Analysis of Hydrocarbons by In-Line GC/MS

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Motivation

- Liquid fuels are also one of the major sources of energy driving the aviation industry.
- Use of these fuels are connected to emissions.
- Studies have linked soot to adverse impact on human health and environment.

![Graph showing energy sources](image)

Annual Energy Outlook, 2015

David et al., Atmos. Environ. 43, (2009)
Motivation

- Soot formation is a combination of complex chemical and physical processes
- The dominant pathway to soot formation varies with fuel composition
- C₂H₂ as an important soot precursor
- aC₃H₄, pC₃H₄, C₄H₆ plays significant role soot growth pathways

Detailed Soot Model = Gas Chemistry Model + Soot Particle Dynamic model
Background: Detailed Mechanisms

- Commercial and military aviation fuels are complex mixers of hydrocarbons
- Consists of n-paraffins, isoparaffins, cycloparaffins and aromatics
- A reactive system involving these fuels will have huge number of additional stable and radical species
Multicomponent Fuel

Fast thermal pyrolysis

Pyrolysis

C₀⁻C₄ Oxidation

- Dodecane oxidation (JetSurF 2.0)
- $\varphi = 0.5$
- Nitrogen = 98%
- $T = 1050$ K, $P = 1$ atm
Reactor Design

Atmospheric pressure reactor

High pressure reactor
Experimental setup

Schematic of experimental setup showing: 1 - nitrogen gas cylinder; 2 - mass flow controllers; 3 - micro flow reactor in vented high-pressure enclosure chamber; 4 - fuel atomizer; 5 - atomizer housing; 6 - liquid fuel pump; 7 - fuel reservoir; 8 - quartz microprobe; 9 - needle valve; 10 – GCMS system; 11 - pressure gauge; 12 - vacuum pump.
The Reactor
Vacuum Pump

The pump maintains a pressure of 0.5 atmosphere on the sampling system.
The GC/MS

6-port valve in a heated enclosure

Gauges for monitoring vacuum status. One is on the in-line to the valve. One on the exit-line.

Connection to the reactor. The GC/MS is running in liquid mode so the line is disconnected in this photo.
Connection to the GC/MS

The heater jacket is not installed on the line in this photo.

Mass flow controller
Controls the flow out of the reactor.
GC-MS Chromatogram (JP-8)

- Propylene
- 1,3-Butadiene
- 1,3-Cyclopentadiene
- 1,3-Pentadiene
- 2-Butene
- Butane
- Propadiene
- Cyclopentene
- 1,3-Cyclohexadiene
- 1,2-Butadiene
- Toulene
- Ethylbenzene
- p-xylene
- m-xylene
- Trimethylbenzene
- Benzene
- Indene

Retention Time:
$t \approx 590 \text{ ms}$
Analytical Goal

- Actual Samples will be gaseous and at high temperatures
- Gas standards are only available for lighter compounds
- There is a need to calibrate the instrument for heavier compounds
  - Naphthalene
  - Anthracene
- We are establishing correlations between available gaseous standards and standards of the same components in solutions
  - Hexane
  - Benzene
  - Cyclohexene (future work)
Preliminary Results (290 ppmv hexane)

![Bar chart showing intensity vs runs for gas and liquid samples.](chart.png)
References