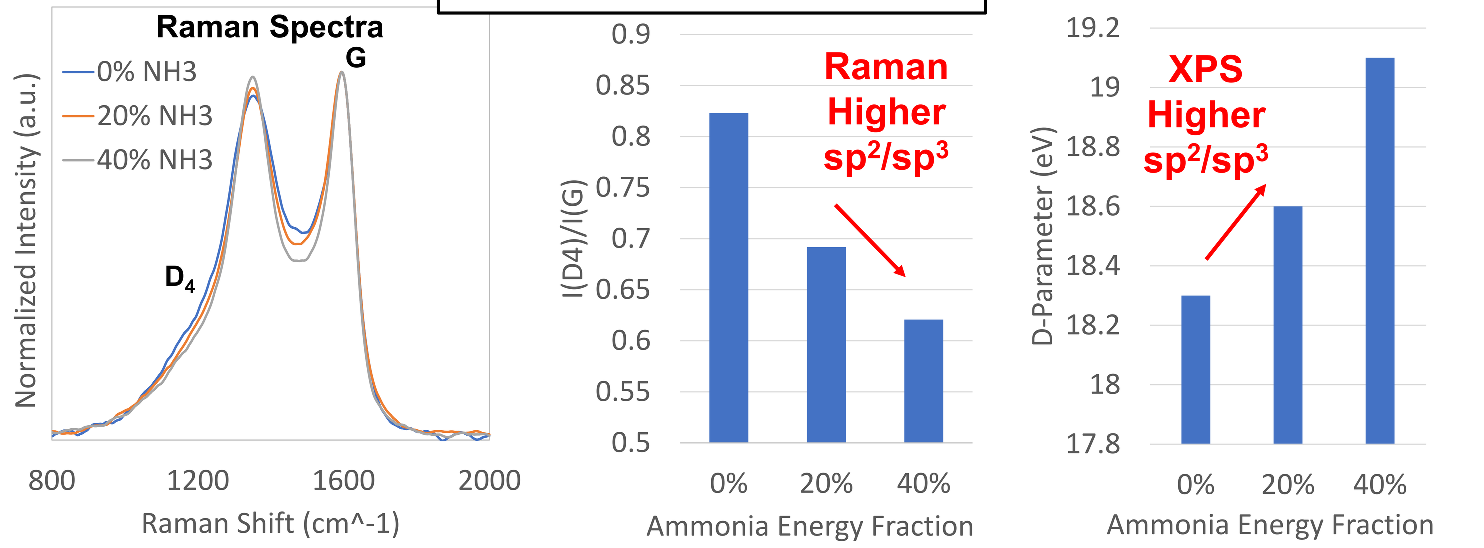

- $CO_2$ and NOx emissions were reduced but $N_2O$ remains a concern.
- Unburnt $NH_3$ emissions increases with $NH_3$ addition.

### Exhaust Soot Emissions



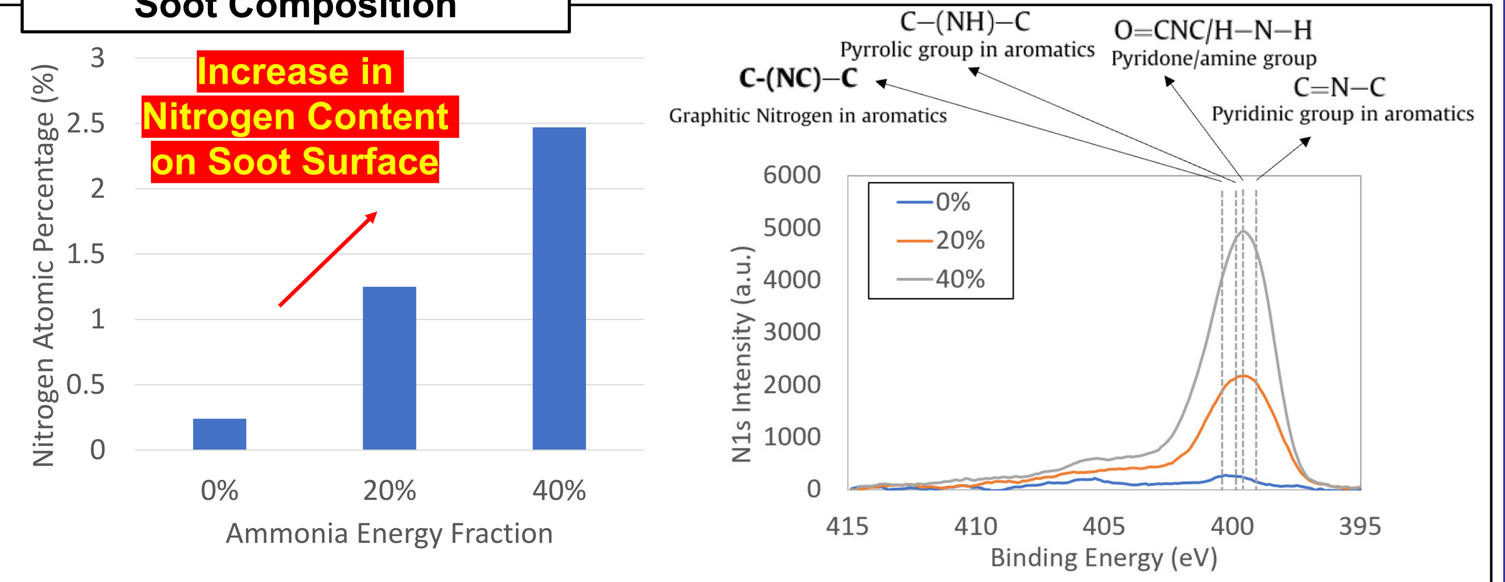

- Engine soot emissions were reduced by 82% at 40% $NH_3$. Average primary particle diameter (dp) and number of particle incepted (Np) decreased with $NH_3$ addition.

### Soot Nanostructure




- From the analysis of Raman spectra, the soot nanostructure showed an increase in graphitization as the ratio of $sp^2/sp^3$ carbon bonding hybridization increases.
- Using XPS analysis, the surface carbon Auger KLL spectra were investigated. The results show an increase in the D-parameter indicating an increase in $sp^2$ to $sp^3$ carbon bonding.

### Soot Composition




- The soot composition analysis using XPS reveals a significant increase in the nitrogen content of the surface with $NH_3$ addition.
- The increase in the nitrogen (N) intensity spectra corresponds with the binding energies of C-N bonds at active sites on the soot surface.
- The results shows an increased risk of nitrogenated PAHs formation on soot surface.

## Conclusions

- The addition of $NH_3$ **reduced the rate of engine soot growth and inception**.
- The increase in the engine soot graphitization with $NH_3$ addition indicated a **reduction in the surface reactivity towards carbon bonding**.
- $NH_3$ was found to react with the soot surface at active sites creating **C-N aromatic bonds and increasing the soot nitrogen content**.

## Ongoing Work

- Engine soot modeling using SRM and KIVA.
- Investigation of $NH_3$-hydrocarbon flame and engine soot surface compounds using ToF-SIMS.
- Investigation of the effect of $NH_3$ direct liquid injection on soot emissions.

## References


[1] ITF, Decarbonising Maritime Transport: Pathways to zero-carbon shipping by 2035, Int. Transp. Forum Policy Pap. (2018) 84.
[2] A.J. Reiter, S.C. Kong, Demonstration of compression-ignition engine combustion using ammonia in reducing greenhouse gas emissions, Energ. Fuel. 22 (2008) 2963–2971
[3] M.H. Zaher, C. Chu, M. Dadsetan, N.A. Eaves, M.J. Thomson, Experimental and numerical investigation of soot growth and inception in an ammonia-ethylene flame, Proc. Combust. Inst. 39 (2022).


## Acknowledgements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Contact: Mohammed Zaher (mohammed.zaher@mail.utoronto.ca)