Analysis of Hydrocarbons by In-Line GC/MS

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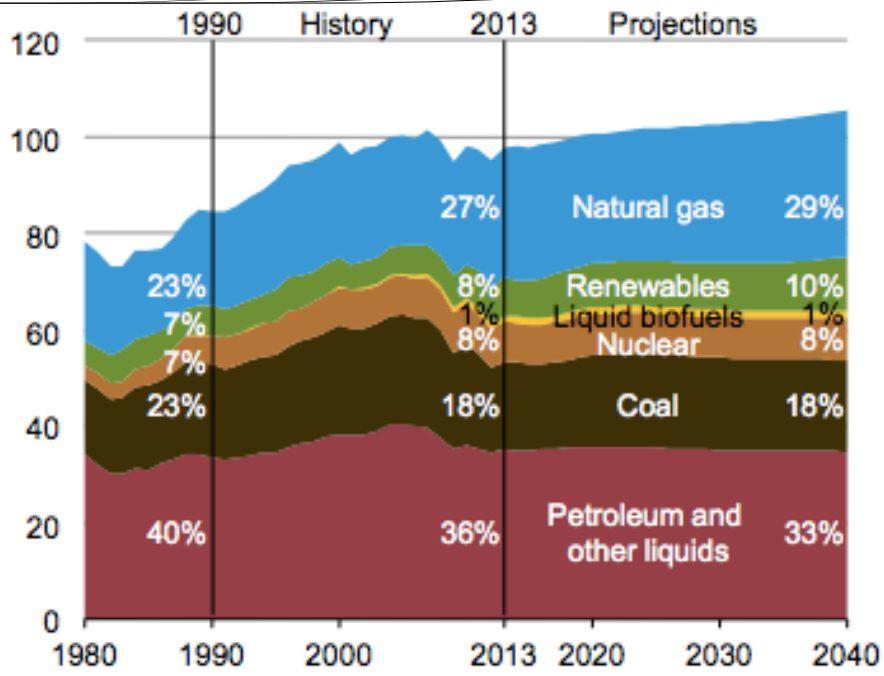
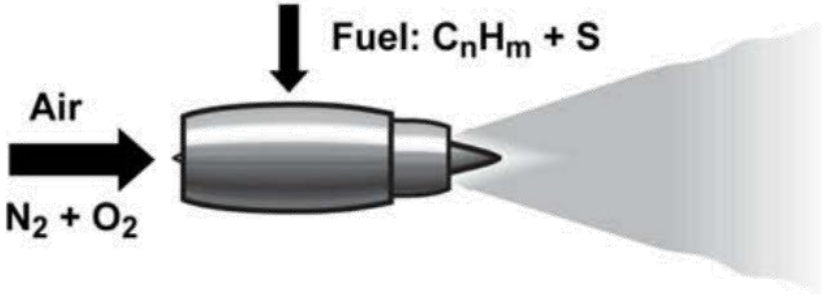
Motivation

- 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



Annual Energy Outlook, 2015



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

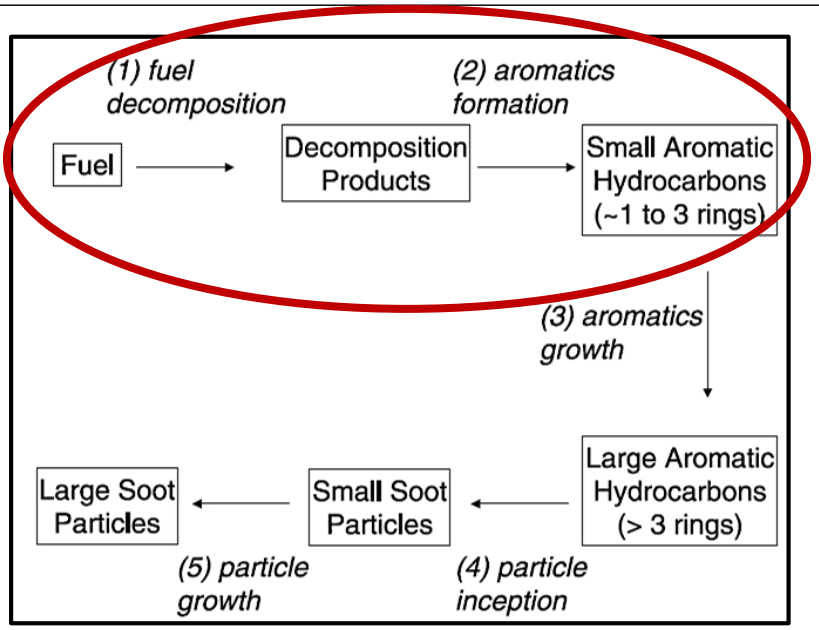
Complete combustion products:

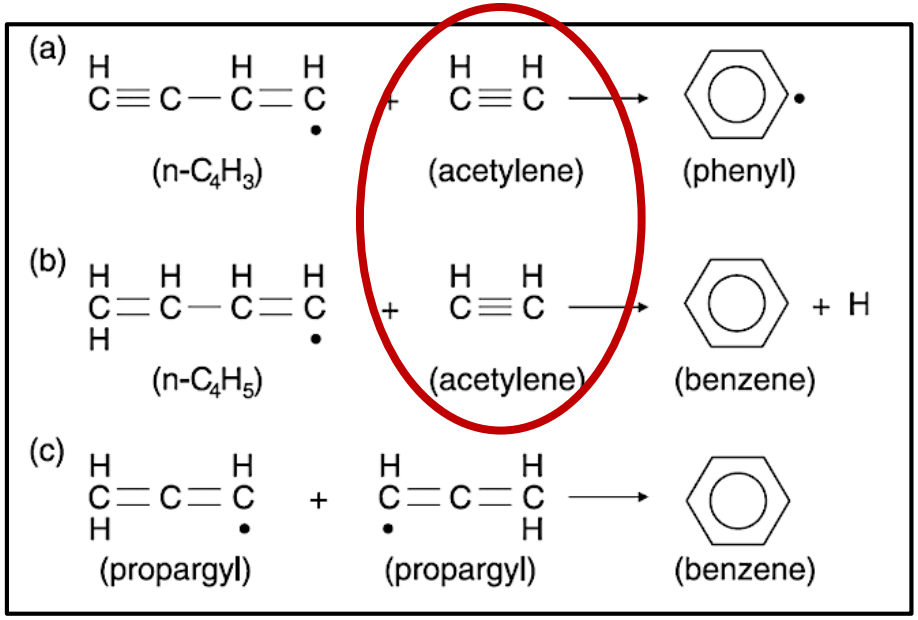
$CO_2 + H_2O + N_2 + O_2 + SO_2$

Actual combustion products:

$CO_2 + H_2O + N_2 + O_2 + NO_x + CO + HC + soot + SO_x$

Motivation

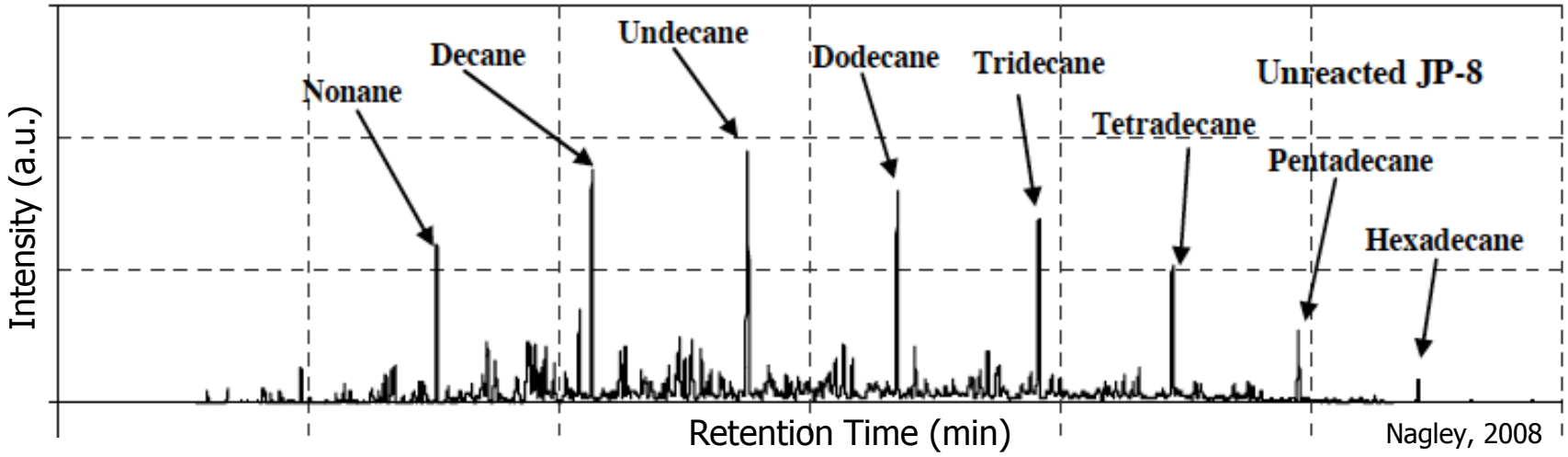




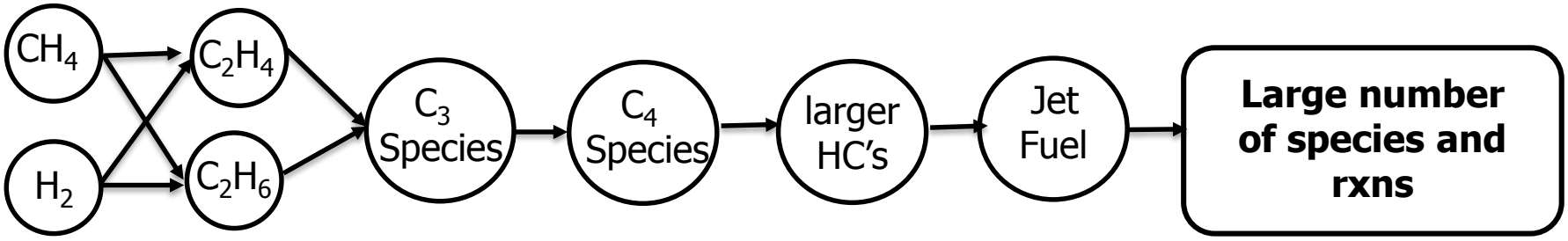
- Soot formation is a combination of complex chemical and physical processes
- The dominant pathway to soot formation varies with fuel composition
- C_2H_2 as an important soot precursor
- aC_3H_4, pC_3H_4, C_4H_6 plays significant role soot growth pathways

Detailed Soot Model = Gas Chemistry Model + Soot Particle Dynamic model

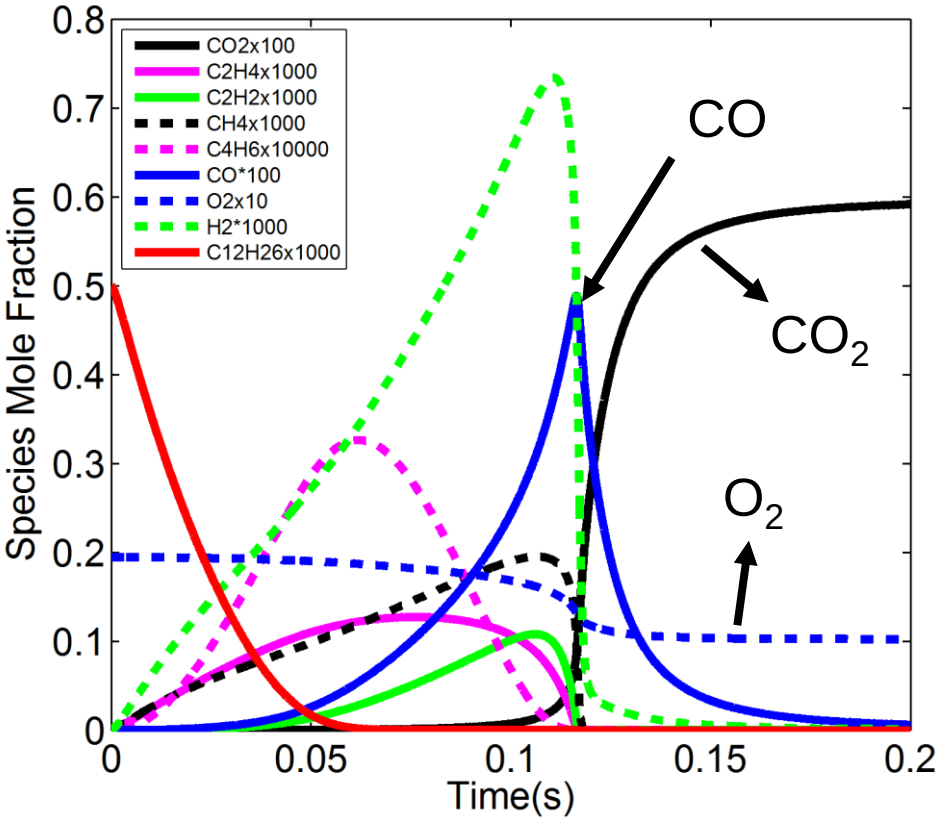
Background: Detailed Mechanisms



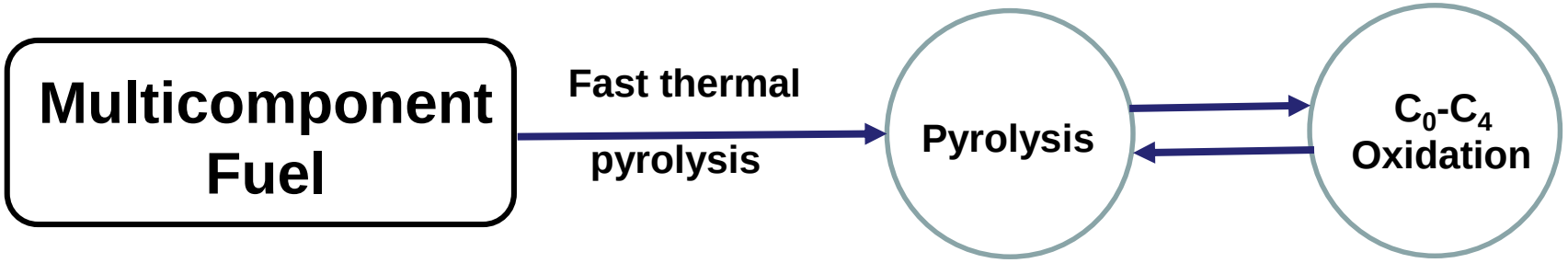
- Commercial and military aviation fuels are complex mixers of hydrocarbons
- Consists of n-paraffins, isoparaffins, cycloparaffins and aromatics
- A reactive system involving these fuels will have huge number of additional stable and radical species



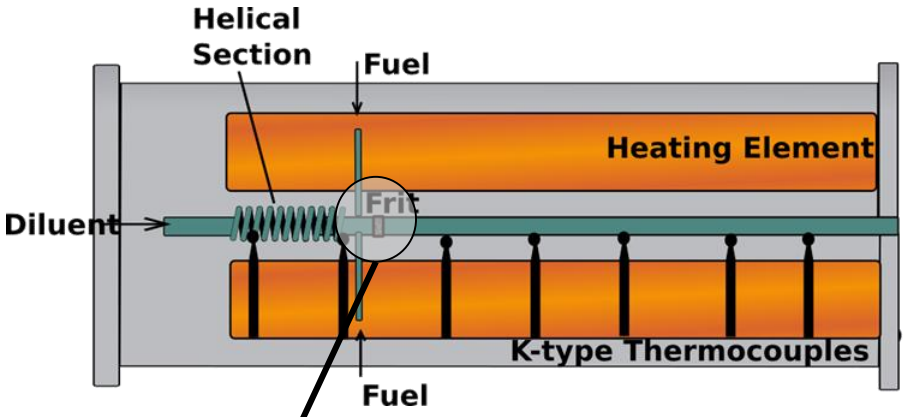
Reaction Chemistry



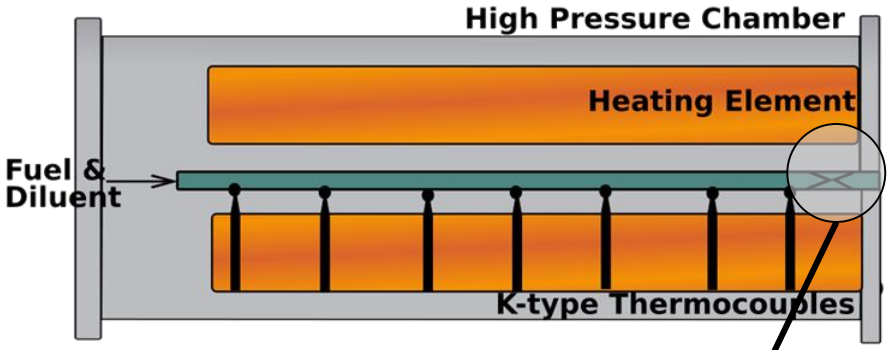
- Dodecane oxidation (JetSurF 2.0)
- φ = 0.5
- Nitrogen = 98%
- T=1050 K, P=1 atm



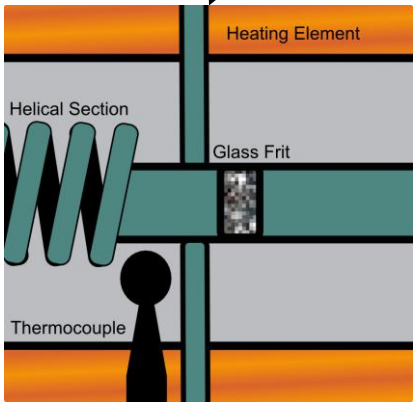
Reactor Design

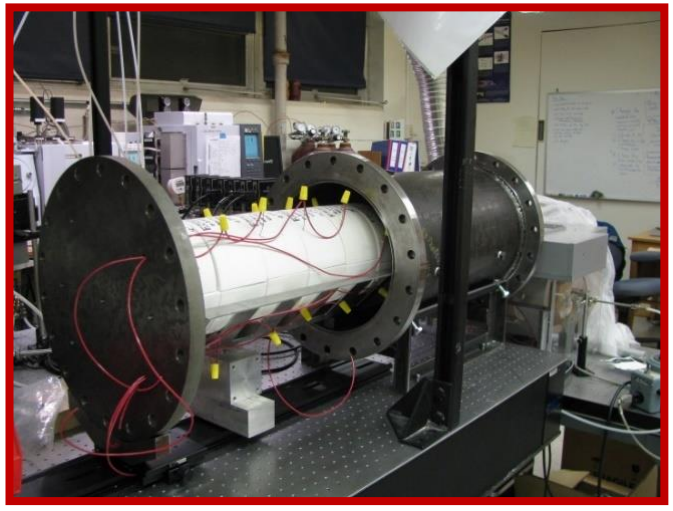


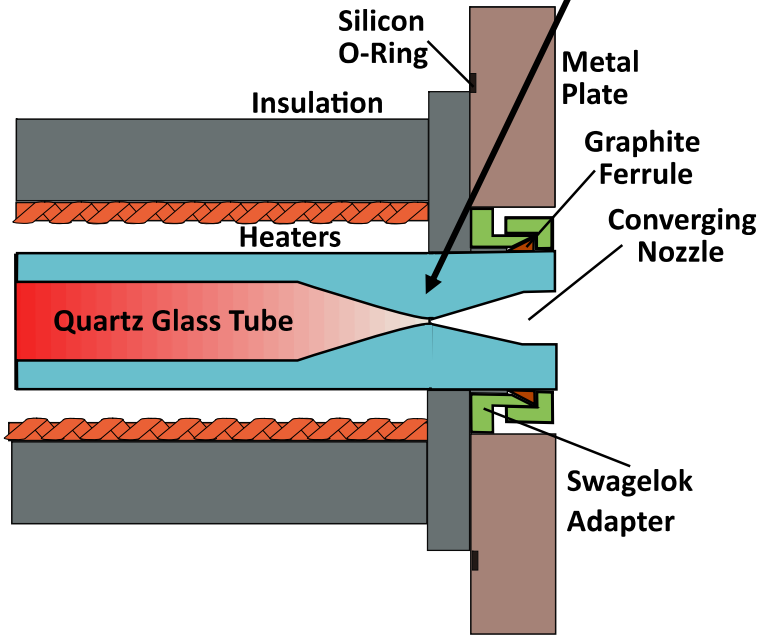
Atmospheric pressure reactor



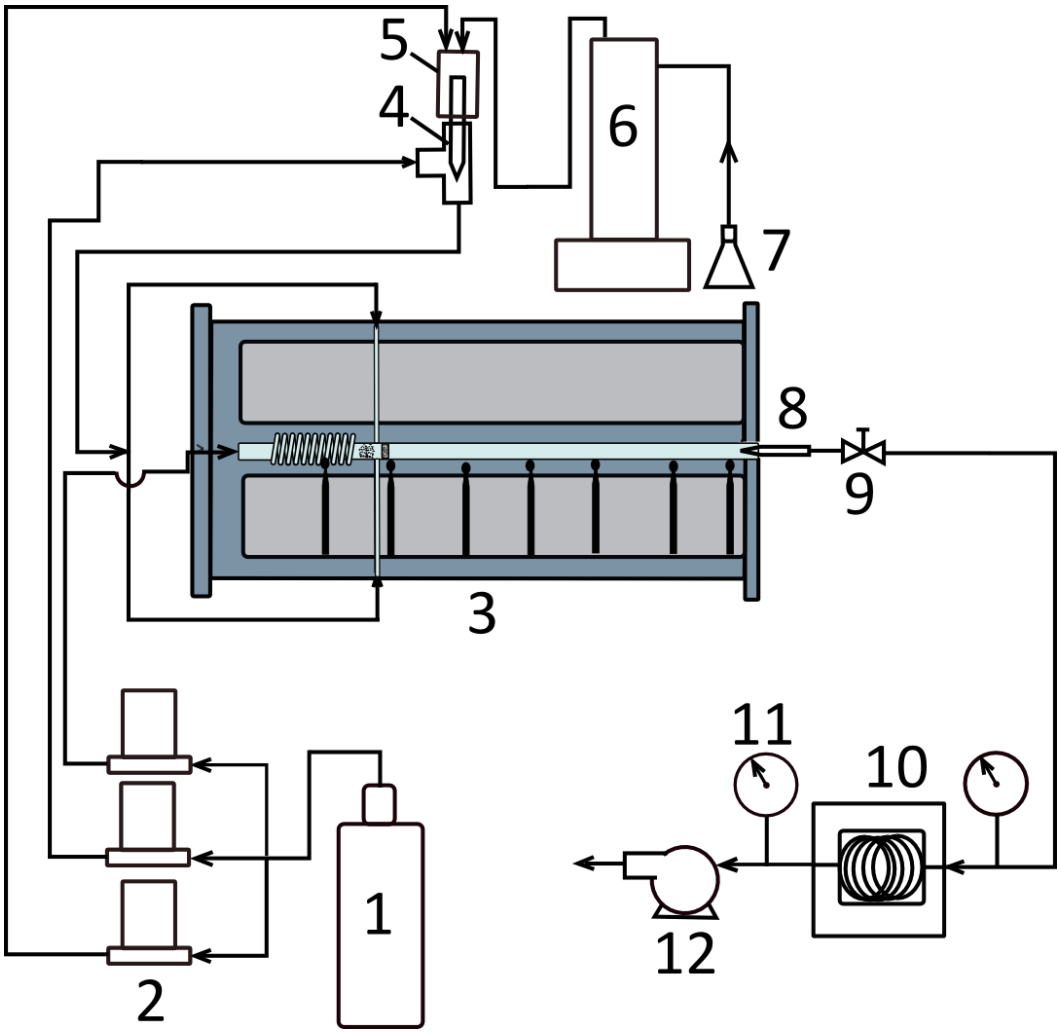
High pressure reactor





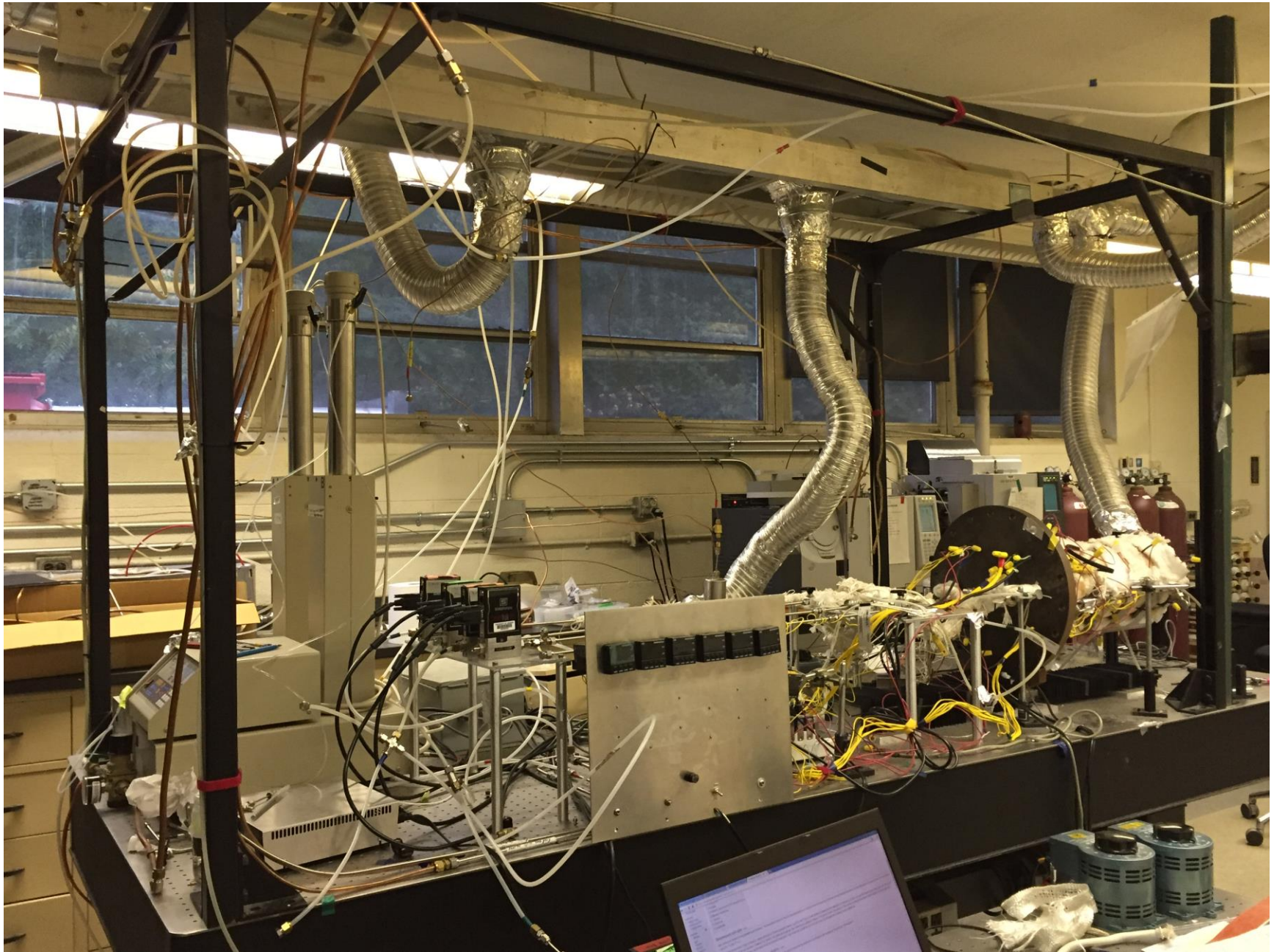


Experimental setup

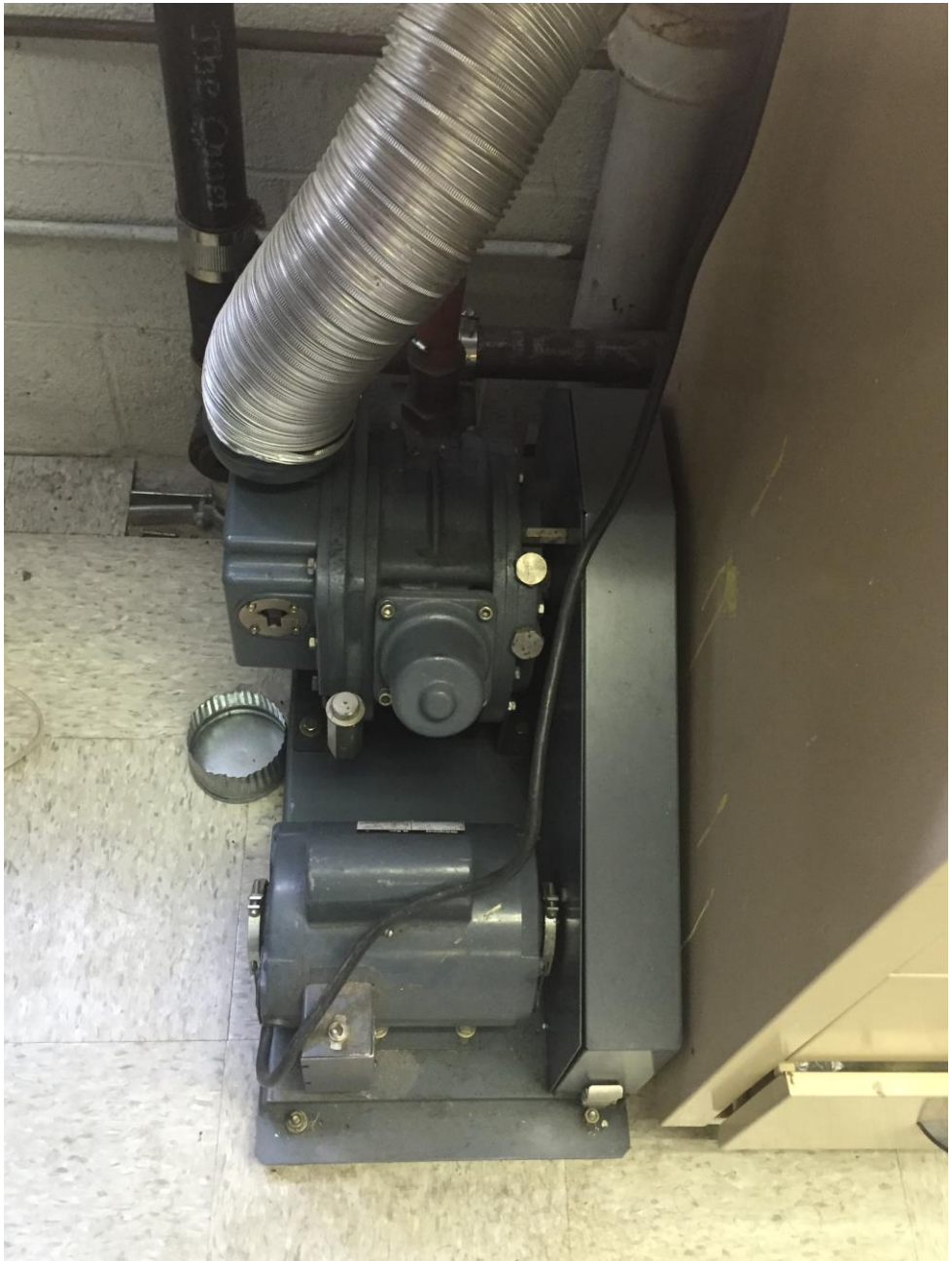


Schematic of experimental setup showing: 1 - nitrogen gas cylinder; 2 - mass flow controllers; 3 - micro flow reactor in vented high-pressure enclosure chamber; 4 - fuel atomizer; 5 - atomizer housing; 6 - liquid fuel pump; 7 - fuel reservoir; 8 - quartz microprobe; 9 - needle valve; 10 – GCMS system;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

The Reactor

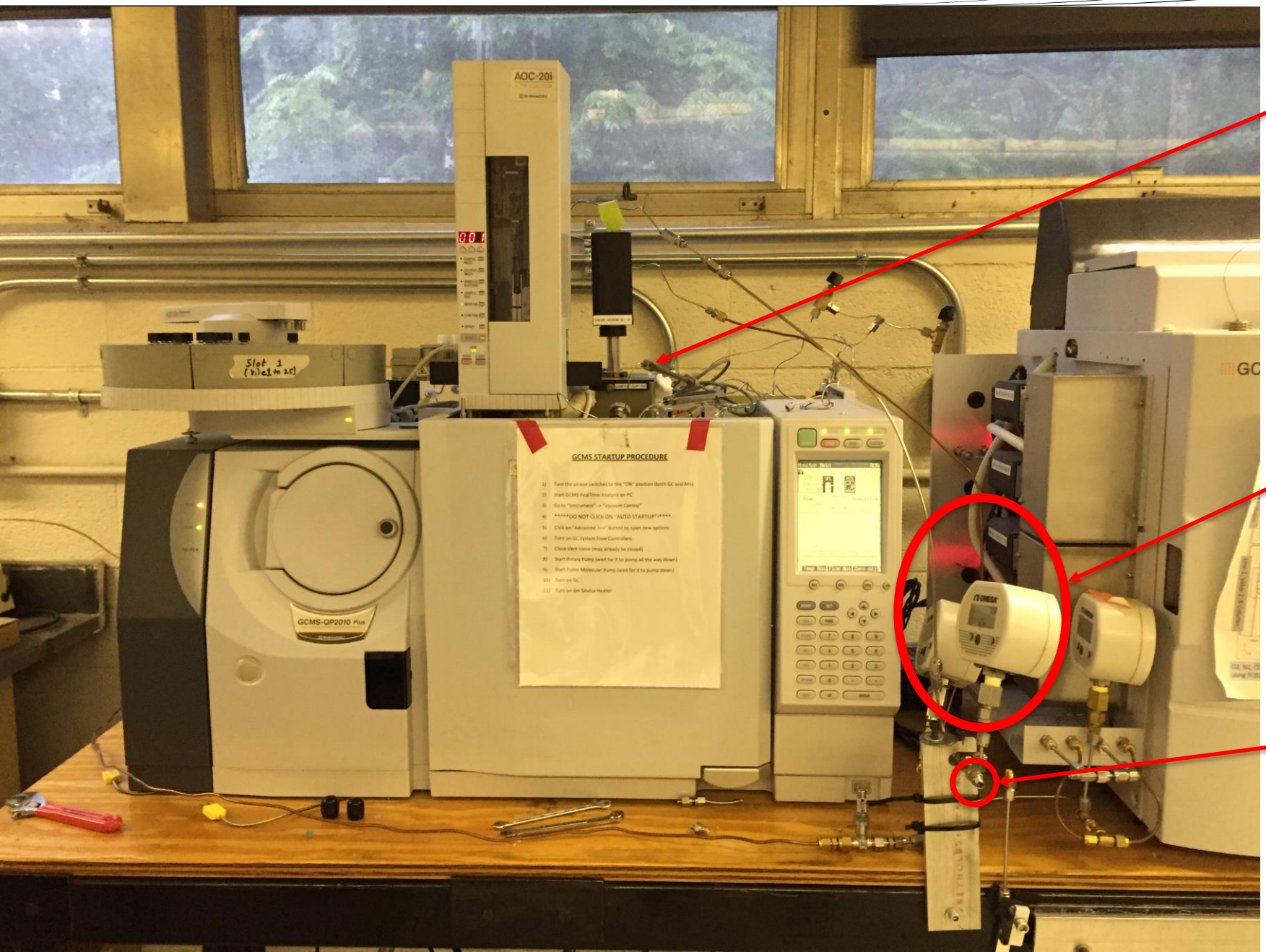


Vacuum Pump



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

The GC/MS

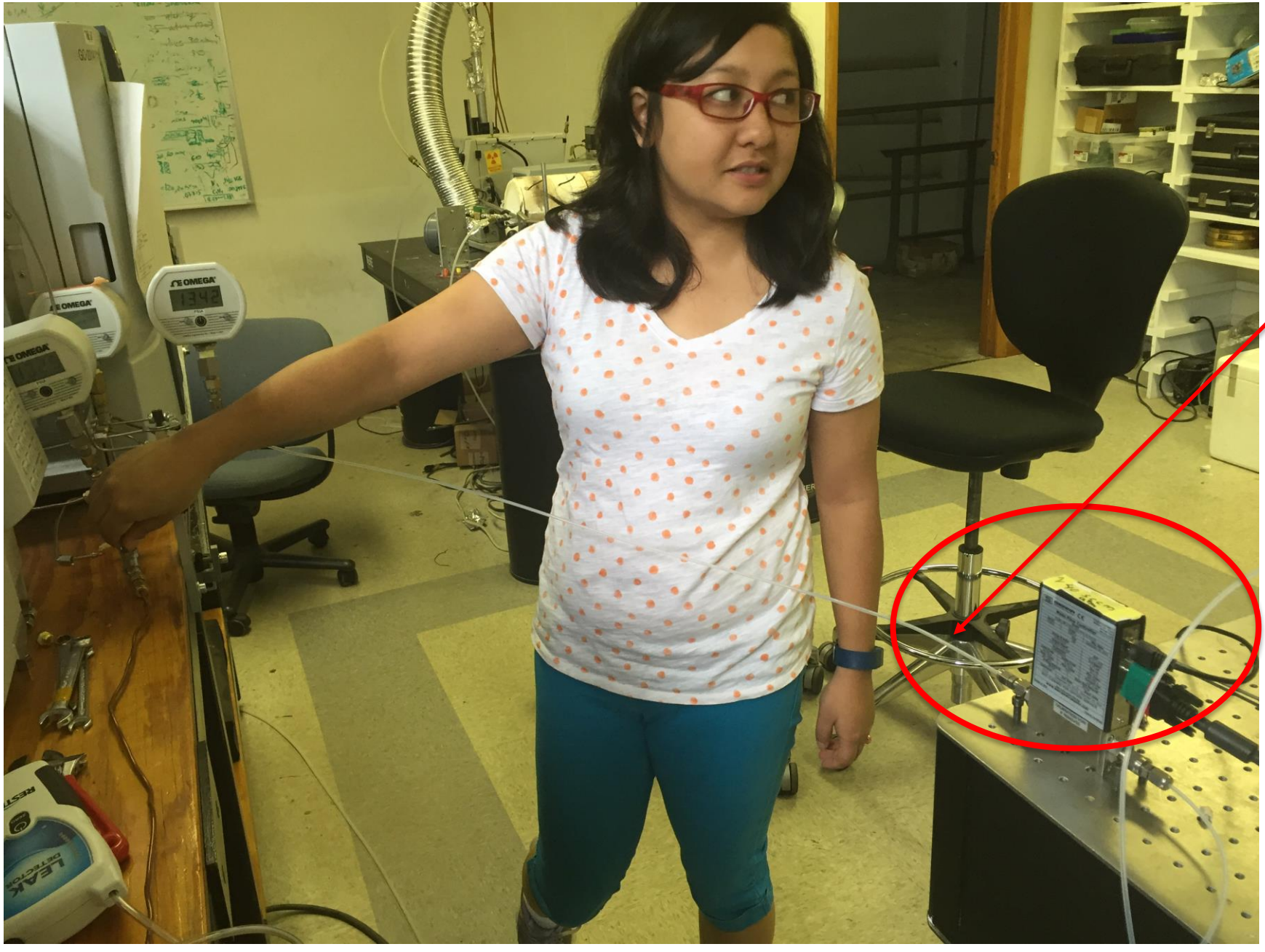


6-port valve in a heated enclosure

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

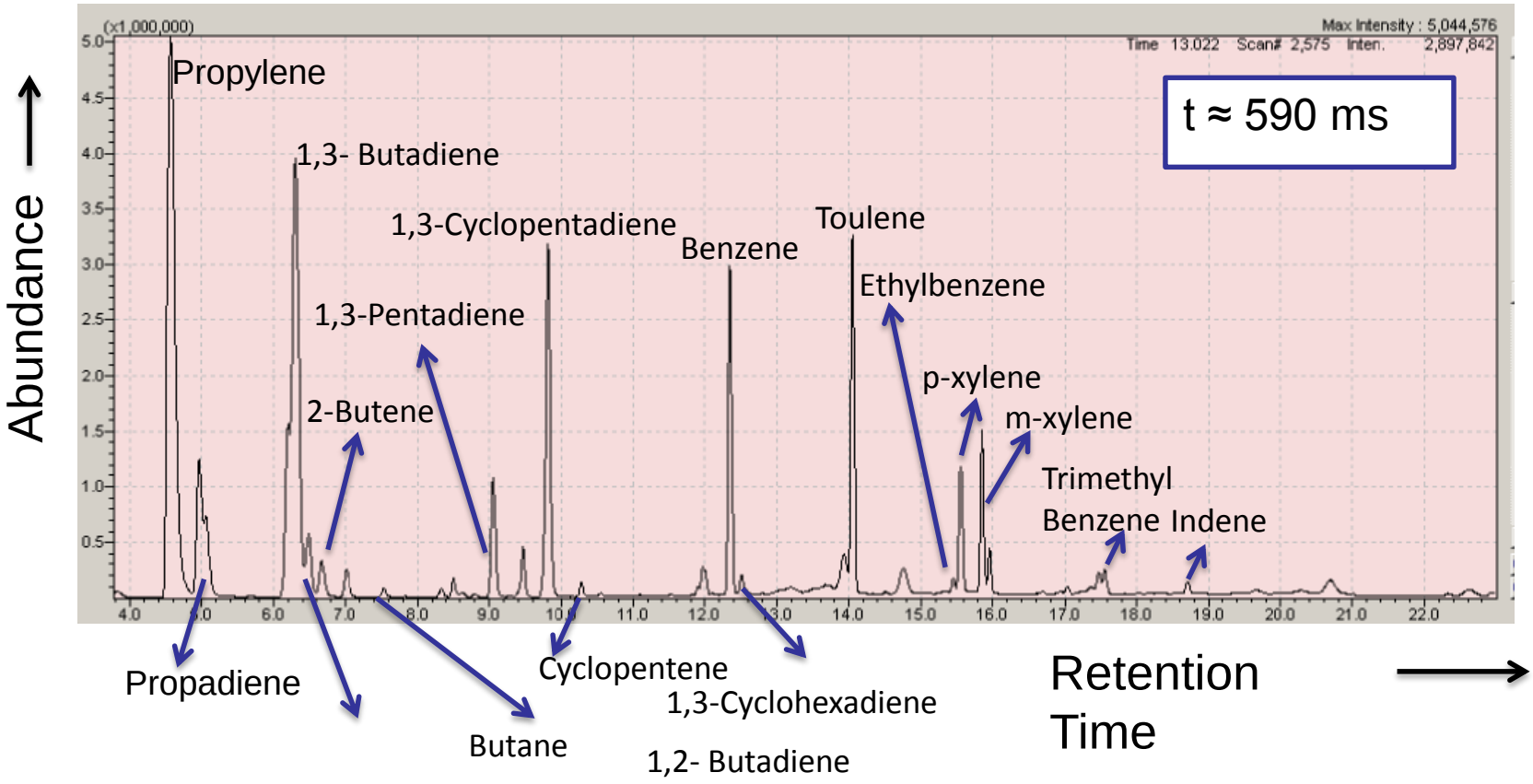


Line to GC/MS

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

Mass flow controller
Controls the flow out of the reactor.

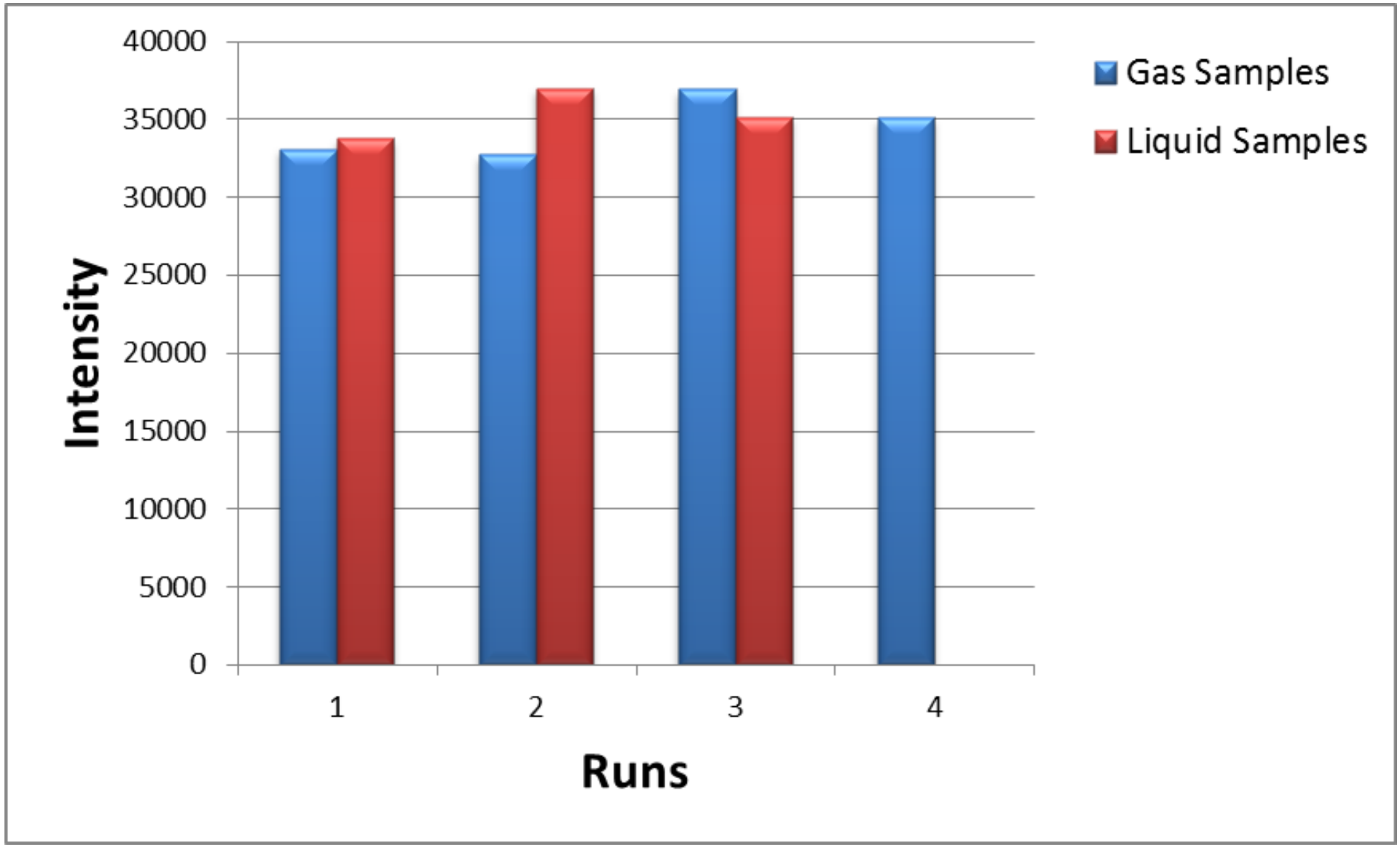
GC-MS Chromatogram (JP-8)



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)



References

- A. E. Outlook, "US Energy Information Administration Washington." DC, 2015
- D. S. Lee, D. W. Fahey, P. M. Forster, P. J. Newton, R. C. N. Wit, L. L. Lim, B. Owen, and R. Sausen, "Aviation and global climate change in the 21st century," *Atmos. Environ.*, vol. 43, no. 22, pp. 3520–3537, 2009.
- C. S. McEnally, L. D. Pfefferle, B. Atakan, and K. Kohse-Höinghaus, "Studies of aromatic hydrocarbon formation mechanisms in flames: Progress towards closing the fuel gap," *Prog. Energy Combust. Sci.*, vol. 32, no. 3, pp. 247–294, Jan. 2006.
- E. A. Nagley, "Fuel Composition Analysis of Endothermically Heated JP-8 Fuel for Use in a Pulsed Detonation Engine", 2008.
- U. Shrestha, "Fuel Pyrolysis at Atmospheric and High Pressure Condition", Ph. D. Proposal, 2016.