EVALUATION OF ATMOSPHERIC IMPACTS OF SELECTED COATINGS VOC EMISSIONS

CARB Contract Number 00-333

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Summary of Progress through June 2002

Outline of Presentation

• Status of preparation of UCR EPA Chamber
• Progress on interfacing a total carbon analysis method to direct reactivity measurements.
• Results of reactivity analysis of petroleum distillates studied by Censullo et al (2002)
• Ongoing Work

Note: Current information about project available at http://www.cert.ucr.edu/~carter/coatings/
STATUS OF PREPARATION 
OF UCR EPA CHAMBER

Essentially all instruments to be used have been acquired, but some still being evaluated

Enclosure and temperature control systems are completed and perform satisfactorily. Some formaldehyde and NO\textsubscript{x} offgasing observed.

Preliminary experiments were conducted with a large “pillow bag” and blacklights. Data indicate background low enough for low NO\textsubscript{x} experiments

Argon arc light is now operational, but not with final spectrum. Performance being evaluated

Final spectral filter may be delivered in July

Construction is underway on final chamber configuration and mixing and injection systems. Process taking longer than expected

Now looks like first experiments with final configuration may be conducted in July

Draft QA plan, data processing procedures, and standard operating procedures developed

Current information about project available at http://www.cert.ucr.edu/~carter/epacham/
Two large air Handlers are located in the corners on each side of the light (not shown).

This volume kept clear to maintain light uniformity

Temperature controlled room flushed with purified air and with reflective material on all inner surfaces

Dual Teflon Bag Reactors

Sample lines go to lab below

Access Door

200 KW Light Source Near Wall
MEASUREMENT OF DIRECT REACTIVITY

Background
Direct reactivity measures the $O_3$ formed directly from the VOC’s reactions. Such measurements could reduce mechanism evaluation ambiguities.

A plug flow HONO photolysis system has been developed for direct reactivity measurements.

Such measurements have potential to provide reactivity data at lower cost than chamber runs.

The current system works well for high volatility compounds suitable for GC analysis, but not for low volatility compounds or complex mixtures.

Interfacing the system with a total carbon analysis method should reduce the cost and may permit use with lower volatility compounds.

Current Objectives
- Develop total carbon analysis method that can be interfaced to existing system
- Improve low volatility injection procedures
- Evaluate performance with high and low volatility compounds and petroleum distillates
• Catalyst from air purifier for Byron Model 15, heated to ~370°C.
• Sub-ppm sensitivity CO₂ analyzer funded by ACC gift
Comparison of concentrations derived by CO₂ converter with calculated amounts injected.
RESULTS OF EXPERIMENT WITH N-OCTANE USING CO$_2$-BASED CARBON ANALYSIS

VOC INJECTED AND MEASURED CARBON

![Graph showing CO$_2$ (ppm) and calculated C Injected over time.]

- CO$_2$ (ppm) axis: 0 to 30
- Minutes after lights on axis: 0 to 300
- Calculated C Injected
- CO$_2$

![Graph showing Δ([O$_3$]-[NO]) over time.]

- Δ([O$_3$]-[NO]) axis: 0 to 0.16
- Minutes after lights on axis: 0 to 300
- Δ([O$_3$]-[NO])
- Calc. VOC Injected (ppmC)
RESULTS OF EXPERIMENT WITH N-OCTANE USING CO₂-BASED CARBON ANALYSIS

- CO₂ data in good agreement with n-octane analysis by GC
- Results in fair agreement with model predictions. (Not shown because conditions not yet fully characterized for modeling)
RESULTS OF EXPERIMENT WITH MINERAL SPIRITS “B” USING CO₂-BASED CARBON ANALYSIS

TOTAL CARBON AND VOC INJECTED

CO₂ or VOCs (ppmC)

Injection Overload at start
Calculated C Injected

CO₂

Minutes after lights on

Calc. VOC Injected (ppmC)

Δ([O₃]-[NO])

Δ([O₃]-[NO]) (ppm)

Minutes after lights on
RESULTS OF EXPERIMENT WITH MINERAL SPIRITS “B” USING CO\textsubscript{2}-BASED CARBON ANALYSIS

1) Recovering from overload. VOC declining
2) Stepwise injection increases
3) Injection off, VOC declining rapidly

- MS “B” contains primarily C\textsubscript{11}-C\textsubscript{14} alkanes
- CO\textsubscript{2} response is higher compared to \(\Delta([O_3]-[NO])\) response when VOC is declining compared to when VOC is increasing
SUMMARY OF STATUS AND CURRENT PLANS FOR DIRECT REACTIVITY MEASUREMENT WORK

Catalytic combustion with CO₂ analysis works well in experiments with higher volatility compounds, eliminating the need for GC analysis.

However, current combustor system apparently has hang-up for lower volatility compounds and needs to be improved.

Use of smaller catalytic combustor with shorter inlet system and higher temperature is being investigated.

Once the combustor system is improved, it will be used to evaluate how to improve syringe pump injection system for low volatility compounds.
REACTIVITY ANALYSIS OF PETROLEUM DISTILLATES STUDIED BY CENSULLO ET AL.

Compositional data obtained for 41 types of petroleum distillates

- 9 types with $\geq 99\%$ alkanes (Bins 6, 11)
- 6 types with 2-8% aromatics (Bins 4, 9, 14)
- 10 types with 8-23% aromatics (Bins 10, 15)
- 16 types with 100% aromatics (Bins 21 - 23)

Two methods used to compute MIRs from the compositional information:

- Based on detailed GC analysis (using generic types only for unspeciated branched and cyclic alkanes)
- Based only on generic type (n-, iso-, or cyclic alkane or aromatic) and carbon number data

Computed MIRs are compared with MIR’s derived using CARB’s binning method
COMPARISONS OF MIRs DERIVED FROM DETAILED SPECIATION DATA WITH MIRs ESTIMATED USING CARB’s BIN METHOD

- 0-1% Aromatic
- 2-8% Aromatics
- 8-13% Aromatic
- 100% Aromatic

1:1 Line

CARB’s Bin MIR (mass O3 / mass VOC)

Calculated MIR from Compositions
COMPARISON OF MIRs DERIVED FROM GENERIC TYPES WITH MIRs DERIVED FROM DETAILED SPECIATION DATA

- Low Aromatic Solvents
- Standard SAPRC-99 Aromatic Lumping
- Aromatics Primarily Monoalkylbenzenes
- Aromatics Primarily Polyalkylbenzenes

1:1 Line
### SUMMARY OF TYPES OF AROMATICS IN AROMATIC-CONTAINING SOLVENTS ANALYZED BY CENSULLO ET AL

<table>
<thead>
<tr>
<th>Aromatic Type</th>
<th>Wt. Percent of All Solvent Aromatics</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Total</td>
</tr>
<tr>
<td>Monoalkyl Benzenes</td>
<td>9%</td>
</tr>
<tr>
<td>Dialkyl Benzenes</td>
<td>44%</td>
</tr>
<tr>
<td>Tri- and poly Alkylbenzenes</td>
<td>41%</td>
</tr>
<tr>
<td>Indans, Naphthalenes and Tetralins</td>
<td>6%</td>
</tr>
<tr>
<td>Unknown</td>
<td>0.3%</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>100%</td>
</tr>
</tbody>
</table>

Aromatics with no chamber data have uncertain reactivities because aromatic mechanisms have to be adjusted to fit chamber data.
SUMMARY OF RESULTS OF ANALYSIS OF CENSULLO ET AL DATA

CARB’s binning method performs reasonably well in predicting MIRs derived from Censullo et al’s compositional data.

Generic type analysis may be sufficient to estimate reactivities for all-alkane solvents, but not for high aromatic solvents.

SAPRC-99 representation of unspeciated aromatics may underestimate reactivities of aromatic constituents in petroleum distillates.

Most aromatics in these petroleum distillates are di- to polyalkyl benzenes.

Almost half of the aromatic mass in these petroleum distillates has no chamber data and therefore very uncertain reactivities.
COMPARISONS OF CALCULATED AND BIN
MIRs FOR HYDROCARBON SOLVENTS
DATA PROVIDED BY THE ACC

• Data for 78 aliphatic hydrocarbon solvents provided (aromatics <20%)
• Re-calculated MIRs are preliminary. Need information on aromatic carbon number dist.
• Some inconsistencies with ACC MIR values
ONGOING WORK

Chamber Experiments
Complete construction of UCR EPA chamber and begin characterization
Continue evaluating analytical instrumentation
Work with RRAC in selecting petroleum distillates for experiments

Direct Reactivity Measurement
Attempt to improve total carbon analysis system for use with low volatility compounds
Attempt to improve injection system
Use C_{12} – C_{16} n-alkanes and selected mineral spirit samples for evaluation

Reactivity Evaluation of Pet. Distillates
Compile data for additional samples as they become available
Develop standard spreadsheet format and reactivity and uncertainty analysis procedures