Characterization of Particles Generated by Combustion of Heavy Fuel Oil

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Introduction

Exposure to Particulate Matter (PM) is known to cause various cardiovascular and respiratory diseases. However, as Corbett et al. (2007) pointed out, there are significant uncertainties, for example toxicity and response effects, behind the global-scale models assessing mortality due to ship emissions. There are very few reported health effect studies of PM from OGVs. Ideally, freshly diluted PM is always desirable for either *in vivo* or *in vitro* health effect studies. It is extremely difficult to have access to marine engine dynamometers to do health effect studies of PM from OGVs. Access to in-use diesel engines on OGVs or even ports to collect PM samples is very difficult as well.

Recently, Agrawal et al. (2008) and Murphy et al. (2009) reported the morphology and chemical composition of particles emitted from OGVs in detail. They found particles in two size ranges, 5 to 8 nm and 30 to over 100 nm range. They also reported chemical elements contained in the particles that originate from burning of heavy fuel oil (HFO).

The objective of this study is to synthesize and characterize particles by spray flame pyrolysis using a lab-scale oxyhydrogen flame burner. These lab-generated particles can be used by researchers, who do not have access to PM from OGVs, to conduct their preliminary health effect studies in the lab. We aim to synthesize nanoparticles using HFO in the lab as similar as possible to those from OGVs in terms physical and chemical characteristics.

Methods

Particles were synthesized using an lab scale oxyhydrogen flame burner. Generated particles were analyzed by various online analysis instruments including Scanning Mobility Particle Sizer (SMPS), NanoDMA, and Cloud Condensation Nuclei Counter (CCNC). Filter samples were also taken for offline chemical analysis. TEM samples were prepared by using a handheld electrostatic precipitator (ESP) (Miller et al. 2010).

Chemical equilibrium calculations were performed for a low-speed 2-stroke main engine on OGVs burning HFO and our lab-scale oxyhydrogen flame to determine equilibrium concentrations of vanadium and nickel containing compounds. The NASA computer program Chemical Equilibrium with Applications (CEA, version 2) (Gordon 1994) with Java graphical user interface (NASA 2010) was used. A thermo input file including vanadium and nickel sulfur compounds was used (Linak et al. 2000; Linak et al. 2004).

Results and Discussions

For heating temperature of 60 °C and feeding rate of 15 ml h^{-1}, size distribution had a peak concentration at 27 nm. Higher heating temperature led to smaller particle sizes. Using a quenching ring reduced the peak particle diameter to 11 nm, close to observed ambient metal particle sizes of 5 to 8 nm (Murphy et al. 2009). By comparing TEM images of lab generated

particles and particles sampled in the stack of a main engine on OGV, we can see that synthesized particles have similar morphology to actual particles emitted from OGV but with a little larger diameter. EDS analysis of synthesized particles showed sulfur and vanadium peaks similar to actual OGV emitted particles (Murphy et al. 2009). About 60% of total PM mass was OC and no EC was present on the filter. Ash content was obtained by subtracting EC and OC mass from the total PM mass. The absence of EC and OC to ash ratio measured in our study were very similar to those of Murphy et al. (2009) for OGV PM measured onboard (see their table 3). Chemical As can be seen in figure 6a and 6b, changes of Ni and V compounds for oxyhydrogen flame have similar trends as the 1 bar case for the OGV 2-stroke diesel engine.
CCN experiments showed that the HFO particles formed by flame pyrolysis are thus much less hygroscopic than soluble inorganic species.

Conclusions

Synthesized particles were compared with actual OGV emitted particles for size, morphology, CCN activity and chemical compositions and agreed well with results of onboard measurement at the OGV. Chemical equilibrium calculations for both engine combustion and oxyhydrogen flame validated that similar nickel and vanadium compounds can be formed in the flame burning process. The approach of synthesizing particles from HFO described in this study can be useful for researchers studying the health effects of OGV emitted PM to carry on preliminary studies.

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Introduction

- Adverse health effects of particles from engines on the ocean-going-vessels (OGVs)
  - ✓ Cause approximately 60,000 mortalities due to cardiopulmonary and lung cancer.
  - ✓ Affects areas of up to 80 km from the coast.
  - ✓ More detailed health effect studies of PM from OGVs are needed.
- Limited access to freshly diluted OGV particles for health effect studies
  - ✓ Freshly diluted PM is always desirable for either *in vivo* or *in vitro* health effect studies.
  - ✓ Scientists have rare access to marine engine dynamometers.
  - ✓ On-board measurement is difficult and costly.
  - ✓ No standard reference material (SRM) available.
- Particle characteristics
  - ✓ Composed of organic carbon, sulfate, and ash.
  - ✓ Vanadium and nickel are major components of ash.
  - ✓ Two size ranges, 5 to 8 nm and 30 to over 100 nm.

Selected properties of HFO

Density at 15 ℃ (g/ml)	0.99
Viscosity at 40 ℃ (mm^2/s)	743.4
Viscosity at 100 ℃ (mm^2/s)	31.78
Carbon (wt %)	85.87
Hydrogen (wt %)	9.63
Oxygen (wt %)	1.64
Nitrogen (wt %)	0.46
Ash (wt %)	0.072
Sulfur (wt %)	2.03
Vanadium (mg/kg)	178
Nickel (mg/kg)	58
Iron (mg/kg)	19

Objective

- Compare particles generated by combustion of Heavy Fuel Oil (HFO) from the main engine of the ship and a lab scale burner.
- Aim to provide particles for preliminary health effect studies.

Methods

Use an oxyhydrogen flame burner to generate particles.

- No carbon contamination.
- Simple and low cost.

Schematic of experimental setup

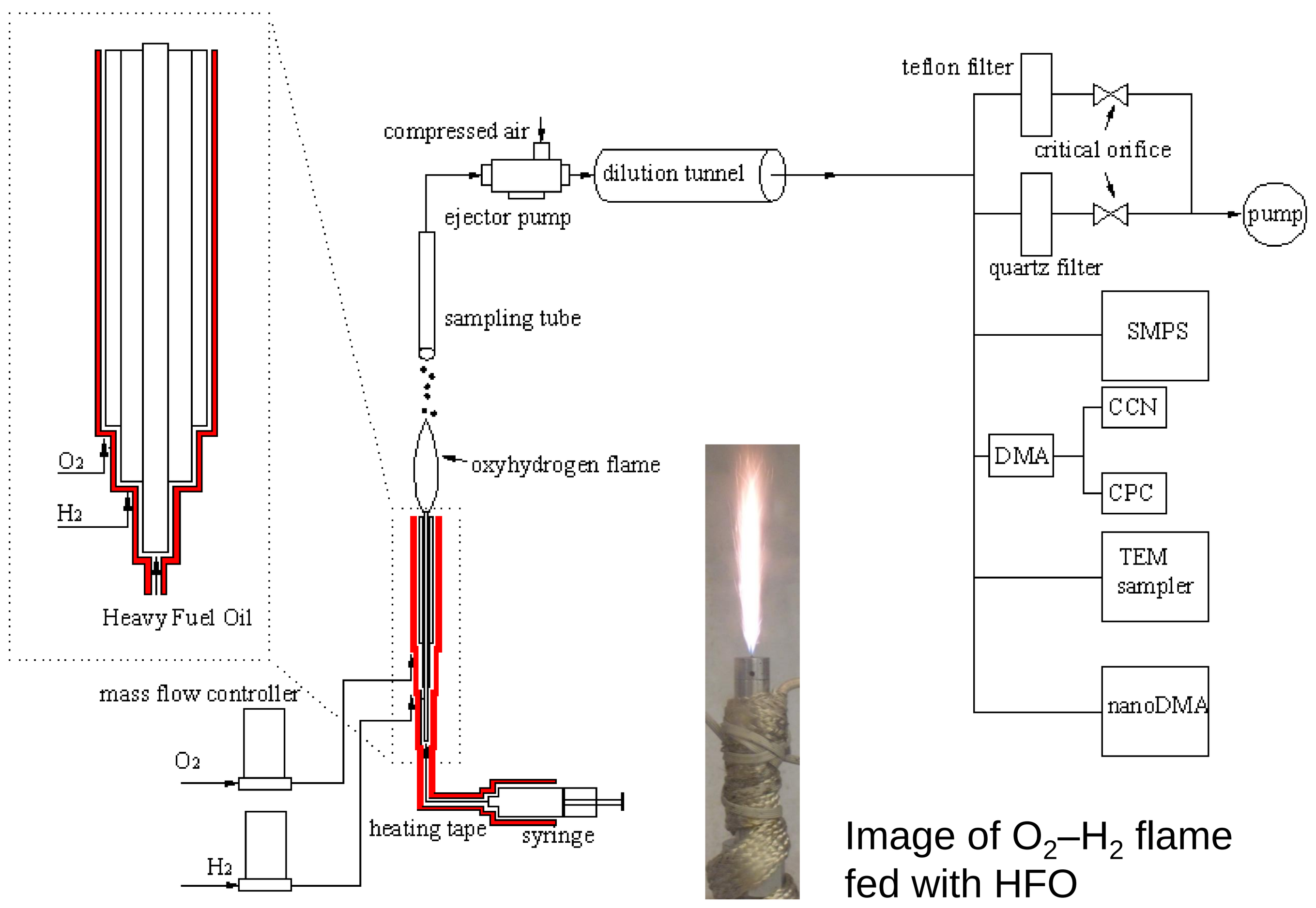
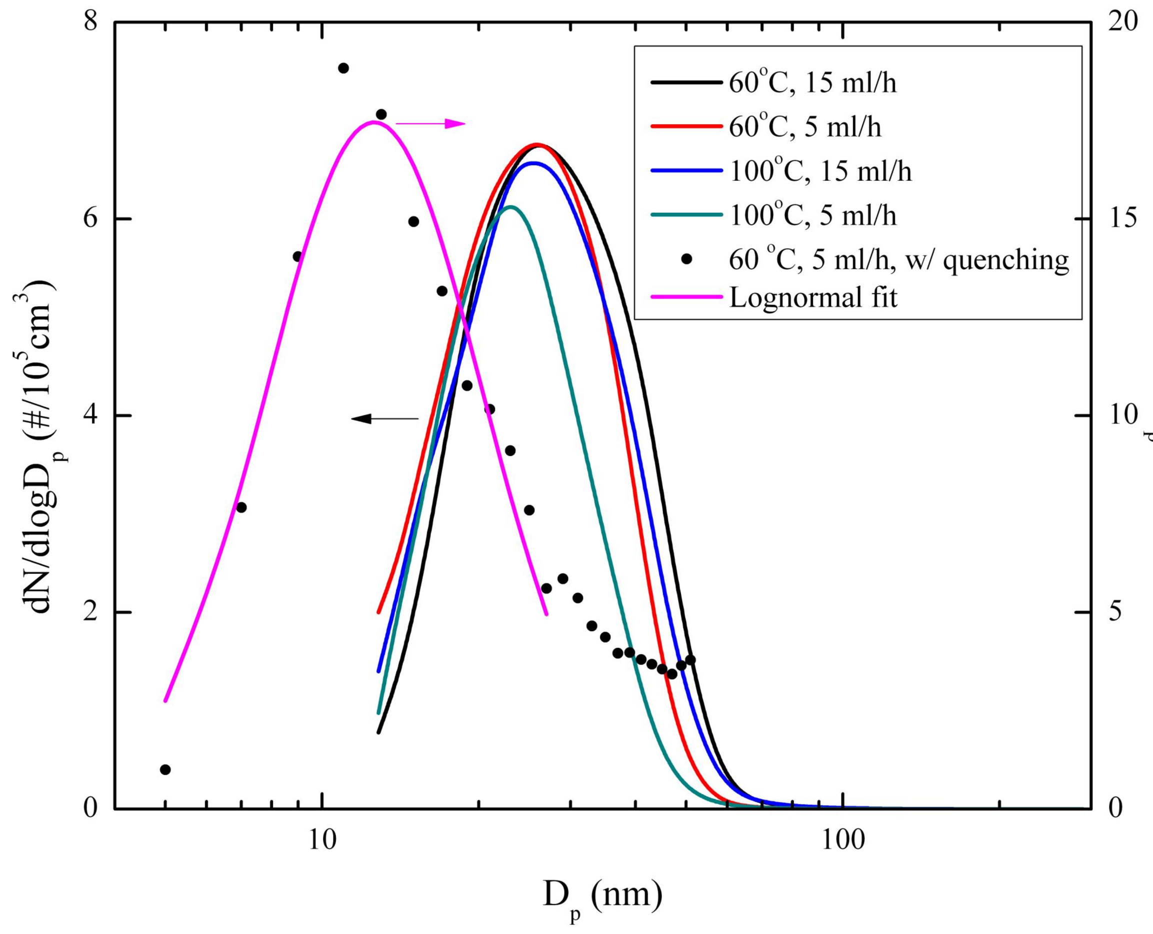


Image of O_2–H_2 flame fed with HFO

Results

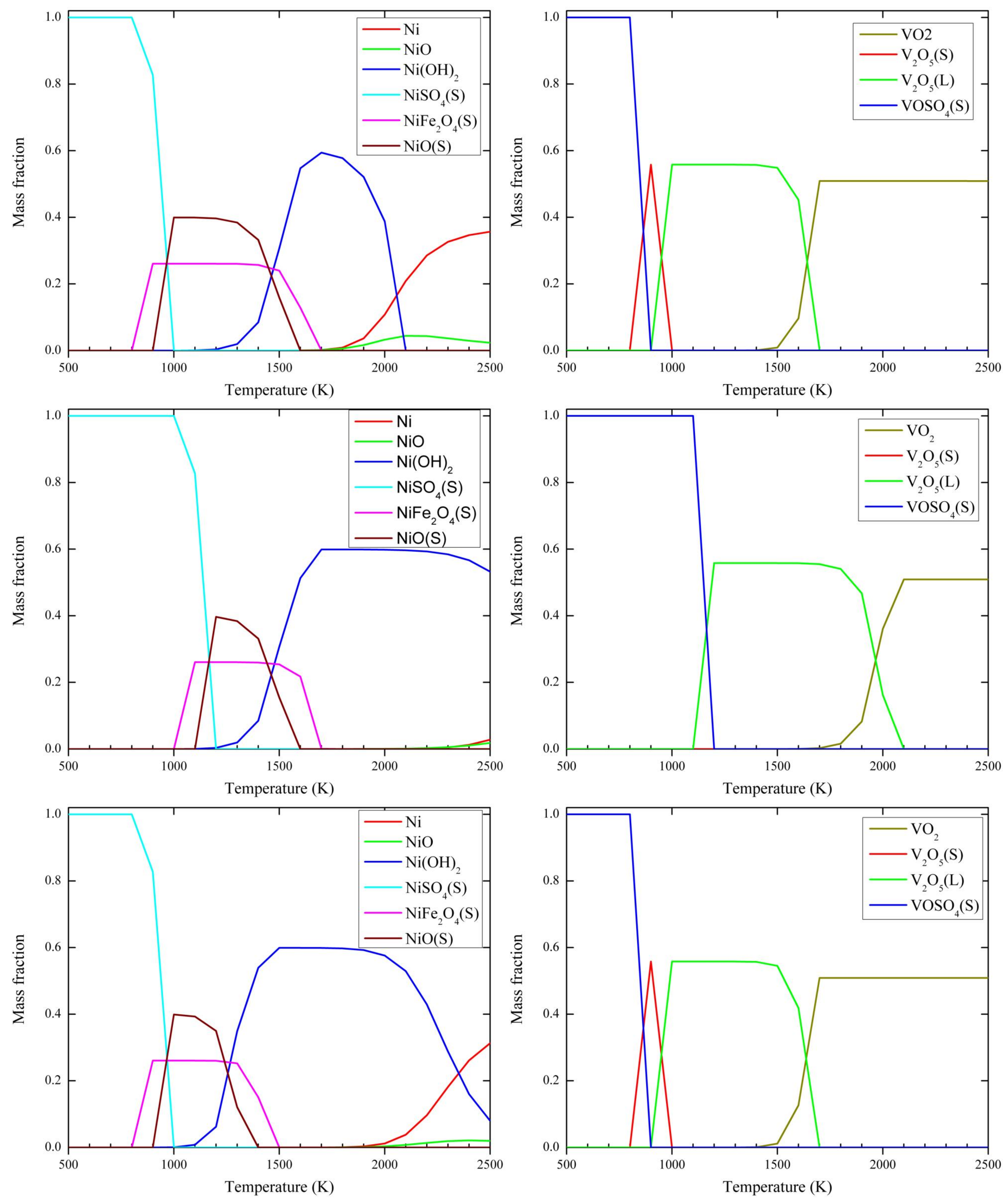
Size distribution

- Higher heating temperature and lower HFO feeding rate lead to smaller particles.
- Use of a quenching ring reduces the particle size significantly.



Chemical Equilibrium Calculation

- Calculations were performed to determine the equilibrium concentrations of vanadium and nickel compounds.
- Changes of Ni and V compounds for oxyhydrogen flame have similar trends as the 1 bar case for the OGV 2-stroke diesel engine.



Engine 1 bar

Engine 100 bar

Oxyhydrogen flame

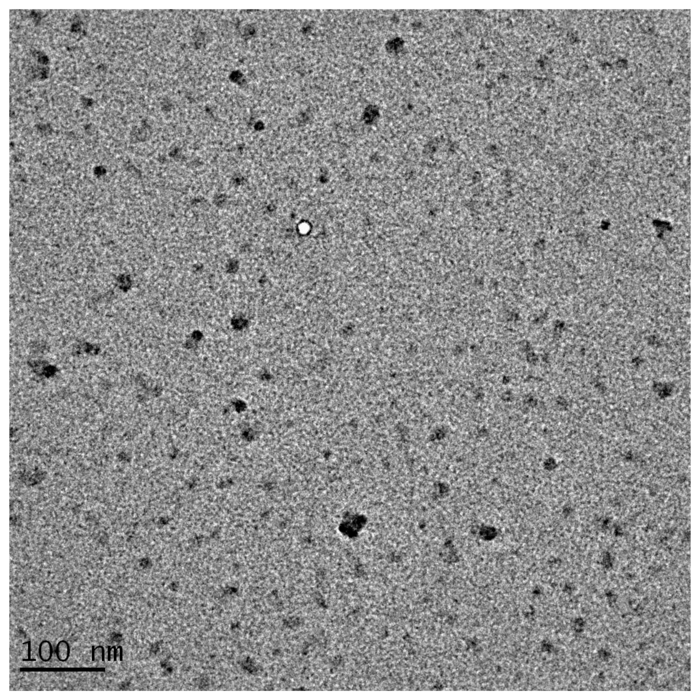
Hygroscopicity

- Adverse health effects from PM air pollution can be caused by the deposition of aerosol particles in the respiratory tract during breathing. The water vapor uptake by hygroscopic particulate components can alter dry PM size and deposition efficiencies.
- For flame condition of 15 ml/h and 60 ℃, At low supersaturations (s < 0.8%) a small fraction of nuclei (<10% of particles with size >100 nm) formed droplets above the size of the optical particle counter detection limit (0.75 μm).
- At s = 0.94 ± 0.03%, the particle critical diameter was ~90 nm; above this size 70% of the total particle concentration became active and formed droplets.

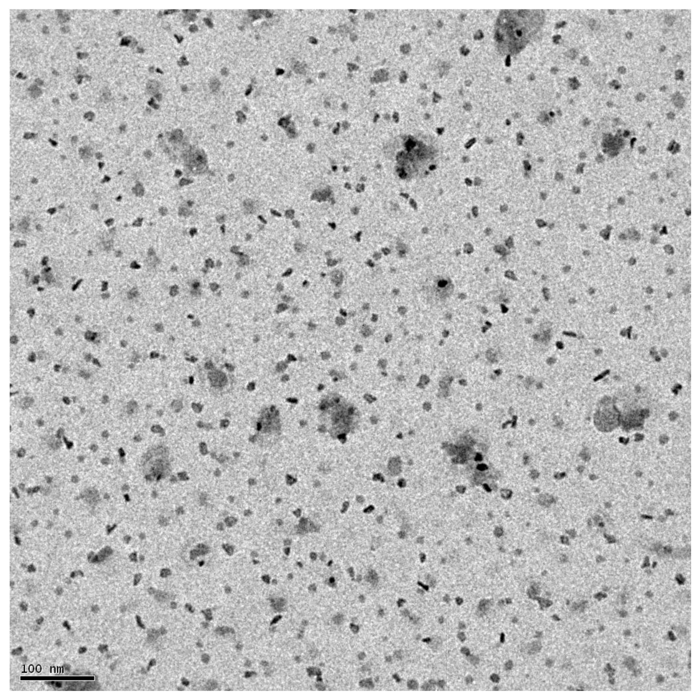
For questions and comments, please email: heejung@engr.ucr.edu

Transmission Electron Microscopy

- Similar morphology.
- EDS shows S and V signals in both samples.



TEM image of lab-generated particles



TEM image of particles sampled from exhaust of an OGV main engine

EC/OC analysis and anion analysis

- The absence of EC and OC to ash ratio measured in our study were very similar to those of Murphy et al. (2009) for OGV PM measured onboard.

PM (μg)	55.6
OC (μg)	34.1
EC (μg)	0
Ash (μg)	21.5*
$H_2SO_4 \cdot 6.5H_2O$ (μg)	0.00032

* Ash content was obtained by subtracting EC and OC mass from the total PM mass

Conclusions

- Oxyhydrogen flame burner can be a useful device to generate particles for preliminary health effect studies.
- Generated particles have similar characteristics to actual OGV emitted particles in terms of size, EC/OC content, and chemical composition.

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