Impact of Metal Fuel Impurities on Diesel Engine Emissions Control

Chao Xie[1], Todd J. Toops[1], Michael Lance [2], Aaron Williams[3], and Giovanni Cavataio[4]

1-Oak Ridge National Laboratory (ORNL): Fuel, Engines and Emissions Research Center; 2-Oak Ridge National Laboratory (ORNL): High Temperature Materials Laboratory; 3-National Renewable Energy Laboratory (NREL); 4-Ford Motor Company

Email: xiec@ornl.gov (Chao Xie), toopstj@ornl.gov (Todd J. Toops)

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Motivation

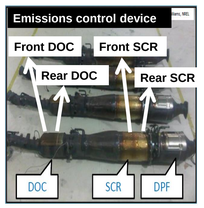
- **Biodiesel is a renewable, clean-burning fuel that can be blended with petroleum diesel**
- **Biodiesel contains alkali and alkaline earth metals**
  - **ASTM D6751 allows < 5 ppm Na + K and < 5 ppm Ca + Mg**
- **Growing concern that trace amounts of these impurities in biodiesel may adversely affect the performance of engine emissions control devices**

OBJECTIVES & RELEVANCE

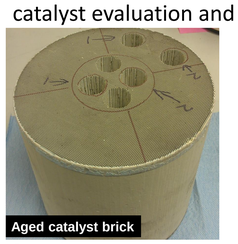
- **Measure presence and impact of K, Na, and Ca on in-use diesel emissions control devices**
- **Current focus on SCR and DOC aged by B20 fuel doped with Na, K or Ca and ULSD control case**
  - Determine the metal distribution along catalyst cores
  - Improve understanding of catalyst degradation by metals
  - Clarify effect accelerated aging factor on severity of test

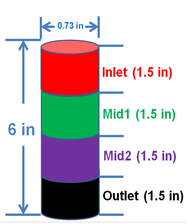
Experimental

- **Accelerated catalyst aging**
  - B20 fuel: Petroleum diesel (ultra low sulfur diesel) mixed with 20% biodiesel doped with Na, K or Ca
  - Three separate catalyst systems from Ford F250 were aged to 150k mile equivalent with B20 and one with ULSD

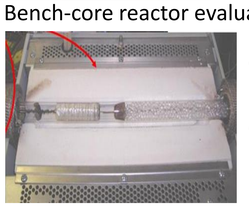


- **Catalyst characterization and evaluation**
  - Catalyst cores were harvested from aged catalyst bricks
  - Catalyst cores were equally divided into four parts for catalyst evaluation and characterization





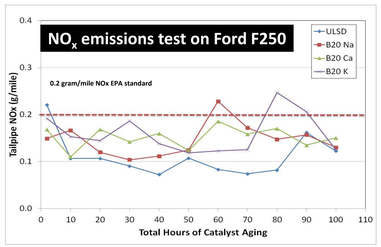
  - Bench-core reactor evaluation

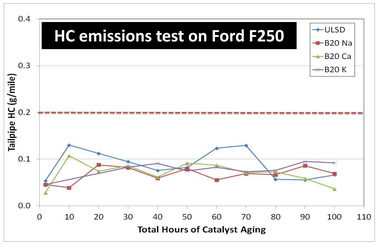


- DOC: CO/HC light-off, NO oxidation
  - 100-650°C; GHSV = 50k h^{-1}
- SCR: NO_x conversion
  - 150-600°C; GHSV = 30k h^{-1}

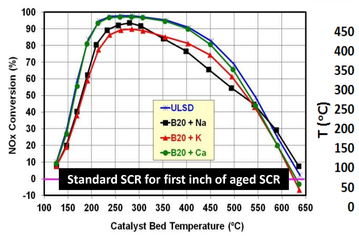
  - K concentrations in aged catalyst cores were measured by SEM-EDAX (Hitachi S4800 FEG-SEM with EDAX)

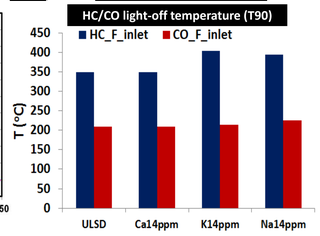
Impact of metal impurities in biodiesel on engine emissions control devices

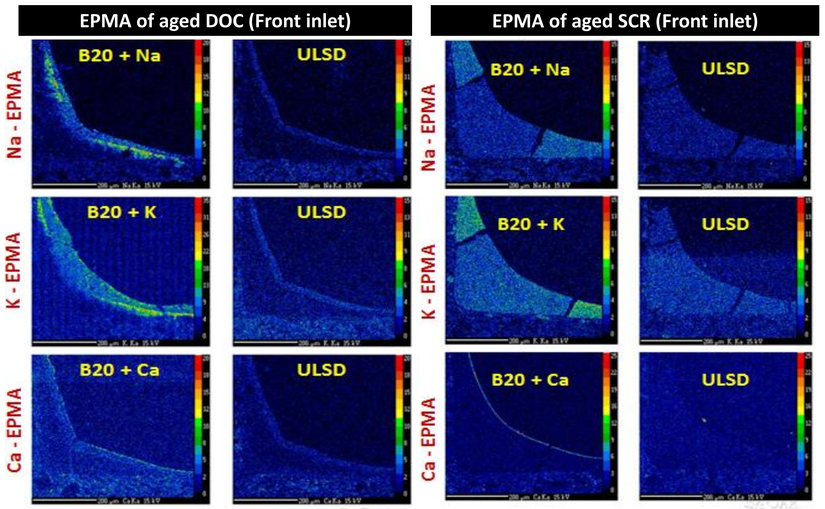




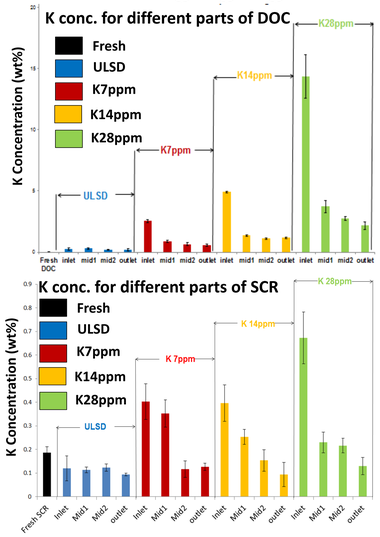
- **Emissions tests: DOC and SCR met final emissions target**
- **Both K and Na runs showed points above threshold**
  - Average NO_x emissions is higher for metal-aged system
- **EPMA revealed the location of metal impurities on DOC/SCR (right)**
  - **EPMA**: **E**lectron **P**robe **M**icro-**A**nalyzer
  - Na and K penetrate throughout washcoat
  - Ca observed but essentially only on surface of washcoat
- **Ford flow reactor evaluation: Significant impact from K/Na-aging on the performance of SCR, but much less on DOC**



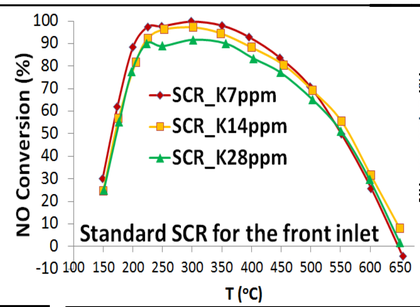


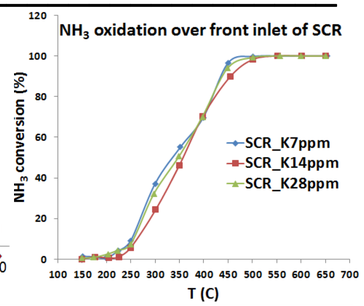


Accelerating aging with high metal concentrations is more aggressive

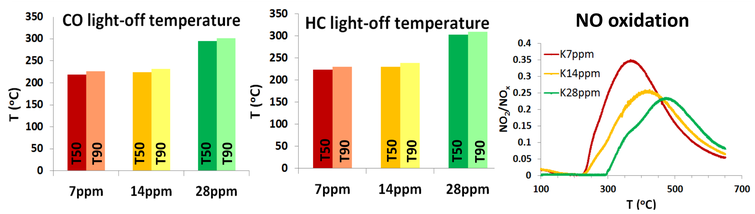


- **K-aging pronouncedly affected the inlet of DOC and SCR**
  - Higher K contents in the inlets of DOC and SCR aged by 28 ppm K
- **K-aging degraded the performance of DOC and SCR**
  - Delayed CO, HC, and NO conversion for DOC
  - Notable negative effect of K-aging on standard SCR
- **Suppressed NH_3 storage capability for K-aged SCR**
  - Reduced strongly held NH_3 with increased K contents in the fuel
  - Strongly held NH_3 may be critical to NO conversion

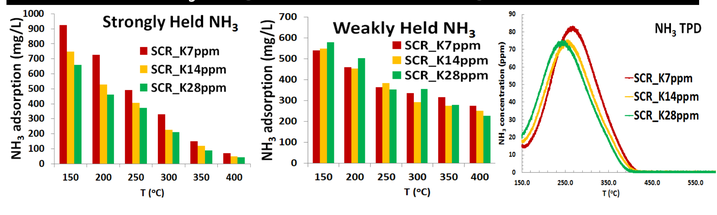




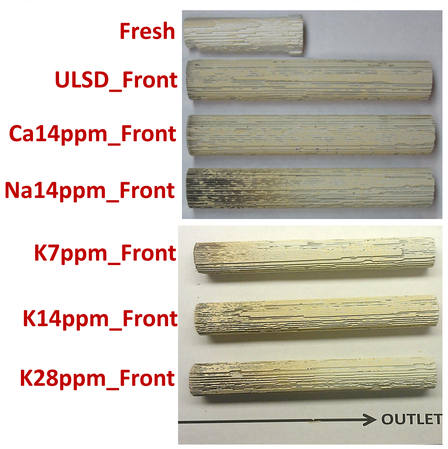
Performance of the front inlet of K-aged DOC



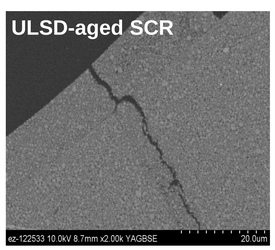
NH_3 storage for the front inlet of K-aged SCR

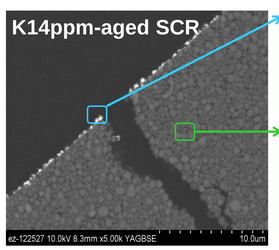


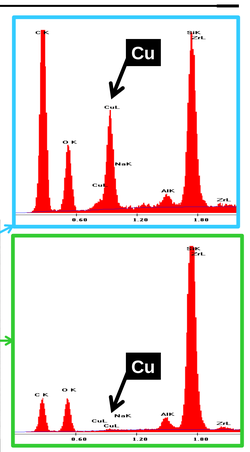
Highly concentrated Cu particles formed on K-aged SCR



- **Discoloration seen in the inlet of the front SCR bricks exposed to Na and K**
- **EDAX analysis indicated the formation of Cu-rich SCR surface upon K-aging**
- **No dark region on the ULSD or Ca samples because there is no Cu on their surfaces**







Summary

- **The metal impurities in biodiesel fuel can significantly affect engine emissions control devices**
  - **Effects need to be accounted for**
- **K-aging dramatically increased the K concentration in the inlets of DOC and SCR**
- **K-aging suppressed HC, CO, NO oxidation over DOC**
- **Increased K content in SCR due to K aging led to inferior NO conversion**
- **Suppressed NH_3 storage of SCR by K-aging, especially for strongly held NH_3**
  - NH_3 storage capability of SCR (strongly held NH_3) may notably affect its catalytic performance