Microreactor Investigations of the Oxidation of Diesel and Model Soots

An Update on the Investigation of the Impact of the Soluble Organic Fraction of Particulate Matter on Diesel Particulate Oxidation Kinetics

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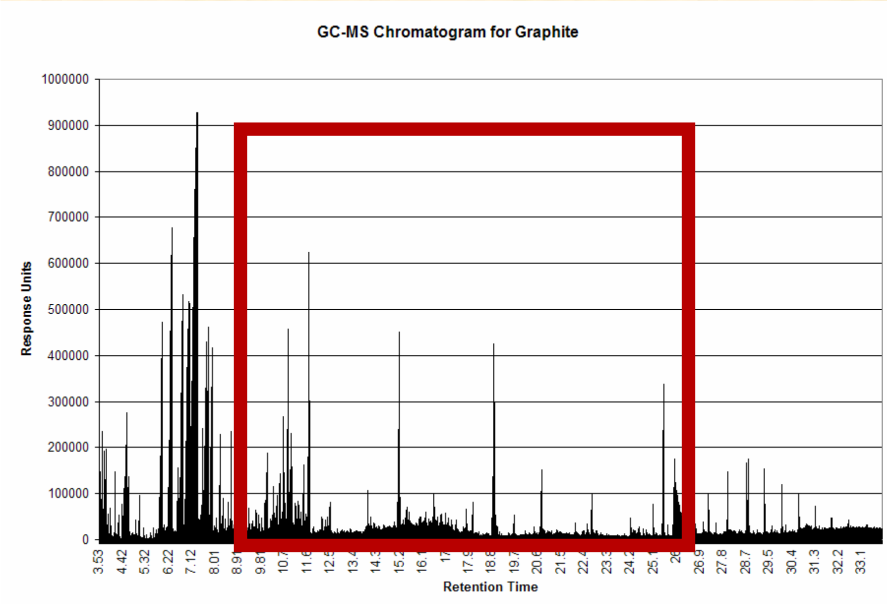
Research Objective

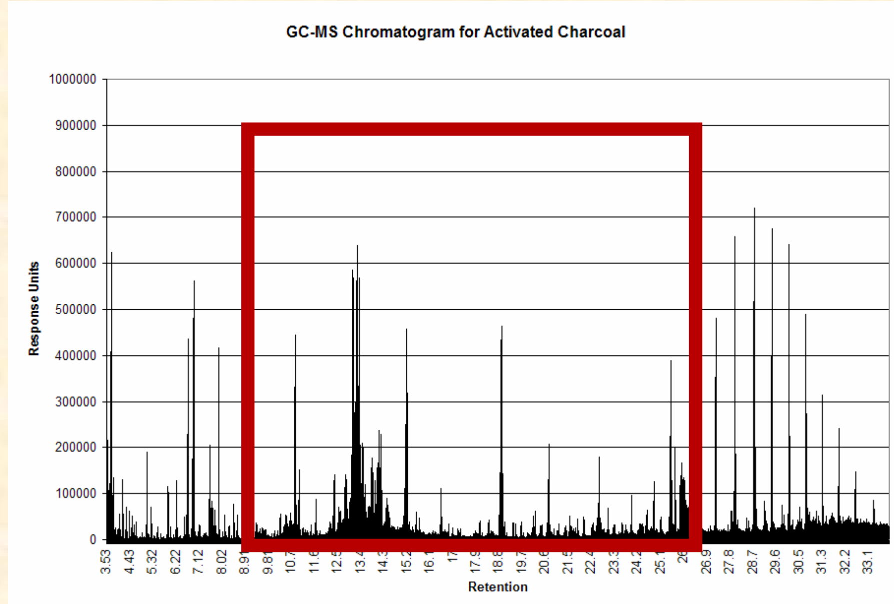
Determine the major constituents and properties of the soluble organic (SOF) component of diesel engine particulate matter as a function of the fuel and combustion conditions and the effect of the volatile properties and composition on PM oxidation kinetics.

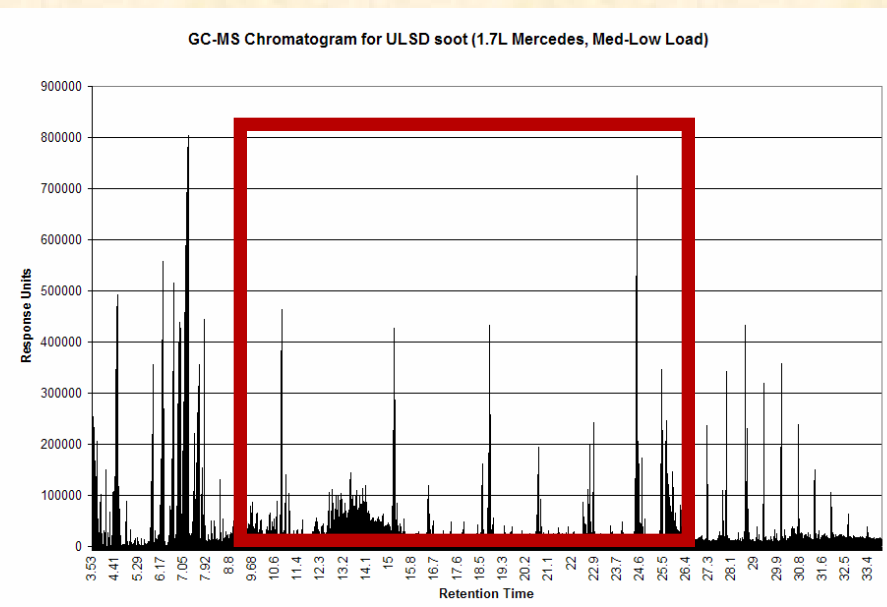
Determining the Impact of Volatiles

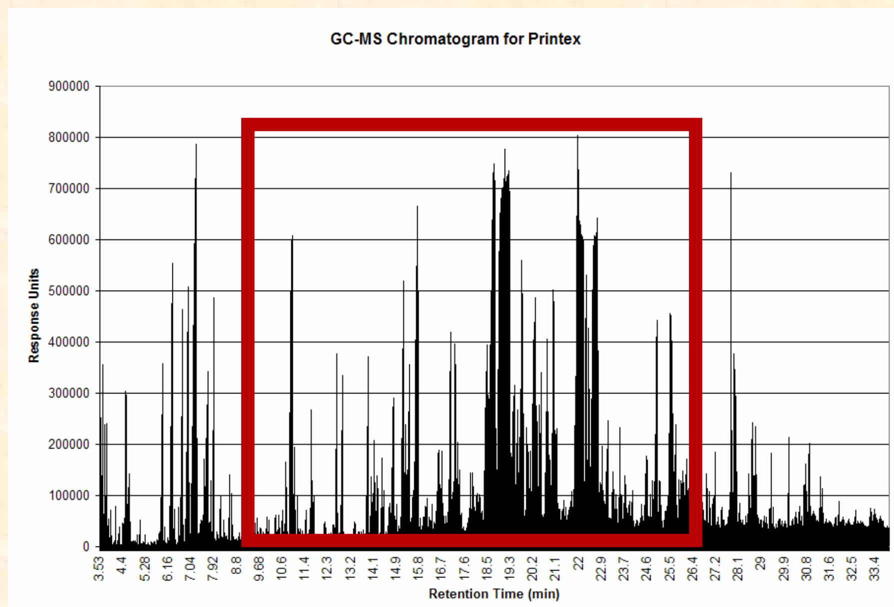
- **Identify SOF** by solid phase extraction and GC-MS analysis.
- **Measurement of fundamental kinetics** for SOF-laden PM devolatilization and oxidation under near-isothermal, differential conditions in a microreactor.
- **Microscopic and physio-chemical characterization** of SOF-laden and extracted samples. (Collaboration with R. Vander Wal)
- **Measurement of global kinetics** for volatile-laden PM on 1x3 filter core samples in a benchflow reactor at realistic device-like conditions.
- **Development of a suitable reaction mechanism** for the dominant SOF and solid carbon reactions.
- **Evaluation of the correlations** among the kinetic, microscopic, and physio-chemical PM properties and the PM oxidation-regeneration behavior in the benchflow reactor filter core experiments.

Identification of Extractable Organics









SOF Extraction

- Extraction of SOF using solid phase extraction and analysis of SOF components using GC-MS. (2007 SAE F&L)
  - Methods
    - Super critical CO_2 extraction
    - Soxhlet extraction
    - Microwave extraction (new technology)
  - Samples
    - Soot on teflon coated quartz filters
    - Powder soot samples
    - Soot on cordierite

- Experiments to determine what impacts SOF species are underway.
  - Fuel type (B100, blends, ULSD)
  - Collection Temperature
  - Engine set point

Kinetic Parameter Determination

- Measurement of Activation Energy for model soots, oxidation of SOF components, devolatilized soot oxidation, and oxidation of SOF-laden soot using a microreactor.
- Oxidation Samples
  - Pre-treated (SOF removed) soot and Printex-U samples to match work by Yezerets et. al
  - SOF desorption/oxidation (TPD/TPO)
    - thermally desorbed in Ar during 50-600C temperature ramp.
    - oxidized in subsequent reactor with supplemental O_2 flow (10%)
  - SOF-laden soot oxidation (TPO)
    - Oxidized completely to CO_2 using the two reactor system.

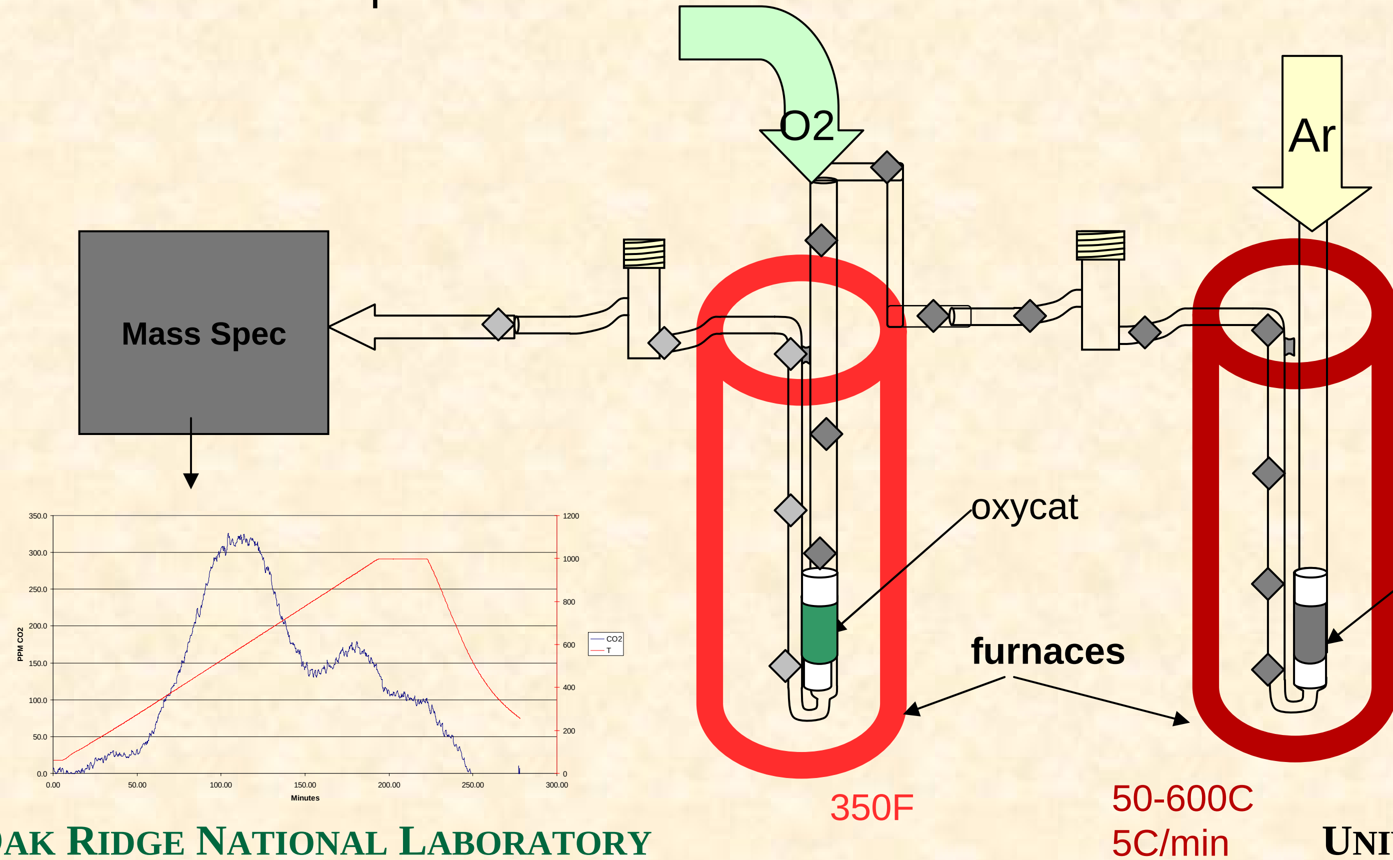
Does SOF have an impact on oxidation?

- In order to determine whether there is an impact from the SOF, a completely dry baseline sample is needed.
  - Printex, Activated Charcoal and Graphite were used as model soot standards.
  - For confidence in total devolatilization of the soot samples, an *in situ* devolatiliation was developed using two reactors in series.
  - The devolatilization temperature range was investigated from 600C to 1000C.
  - An oxycat was used in a secondary reactor for conversion of the volatiles to CO/CO_2.

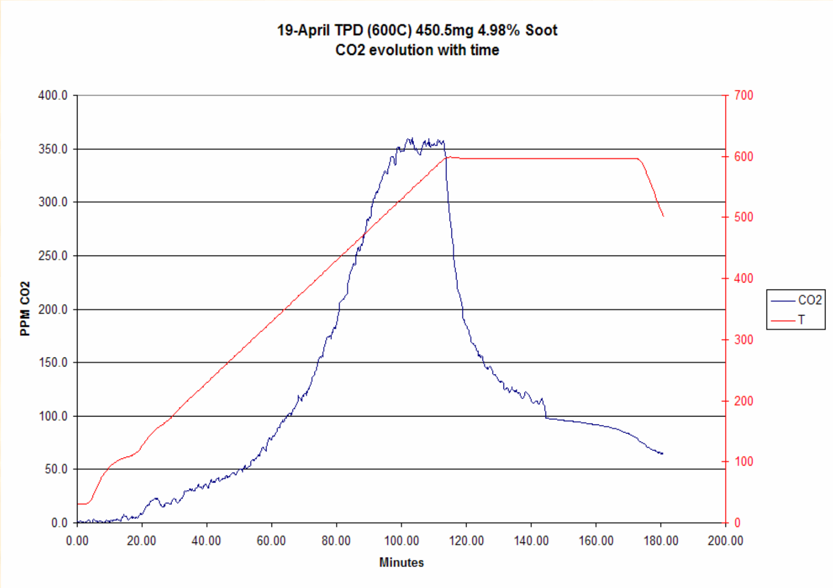
Microreactor Experimental Setup

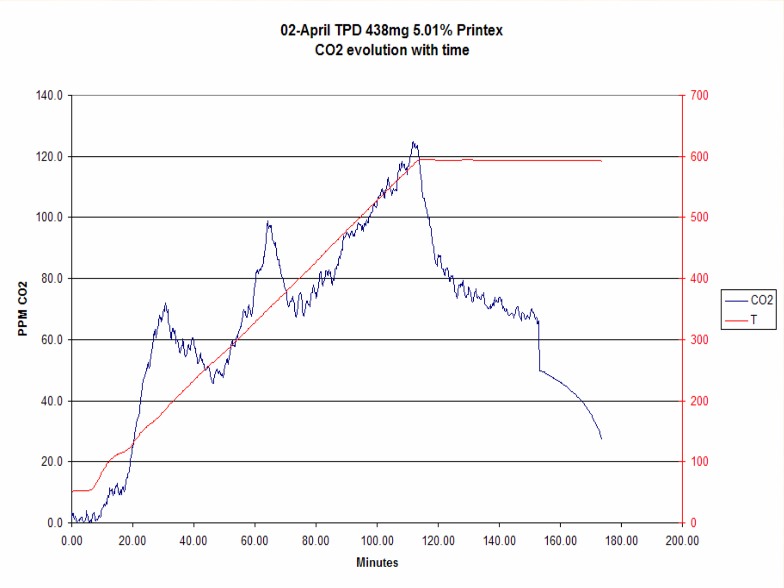
Investigations of *in-situ* SOF devolatilization and oxidation (TPD+O) and oxidation of SOF-laden soot (TPO) were carried out in the dual U-tube reactor.

- For *in-situ* devolatilization, Ar was flowed through the soot bed in reactor 1, which was heated from 50-600C (or 1000C) at 5C/min and O2 was introduced before reactor 2, containing the oxy-cat, held at 350C.
- A mass spectrometer was used to measure the CO2 evolution with time.



TPD Sample Results

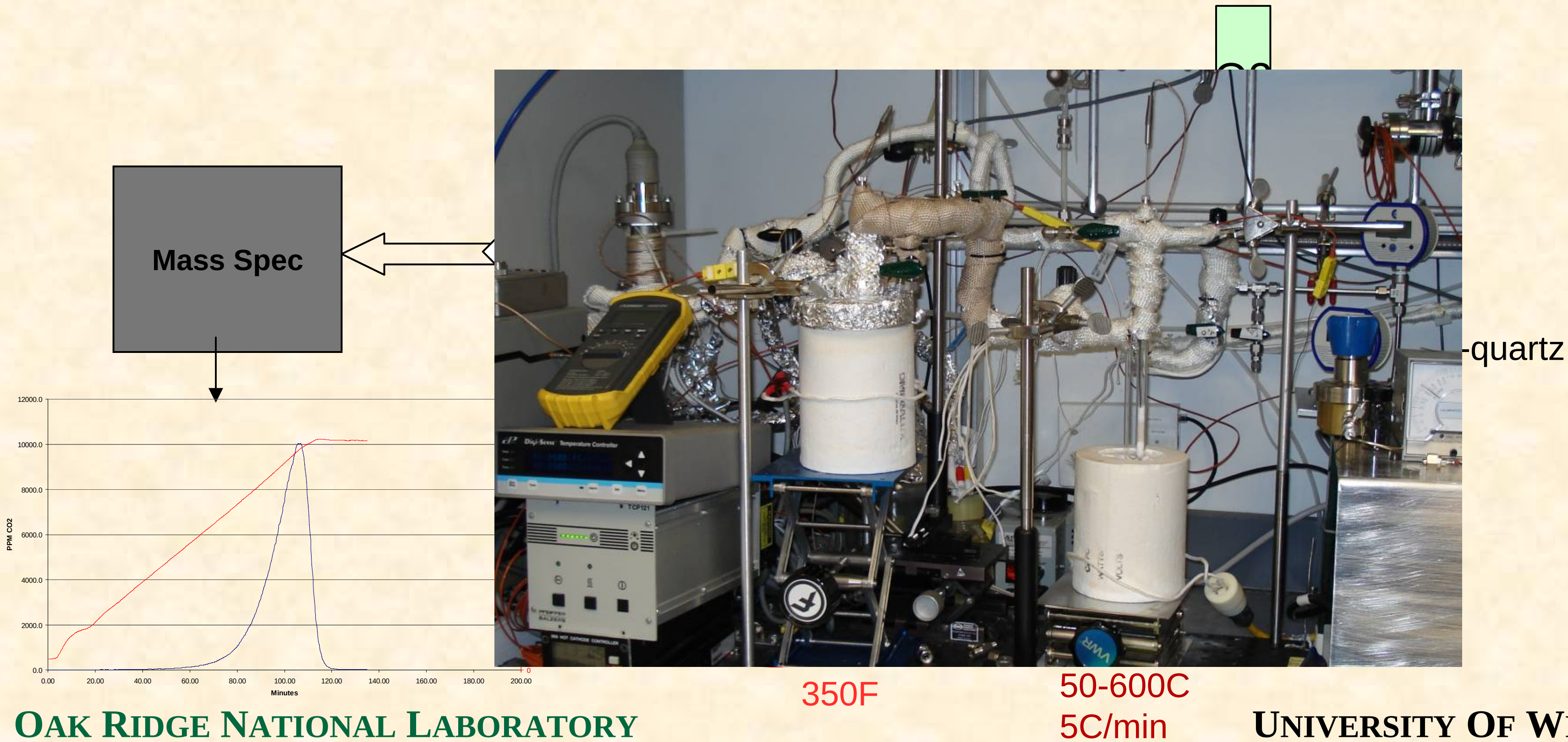




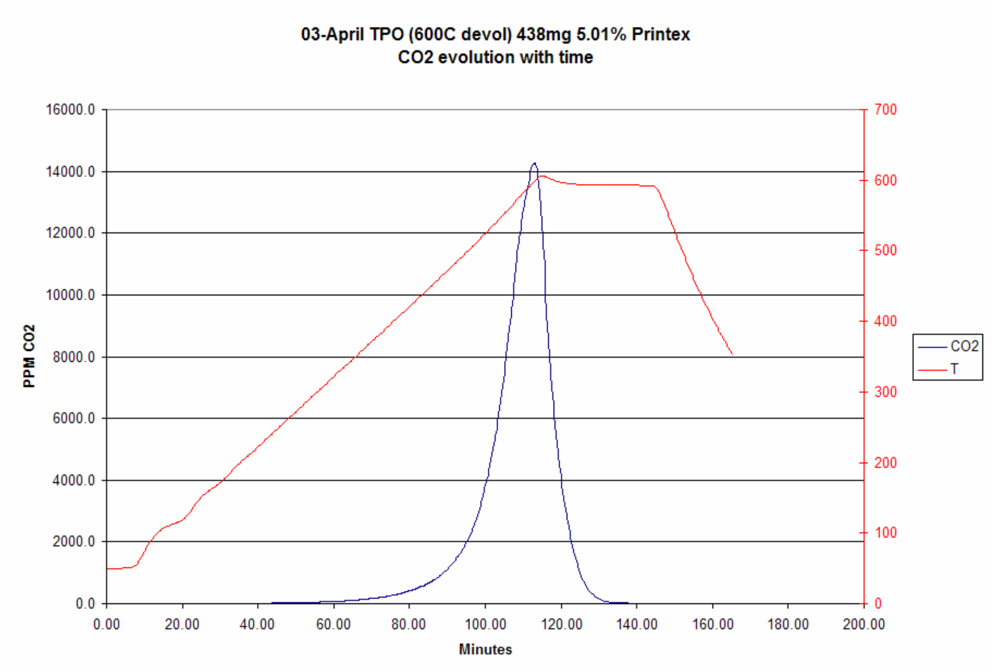
Microreactor Experimental Setup

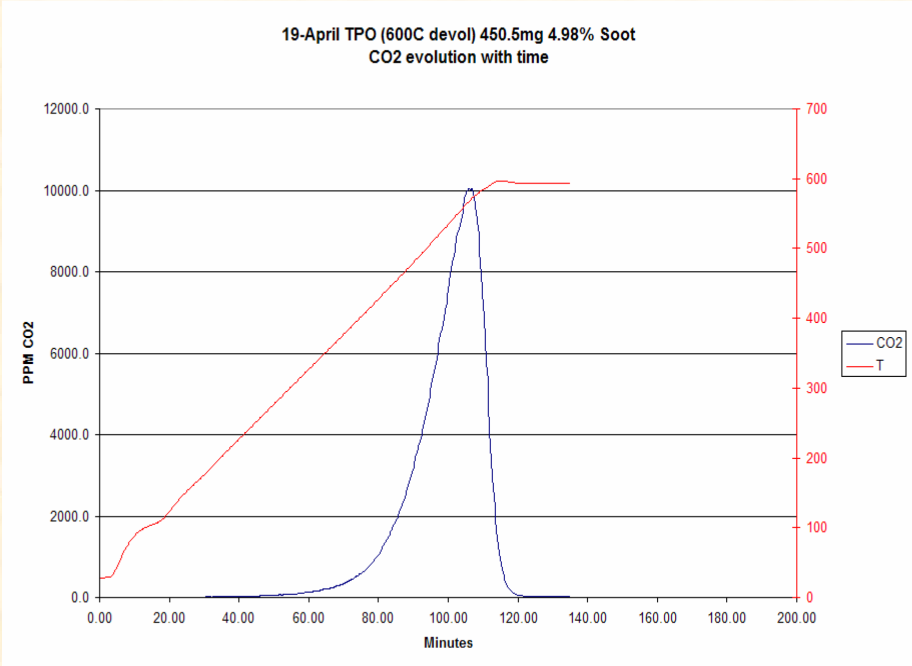
TPOs could be done using only one reactor. Two are used in these experiments for consistency.

- For oxidation, O2 was flowed through the soot bed in reactor 1, which was heated from 50-600C at 5C/min before continuing into reactor 2, containing the oxy-cat, held at 350C.
- A mass spectrometer was used to measure the CO_2 evolution with time.



TPO Results

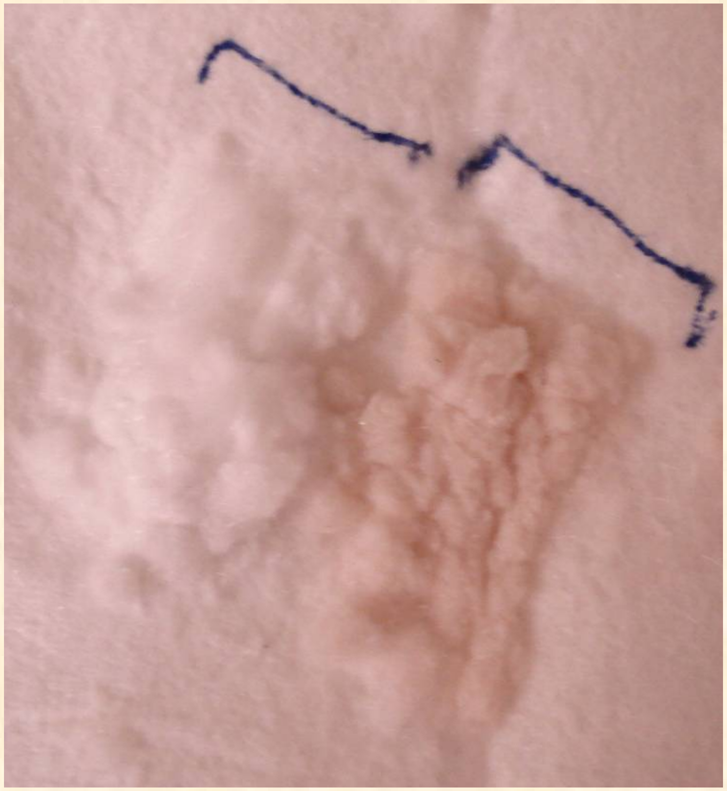




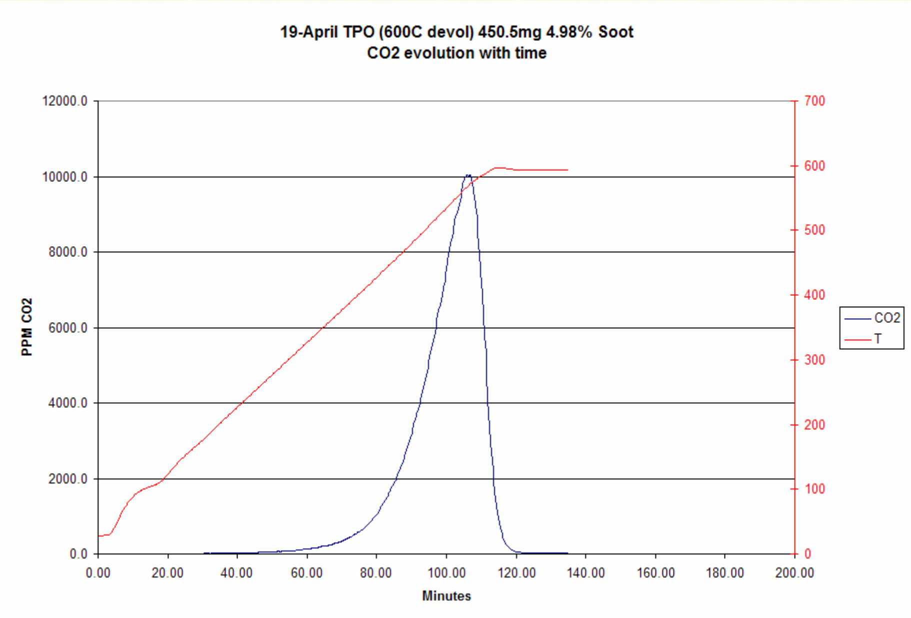
		Soot Conv. Range		Temperature Range	
Activation Energy		Low	High	Low	High
Ea (kJ/mol):	113.6	30%	40%	557	573
Ea (kJ/mol):	74.1	40%	50%	573	583

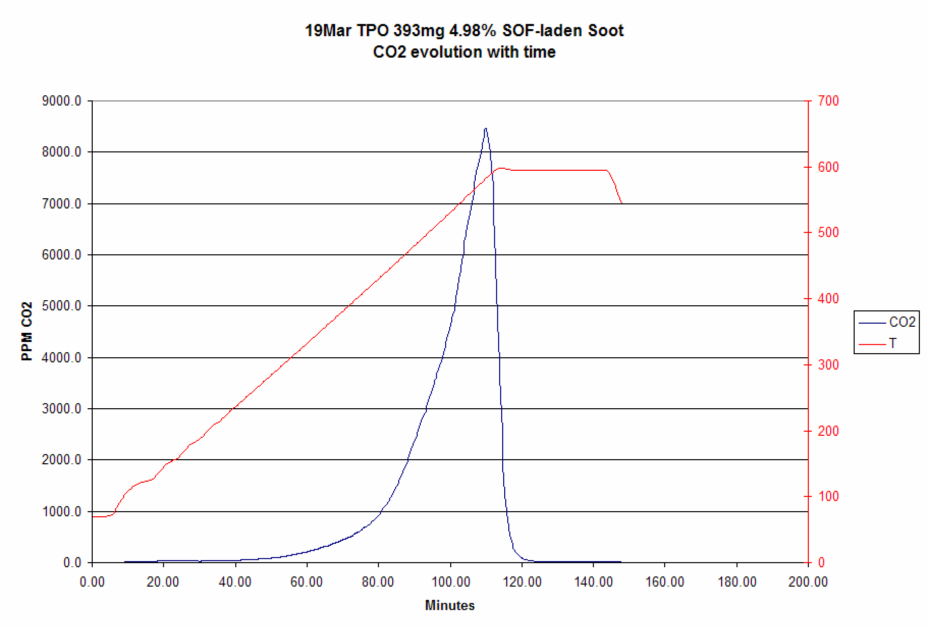
		Soot Conv. Range		Temperature Range	
Activation Energy		Low	High	Low	High
Ea (kJ/mol):	82.9	30%	40%	518	534
Ea (kJ/mol):	79.2	40%	50%	534	547

Pictures of Samples after TPO



Impact of Volatiles?





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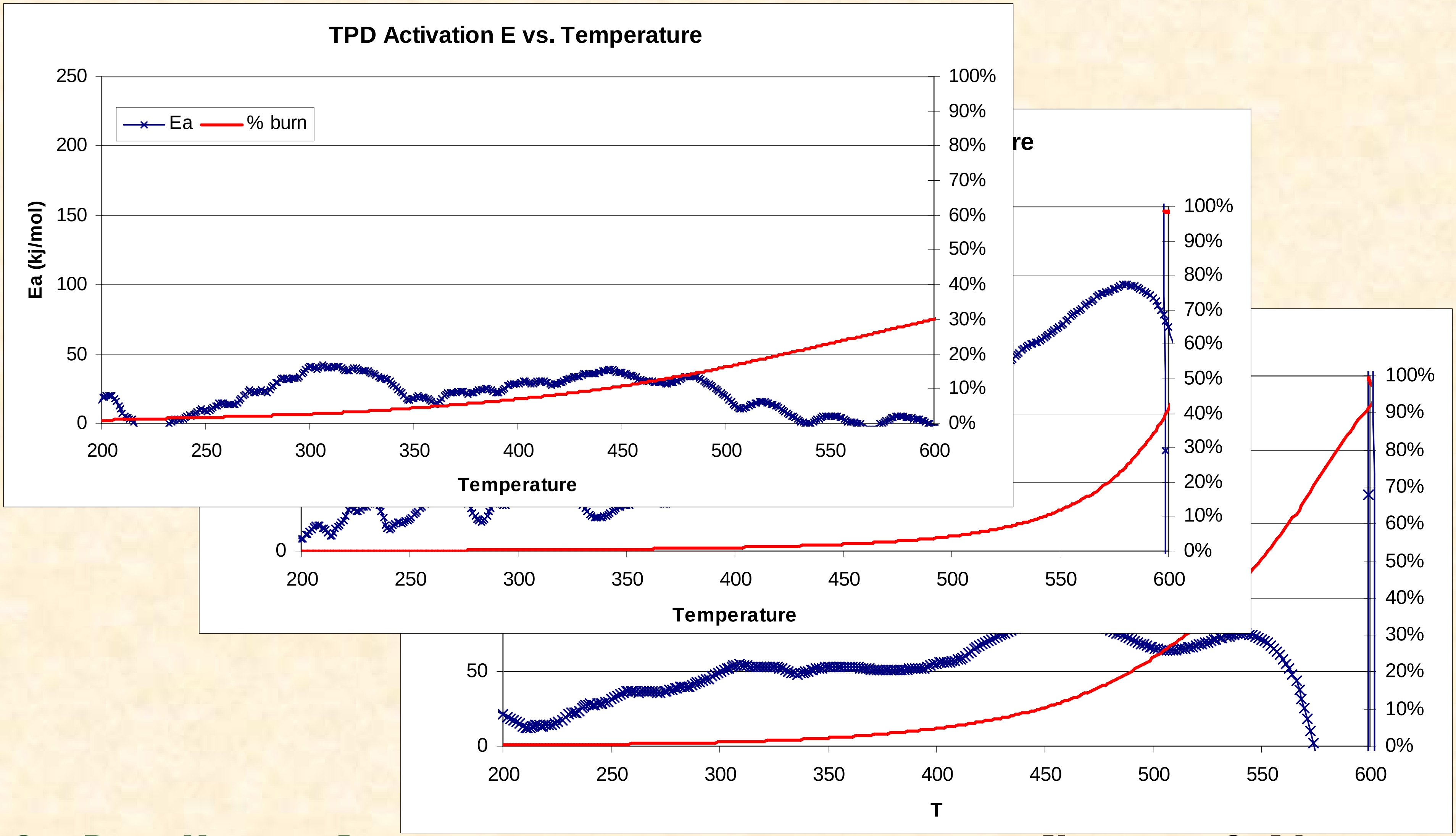
		Soot Conv. Range		Temperature Range	
Activation Energy		Low	High	Low	High
Ea (kJ/mol):	66.4	30%	40%	512.1	530.1
Ea (kJ/mol):	62.6	40%	50%	530.1	546.2

Activation Energy and % Burn Out with T



Comparison Summary

Sample	BET (m2/g)	T start	T peak	T end	Ea (40-50% burn)
de-vol soot	200	407	581	600	82.9
soot	-	384	584	590	62.6
printex	-	423	600	600	112.3
activated C	600	338	523	600	71.7
graphite *	6	628	756	800*	138.7

Additional samples run include a HD diesel soot at 2 load points with ULSD and B20.

- Preliminary results indicate that there is an oxidative advantage for volatile laden soot on the order of 20 kJ/mol.
- Printex, a low-volatile carbon black, has a lot of non-soot volatiles (PAHs, napthalene-range boilers), which actually may impede oxidation.
- similar to devolatilized soot. Devolatilizing the Printex does not change its burn characteristics.
- Devolatilizing samples above 600C leads to graphitization of carbon in the sample.
- Activated charcoal is the standard most similar to diesel soot, though has 3x surface area.

Path Forward

- BET on SOF-laden soot and Printex.
- GC-MS analysis of solvent extracted samples.
- Collaboration with Randy Vander Wal to determine carbon structure of samples.
- C-H analysis (proximate analysis) on samples.
- Fuel-doped soot standards kinetics investigation.
- Investigation of dilution, temperature, fuel and combustion conditions on SOF quantity and components.

Determining the Impact of Volatiles

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Acknowledgements

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- **Todd Toops**
- **Sam Lewis**
- **John Storey**

- **Alex Yezrets**

Is this useful? DOE and I would like to know…….

- **Is this information needed?**
- **Is scope appropriate?**
- **Additional experiments/needs?**