Particulate Emissions Hazards Associated With Fueling Heat Engines

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\section*{ABSTRACT}
All hydrocarbon- (HC-) fueled heat engine exhaust (tailpipe) emissions (<10 to 140 nm) contribute as health hazards, including emissions from transportation vehicles (e.g., aircraft) and other HC-fueled power systems. CO\textsubscript{2} emissions are tracked, and when mapped, show outlines of major transportation routes and cities. Particulate pollution affects living tissue and is found to be detrimental to cardiovascular and respiratory systems where ultrafine particulates directly translocate to promote vascular system diseases potentially detectable as organic vapors. This paper discusses aviation emissions, fueling, and certification issues, including heat engine emissions hazards, detection at low levels and tracking of emissions, and alternate energy sources for general aviation.

\section*{INTRODUCTION}
Synthetic and biomass fueling of heat engines begins with the generation of feedstocks. For aviation fuels we consider three types: petroleum-based kerosene (JP-8/Jet A-1), synthetic paraffinic kerosene (SPK), and hydro-treated renewable jet (HRJ or bio-SPK). Fueling aircraft with JP-8/Jet A-1 represents legacy and current practice. The SPK process usually begins with coal or natural gas and evolves through a Fischer-Tropsch (FT) process into SPK-fuel and is more common, having a long history within WWII. Biomass fueling (HRJ) is less known, as the process begins with a seed source growing into cellulosic and seed biomass that is converted to biodiesel or seed oil and further processed to jet fuel. In general we consider halophytes, algae, bacteria, weeds-to-crops, and organic waste as fuel feedstocks. Selected plants provide multiple feedstock sources, and we will consider potential fuel feedstock sources such as sustainable palm oil and oil seed plants (e.g., castor) as crops, camelina as a "weed to crop," and pennycrest as having "weed to seed oil" potential (Atlantic Greenfuels, 2009a and 2009b; Reuters, 2009; Evogene Ltd., 2009; McVay and Lamb, 2007; and Schill, 2008).

The Makin group sustainable palm-oils are commercially available (Atlantic Greenfuels, 2009a). Processing castor involves disposing or denaturing highly toxic ricin; camelina is a more conventionally harvested weed-to-crop; and for pennycrest, with weed-to-crop potential, the harvesting and containment of a small weed seed needs consideration. Seed-oil processing to biojet involves crushing, proprietary catalysts and processing, and yields of different hydrocarbon distributions depending on feedstock sources, but all must satisfy the jet fueling standards. Most biomass feedstocks can be handled by the Honeywell UOP process.

But even with SPK or bio-SPK fueling, emissions are still a major problem. Testing of SPK and HRJ provides emissions data including particulate distributions. Similar measurements are made across the transportation industry with heat-engine-dependent results. Ground station measurements of CO\textsubscript{2} emissions can be used to map out major cities and roadways across the United States. Tailpipe emissions from petroleum-fueled heat engine sources are EPA-designated health hazards. Particulate health hazards are rapidly becoming recognized as a major concern and need resolution. Recent studies show nanometer particulates to engender cardiovascular disease in addition to well documented respiratory diseases. All hydrocarbon-fueled heat engines produce airborne (exhaust) particulate distributions peaking in the 20–40 nm range, thus we can infer their inhalation is a source of disease. These health concerns are common to all hydrocarbon-fueled heat engines, including aircraft tailpipe emissions, and those flights along the Potomac River are of congressional concern. In this paper we discuss aviation emissions fueling certification, how and why these emissions are hazardous, how they change with (SPK or bio-SPK) additions to JP-8/Jet A-1, and whether we can detect and track them. Hydrocarbon-fueled heat engine emissions are linked to health hazards, implying an emphatic need to curtail hazardous emissions perhaps by transitioning to more electric- or hydrogen-fueled propulsion systems that may offer long-range resolution.

\section*{AVIATION EMISSIONS, FUELING, AND CERTIFICATION}
In 2006, estimated U.S. national emissions from all sources (Bureau of Transportation Statistics, 2007) were CO\textsubscript{2}, 1618.5 Mt; CO, 100.55 Mt; NO\textsubscript{x}, 18.22 Mt; volatile organic compounds (VOCs), 17.38 Mt; PM10 (coarse particulates), 18.42 Mt; PM2.5 (fine particulates), 2.61 Mt; SO\textsubscript{2}, 13.77 Mt; and lead, 4.23 kt.
While these figures represent all emission sources, we want to focus more on the impact alternate fueling of aviation and heat.

**Commercial and Military**

Flight tests have been carried out with CTL, GTL, and biojet blends up to 50% Jet A-1 or JP-8 and 50% alternate fuels with a few ground tests to near 100% alternate fuels. Basically, alternate aviation fuels are termed “drop in” fuels because they pretty much “walk, talk, act, smell, and perform” like Jet A-1 or JP-8. Alternate fuels, based on diverse but approved feedstocks, conform to MIL-DTL-83133F (2008) or ASTM D7566 (2010) standards and along with life cycle greenhouse gas emissions analyses provide a unified aviation industry position on alternative fuels (Boeing, 2009).

Edwards (Atlantic Greenfuels, 2009c) cites a high-level USAF goal of purchasing 400 million gallons of alternative fuel by 2016 while working jointly with the CAAFI (Commercial Aviation Alternative Fuel Initiative) group to harmonize specifications and create an alternate fuels market. Currently, the USAF buys about 2.5 billion (B) gallons of jet fuel per year with the U.S. aviation industry near 26B gallons per year (Boeing, 2009; and Atlantic Greenfuels, 2009c).

**General Aviation**

Dr. Brien A. Seeley’s goal for the Comparative Aircraft Flight Efficiency (CAFÉ) Foundation (CAFÉ Foundation, 2009) is performance and biofuel blends with 100LL Avgas (general aviation piston engine fuel) to reduce and eventually remove lead. Baylor University’s renewable aviation fuels program (RAPDC) (Wikipedia, 2009) is testing ethanol-ethyl tert-butyl ether (ETBE) an oxygenate gas additive in a Cessna 152 (recall ethanol to 10% is good gasoline additive). The Embraer EMB-202A aircraft consumes ethanol (Baylor Institute for Air Science, 2006; Scott, 2005; and Embraer, 2009) and the Antonov 2 N244MJ should be capable of blended biofuels (Wikipedia, 2009b) while the first biofueled jet flight, an L-29, was fueled with a blend of vegetable oils (GreenFlight International, 2009).

**Hydrocarbon-Fueled Engine Emissions**

Gas turbine, diesel, and gasoline engines are well known HC-fueled engines.

Diesel engine emissions operating on petroleum-based fuels are well established (United States Environmental Protection Agency, 2002), and many have been run on bioderived fuels with and without processing. In an EPA engine test-fueled with 20% soy-biodiesel and 80% petroleum diesel, NOx increased 2%, PM, HC, and CO decreased 10.1%, 21.1%, and 11.0%, respectively (United States Environmental Protection Agency, 2002).

Biodiesel emissions are dependent on feedstock (soybean, rapeseed, or animal fats) and engine type but not model year, implying combustor type and injection system similarities of the manufacturer. Figure 1 represents average emissions with %biodiesel for heavy-duty highway engines.

**Aircraft Gas Turbine Engines.** On the ground engine-on-wing emissions test data differ from altitude tunnel engine test data but are considered more representative of actual flight conditions. Both show particulate size and mass changes with air pollutants, and can be regulated by the EPA under CAA - Massachusetts Supreme Court ruling, 2 April 2007 (Massachusetts v. EPA, 549 U.S. 497 (2007) (Massachusetts Supreme Court of United States, 2006; and U.S. Environmental Protection Agency, 2009).

Greenhouse gases (GHGs): CO₂, CH₄ (25x worse than CO₂), NOₓ (N₂O, 300x worse), etc. declared hazardous to climate and health (e.g., excess CO₂ in body lowers pH (acidosis)).

Particulates, affect the climate and major undeclared health hazard (e.g., cardiovascular and lung diseases)

All hydrocarbon (HC)-fueled heat engine exhaust emissions contribute as health hazards where exhaust (tailpipe) emissions (<10–140 nm) includes aircraft and mobility/stationary systems. In the case of particulate pollution (Table, 1), Simkhovich et al. (2008) have shown that ultrafine particulates directly translocate to promote vascular system diseases and Schwartz (1993) among others linked chronic respiratory diseases to particulates and are better known.

ALL HC-heat engines are major sources of these hazardous emissions.

With particulate inhalation of size similar to 5 µm, you cough it out. With nanoparticulates (<100 nm), quantum mechanical forces come into play and particulates can lodge in tissue. With distributions peaking ranging from 20–60 nm, the residence time and toxicity of particulates become similar to the classic grain of sand in the oyster. Does such a lodged nano-seed form a resident benign nodule, eventually released by the lympathic system, or does it serve as a tumor initiator and subsequent source of demise?

### Table. 1 Particulate sizes classified by aerodynamic diameter

<table>
<thead>
<tr>
<th>Classification</th>
<th>Examples</th>
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<tbody>
<tr>
<td>Coarse: 2.5–10 µm (PM10)</td>
<td>Road and agricultural dust, tire wear</td>
</tr>
<tr>
<td>Fine: &lt;2.5 µm (PM2.5)</td>
<td>Gas to particulate conversion in combustion and industrial processing</td>
</tr>
<tr>
<td>Ultrafine: &lt;0.1 µm (&lt;100 nm) -nanomaterial particulates</td>
<td>Exhaust emissions (tailpipe), such as aircraft HC-fueled mobility/stationary systems</td>
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**WHY AND HOW ARE HYDROCARBON HEAT ENGINES HAZARDOUS?**

**Emissions Hazards**

The EPA classifies emissions as health hazards. Greenhouse gases contribute to air pollution that "...threaten the public health and welfare" (The Chicago Tribune, 2009). All of the primary greenhouse gases qualify as...
Aircraft engines fueled with blends of FT-derived fuels (CTL and GTL), classified as SPK-Jet A-1 50:50 blend, show reductions in particulate emissions to 40% at ground idle engine speed but see that margin steadily decrease with increased engine power setting (Fig. 2). Particulate emission reductions to 80% at ground idle are demonstrated at 100% SPK, but again, these reductions diminish with power increases. Similar trends are anticipated for biojet (HRJ) fuels since the hydrocarbon profiles are similar (Hendricks et al., 2009a).

Whereas the static ground aircraft engine test results for the CTL- and GTL-processed fuels do indicate a reduction in particulate levels when compared with the Jet A-1, the distributions for these tests (in terms number and size) are close to being similar with a peak in the 25-nm range, rather independent of biodiesel blend of 0%, 2%, 10%, 20%, and 20% premixed (Fig. 3). Other tests show peaks from 20 to 60 nm. Also to be noted is the unregulated auxiliary power unit (APU) gas turbine exhaust emissions, which are significantly higher than propulsion gas turbines (an issue in need of resolution).

On-wing gas turbine engine ground tests with petroleum-based JP-8 show similar trends (Fig. 4). Petroleum-based JP-8 particulates as well as blends of JP-8 and FT fuels (CTL Sasol and GTL Shell) show significant increases in particulate emissions below 10 nm depending on engine power setting. With increases in engine power from 30% to 65%, JP-8 particulate peaks shift from 18 to 35 nm with an increasing peak with FT fueling. The reduction in particulate emissions and black carbon number are most pronounced at idle but as shown in Fig. 2, diminish considerably near 100% or the Take Off power setting.

The black carbon and smoke number variations are also reflected in combustor testing, as the luminosity decreases with increasing percentage of FT fueling, and pressure (equivalent to increases in engine power) as shown in Fig. 5.
Fig. 4 On-wing engine emissions testing measurements for particulates with JP-8, 50:50 blend JP-8 and S8, and 100% S8, where S8 represents a Fischer-Tropsch fueling with either CTL or GTL jet fuel (Anderson, 2009).

Fig. 5 Combustor sector smoke number and luminosity test results for JP-8+100 fueling and blends with S8 varying from 0% to 100%. Photo inset (P,T)inlet = [75psia, (0.517 MPa), 500 °F ( 533 K)] at 3% combustor pressure drop.
We know from published data and prior discussion that particulates of these sizes (less than 100 nm) lodge in the lung capillaries with the smaller ones able to penetrate into the venous system, returning to the heart with some lodging within the tissue and others in the arterial walls promoting cardiovascular disease.

There are several issues here:

1. These particulates and distributions are common to all HC-burning heat engines including the gas turbine engines for aviation and engines for automobiles and power plants.
2. We need to become more proactive to caution the energy community of the health hazards of HC-fueled heat engine particulate emissions.
3. Carbon dioxide emissions are tackled at ground stations throughout the United States, and one can spot the major cities and interstates by mapping the CO$_2$ emissions. Similar efforts could be employed for other emissions as NO$_x$, CH$_4$, and VOCs most of which are toxic and implicated in diseases. However the distribution of particulates, to our knowledge, have not been tracked, nor has the effect of particulate release at altitude been tracked; more importantly the toxicology of those engine exhaust particulates under various climatic conditions has received little attention.
4. While the CO$_2$ emissions, etc are currently classed as health hazards (The Chicago Tribune, 2009), the associated deadly issues of lung cancer and cardiovascular disease are overshadowed if not hidden and glossed over by the dynamics and politics of climatic-GHG affects.
5. Also to the author’s knowledge, the U.S. disease center has not studied correlations between particulate distributions and disease distributions.

We are interested in the particulate size, distribution, and toxicology of those particulates, VOCs and other gases and how body systems are affected by these elements, including their toxicology.

**CAN WE DETECT LOW-LEVEL HAZARDOUS EMISSIONS AND PARTICULATES?**

**A Basis for Detection**

We want to detect the bad stuff before it happens. Emissions probes for aircraft exhausts are intrusive and difficult to design and implement, yet to a limited extent, have been accomplished. Other exhaust sensors are less intrusive. For example, at NASA Glenn Research Center Dr. Gary Hunter (2009) has developed exhaust gas radiation sensors for detection of specific elements primarily related to integrated health monitoring systems. He has also developed cargo bay gas-sniffers for detection of combustibles, which closely relates to needed emissions sensory work for humans and animals.

In the pioneering work of Dr. Hosam Haick (Lovgren, 2006) and Dr. Donald Broom (Leung, 2005) dogs, which have a very distinctive and highly developed sense of smell, have been trained to sniff out “foreign elements” such as disease-specific odors (organic compounds). Diseased cells emit waste products different from those of normal cells that are excreted from the body and in particular exchanged in the lungs where emissions also play a major role, as also the case in the work of Hunter and Dweik (2008).

Nitric oxide (NO) a hazardous emission. A problem is that NO is necessary for life, but too much of a good thing is usually toxic, and for air-oxidized combustion systems (heat engines, cigarettes, flue gas, etc.), such is the case. In asthmatics, where exhaled NO levels are higher than with non-asthmatics (still in ppb), NO enhances inflammation; detectable by chemiluminescence or laser diagnostics, the methods are both cumbersome and expensive. Hunter and Dweik (2008) are presently developing a system to detect and extracted information from an asthmatic patient’s breath using their portable low-cost solid-state sensor system. (Note, an EPA average air quality goal is 0.16 ppm NO.)

The sensors of Haick (9-element) and Hunter and Dweik along with associated electronics and transmitters could be “chipped” and made a mandatory part of every “closed atmosphere” transport vehicle (spacecraft, aircraft, automobile, even high rise office space and homes) to detect emissions that are health hazards to the human anatomy and physiology. Coupled with telemedicine, such detection systems would provide early warning of disease and perhaps even their pathology (Winters, 2008).

Preventive in-flight cabin and spacecraft emissions sensing significantly reduces overall costs of medical care, drugs, and hospitalization (where applicable) and ensures greater safety of the traveling public or space explorer. Further, feedback loops could sharpen the sensitivity and selectivity of these electromechanical/chemical devices.

Herein, we are basically interested in emissions and data related to the particulates, VOCs, and their distribution and toxicology as they affect the body and organs because the cabin in aviation and space craft is one’s survival membrane.

The hidden dangers of hydrocarbon burning combuster emissions need our immediate attention.

**CAN WE TRACK THESE EMISSIONS?**

**Tracking Carbon and Ultrafine Emissions**

Since the 1950s global emissions have increased with CO$_2$ levels rising from 300 to near 400 ppm. Increased CO$_2$ levels affect both plant biomass and human respiration in terms of expulsion of CO$_2$ (a toxicity issue). In fact pictorial images of HC-fueled heat engine mobility corridors and population centers are readily outlined throughout the United States (Winters, 2008). (Fig. 6). With heat engines there is an implied direct link between C-emissions measurements and ultrafine (nano) particulate emissions, as shown in Fig. 1.
Fig. 7a Solid rocket motor test firing plume, Promontory, Utah (NASA, 2009). Ares first-stage five-segment motor test. Fifteen tons CO$_2$ dumped to extinguish motor firing. 22 million hp, nozzle exit $M = 3$, and 3.6 million lbf of thrust.

Fig. 7b Mount Pinatubo, Philippines, ash plume reaching a height of 19 km, 3 days before the climactic eruption of 15 June 1991 (Wikipedia, 2009c)

Fig. 8 General aviation electric powered aircraft (Hendricks, et al., 2009b)

Some systems are more visibly tracked, such as anthropogenic particulate formations and volcanic eruptions (Figs. 7a and b) where pyroclastic debris is deadly. Still interesting materials can evolve from such extreme events. Pozzolana, the basis for pozzolanic materials, is reported to form from the long-term exposure of erupted ash to atmospheric H$_2$O and CO$_2$, transforming the original complex silicates into a fine dust of simple silicates and oxides (SiO$_2$, Al$_2$O$_3$, Fe$_2$O$_3$). When reacted with lime, Ca(OH)$_2$, they harden into insoluble calcium silicates and aluminates more resistant to aging (Bonincontro, 2002–2010; and Veloso and Veiga, 2005).

General Aviation Emissions Response

Although in its infancy, electric-powered light aircraft sustained by combinations of solar, hydrogen-fuel cell, and battery are poised as general aviation solutions to aircraft emissions pollution. Examples vary from military unmanned aerial vehicles (UAV) to the Chinese Yuneec E430 54-hp two-seat battery-powered electric airplane (Fig. 8) (Yuneec International, 2008).

Electric motors are challenged by water but work well at altitude where the aircraft is more efficient. While low- to no-emissions hydrogen fueling is an attractive alternative and novel to general aviation, we need also remember that commercial aviation was built upon general aviation.

CONCLUSIONS

1. Alternate-fueled diesel and gas turbine engines whether sourced from CTL, GTL, or biomass feedstocks represent near-paraffinic hydrocarbon blends with Jet A-1 or JP-8 that perform as well as or better than petroleum-based fuels, yet produce less aviation
emissions. Life cycle attributes are not addressed herein, but tend to favor biomass feedstock fueling.

2. EPA classifies emissions as health hazards that threaten the public health and welfare.

3. Emissions can be tracked and mapped outlining major transportation routes and cities.

4. All hydrocarbon- (HC-) fueled heat engine exhaust emissions contribute as health hazards where exhaust (tailpipe) emissions (< 10 to 140 nm) includes aircraft and mobility/stationary systems. Particulate pollution effects living tissue and is found to be detrimental to cardiovascular and respiratory systems where ultrafine particulates directly translocate to promote vascular system diseases.

5. Diseased organic vapors are detectable and constitute an early warning system, which when combined with telemedicine could institute a major advance and cost reduction in medical care.

6. ALL HC-fueled heat engines are major sources of these hazardous emissions, and general aviation is developing electric and hydrogen-fueled propulsion systems with unmanned aerial vehicles already in use.

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