

EVALUATION OF ATMOSPHERIC IMPACTS OF SELECTED COATINGS VOC EMISSIONS

CARB Contract Number 00-333

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Summary of Progress through
November, 2003

Outline of Presentation

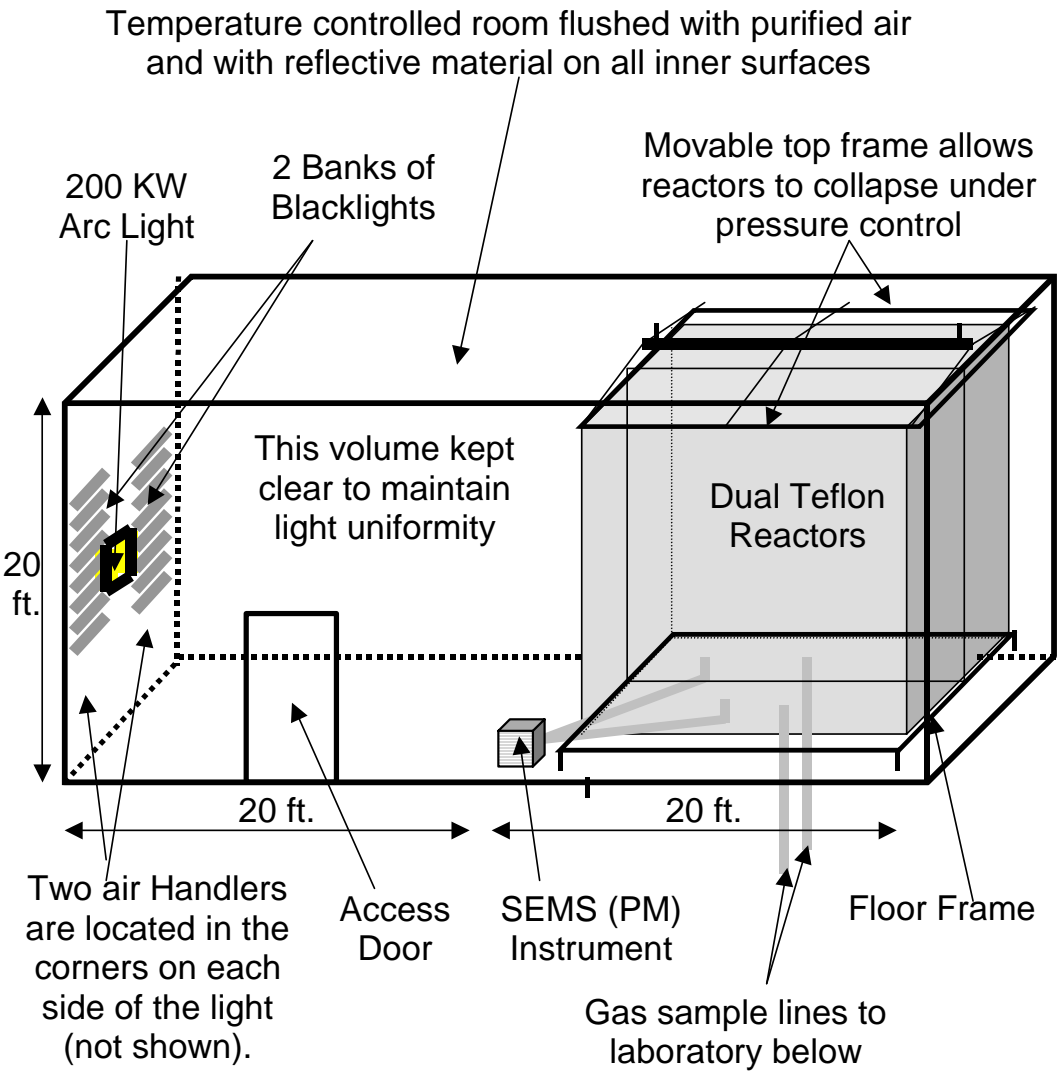
- Status of UCR EPA Chamber
- Environmental chamber experiments with representative petroleum distillates
- Development of experimental methods for Texanol®
- Status of development of a direct reactivity measurement method
- Ongoing Work

Note: Current information about project available at <http://www.cert.ucr.edu/~carter/coatings/>

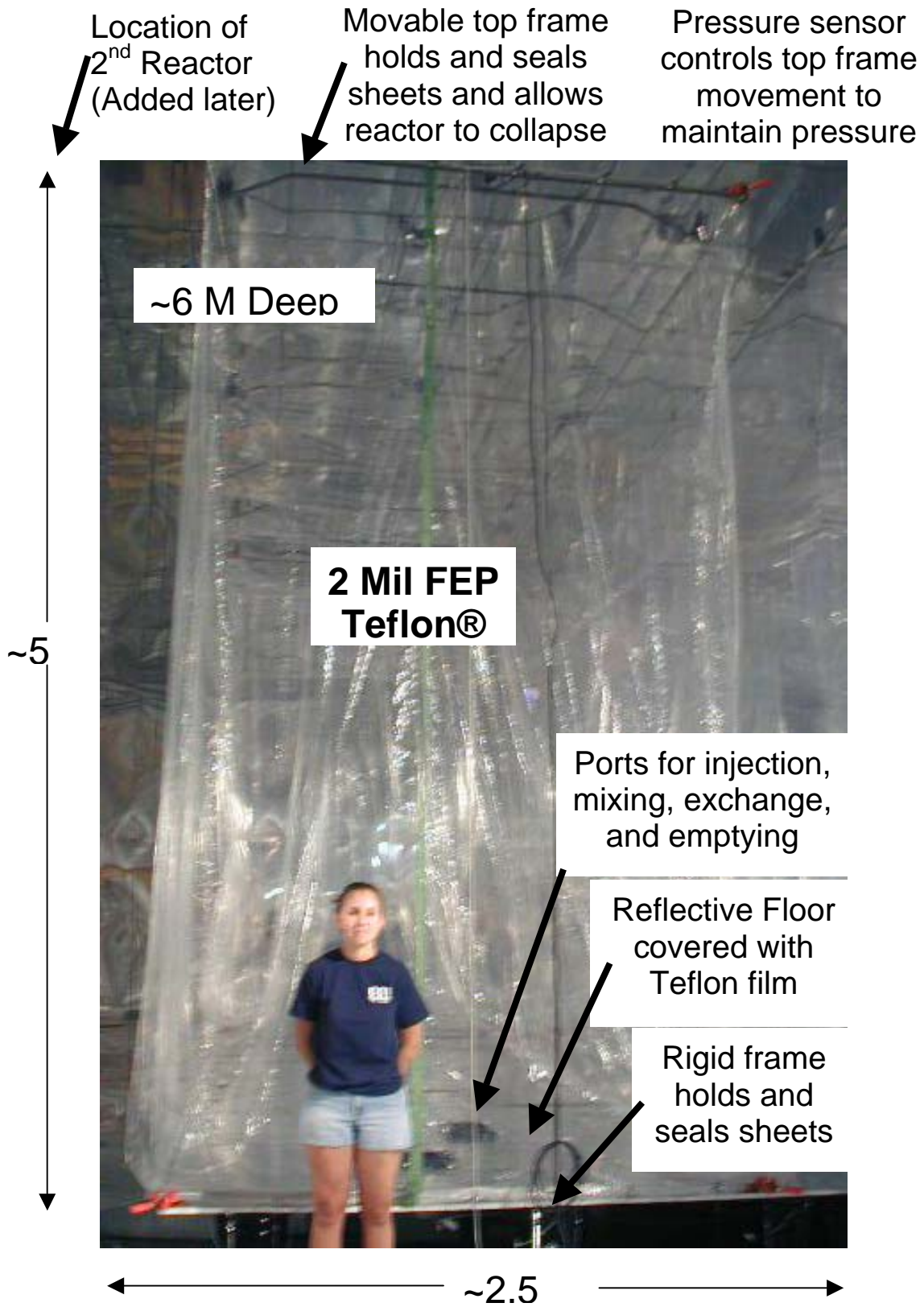
STATUS OF UCR-EPA CHAMBER

Time	Status or Activity
1999-2002	Workshop, design, construction, initial evaluation, problem resolution
Jan 2003	First experiment in current dual-chamber configuration
Jan - Mar 2003	Characterization runs and low NO _x runs on simple chemical systems
Feb 2003 (& ongoing)	PM Instrumentation on line. Begin ongoing blacklight PM experiments
Mar 2003	Initial characterization completed
Mar – Jun 2003	Surrogate runs to assess base case for reactivity experiments
Apr 2003	Surrogate runs for low NO _x mechanism evaluation
Jun – Aug 2003	Incremental reactivity experiments for selected petroleum distillates
Sep – Oct 2003	Surrogate runs with enhanced measurements for EPA OBM study
Nov 2003	Begin Texanol® reactivity evaluation

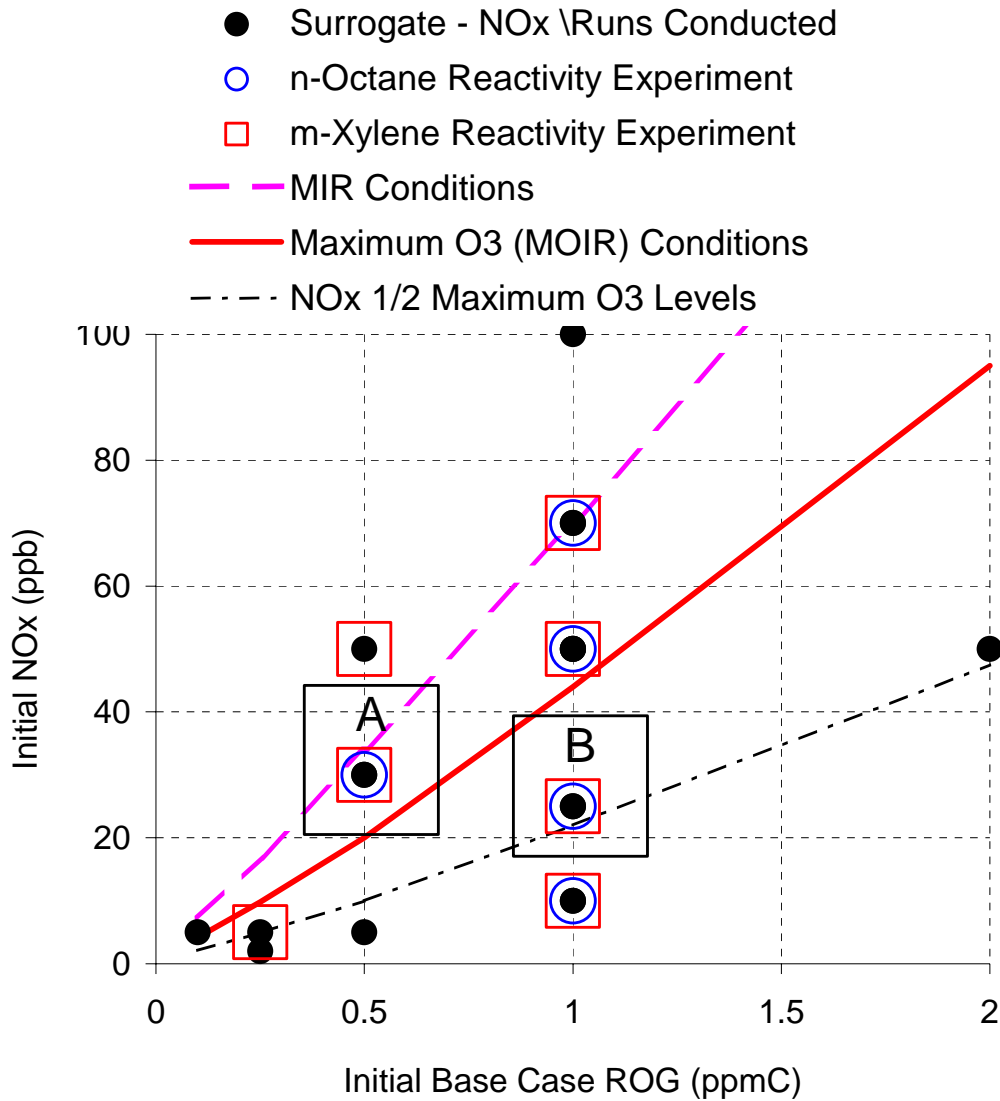
DIAGRAM OF UCR-EPA ENVIRONMENTAL CHAMBER



PICTURE OF SINGLE REACTOR



MATRIX OF SURROGATE EXPERIMENTS

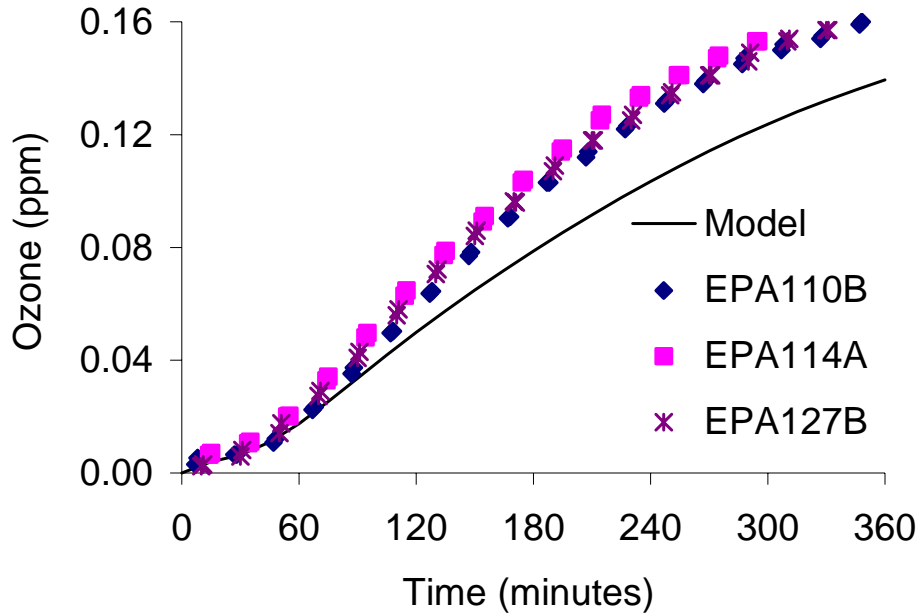


Base case for initial reactivity experiments

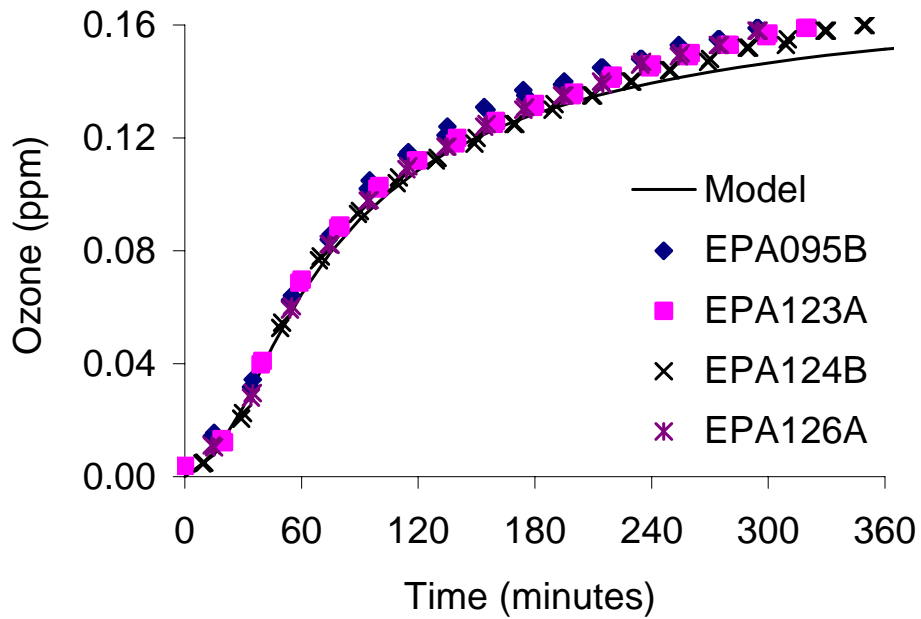
- AMIR Conditions (Higher NO_x / VOC)
- BLower NO_x / VOC; NO_x \approx 1/2 MOIR Level

BASE CASE SURROGATE EXAMPLES

MIR Conditions ($\text{NO}_x=30, \text{ROG}=0.5$)



1/2 MOIR NO_x Conditions ($\text{NO}_x=25, \text{ROG}=1$)



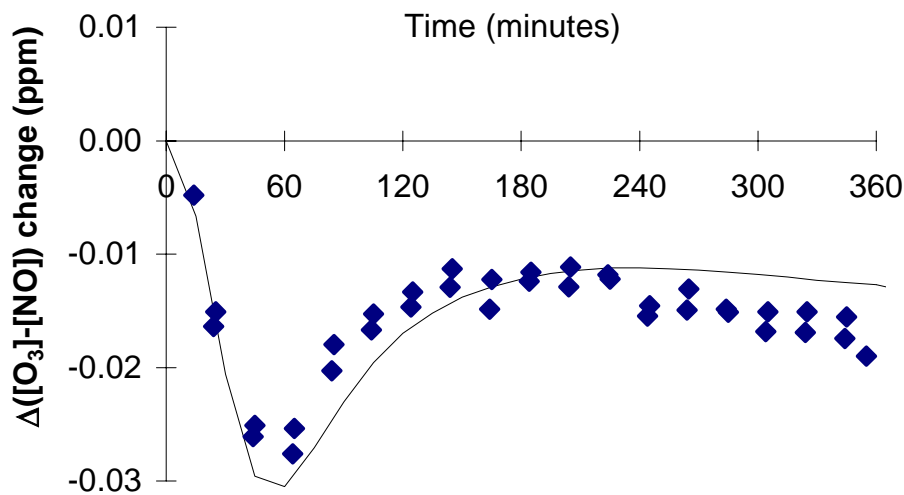
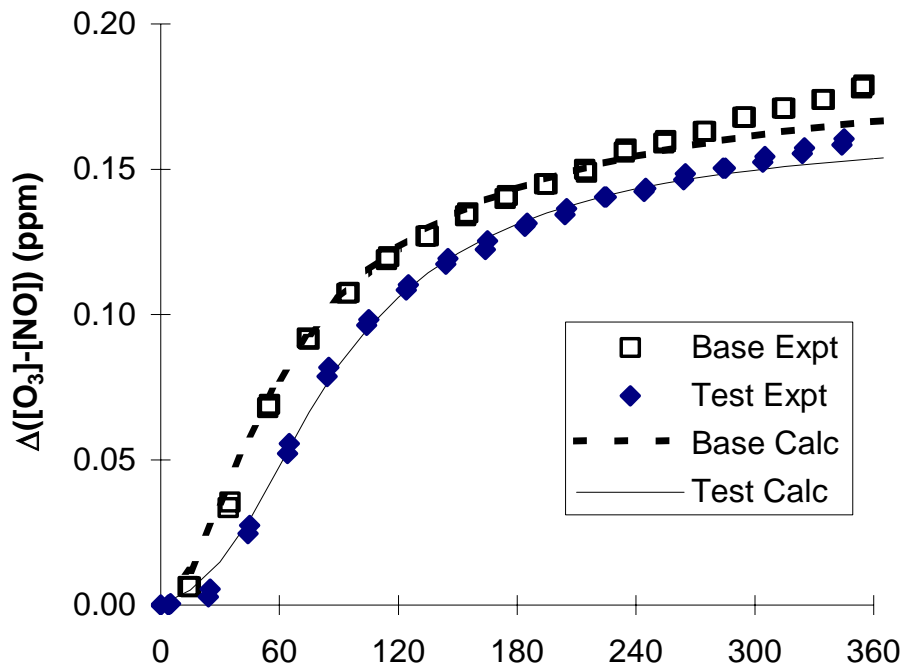
REPRESENTATIVE PETROLEUM DISTILLATES STUDIED

Designation	Avg. Carbons	Aromatic Percent	n-Alkane Percent
VMP Naphtha	8.7	0.1	13
ASTM-1A	10.7	19	15
ASTM-1B	10.8	0	14
ASTM-1C	10.8	6	14
ASTM-3C1	11.0	0	96
Aromatic 100	9.1	100	0

EXAMPLE OF REACTIVITY RESULTS

EPA126

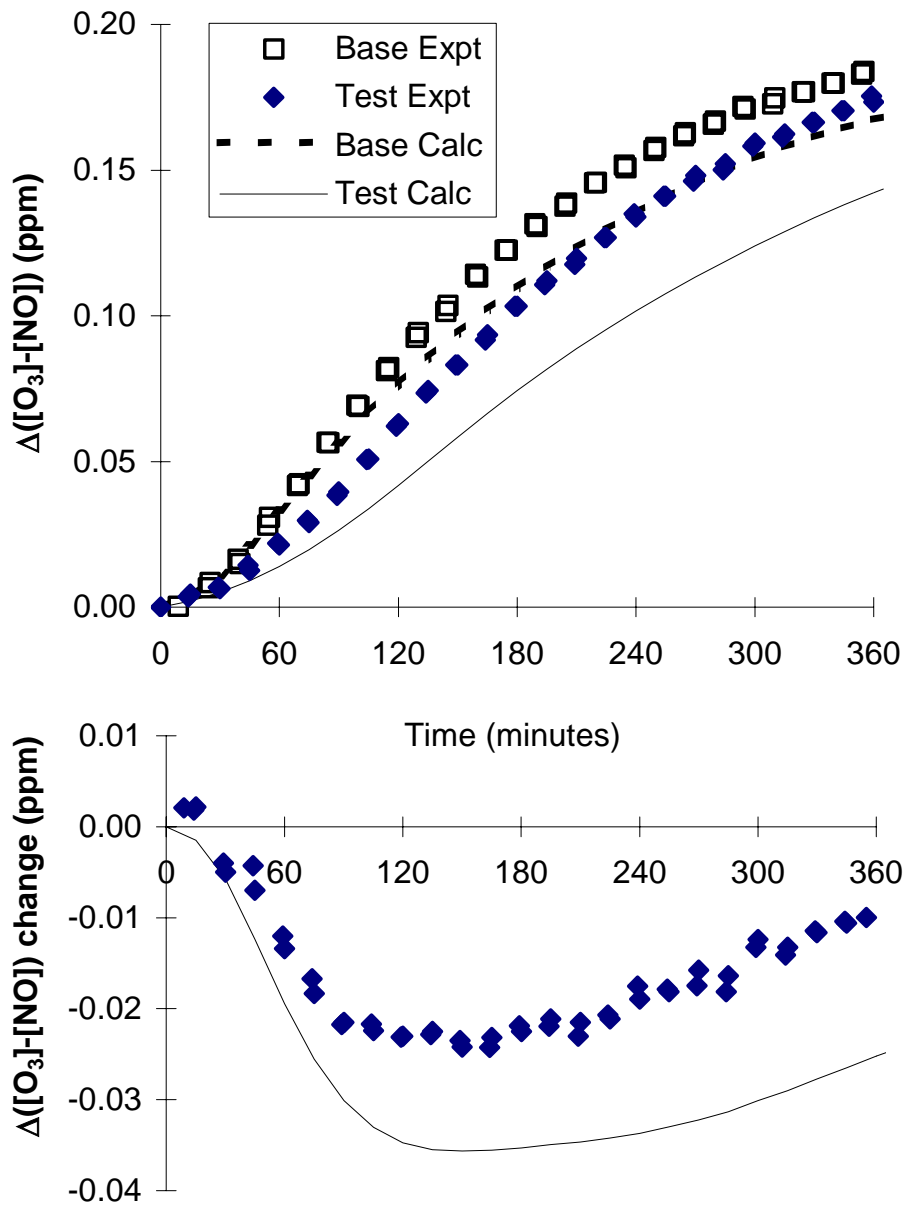
Low NOx Base + 0.9 ppmC VMP Naphtha



EXAMPLE OF REACTIVITY RESULTS

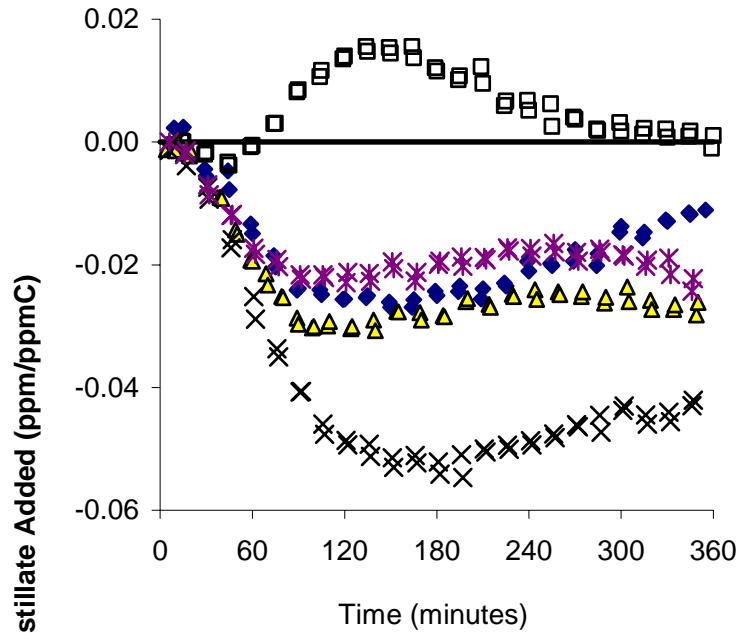
EPA137

MIR Base + 0.9 ppmC VMP Naphtha

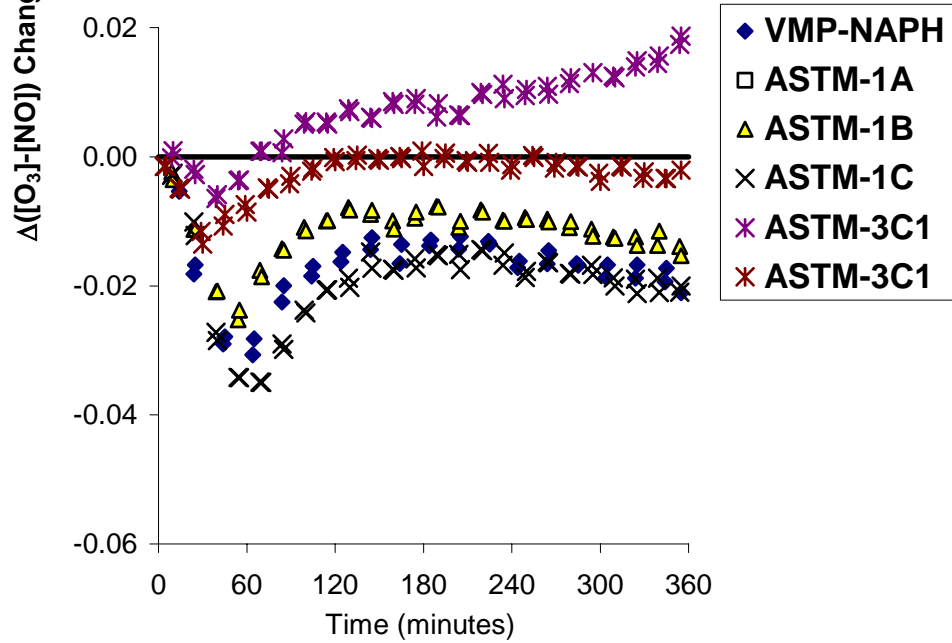


EXAMPLE OF REACTIVITY RESULTS

MIR Base Case

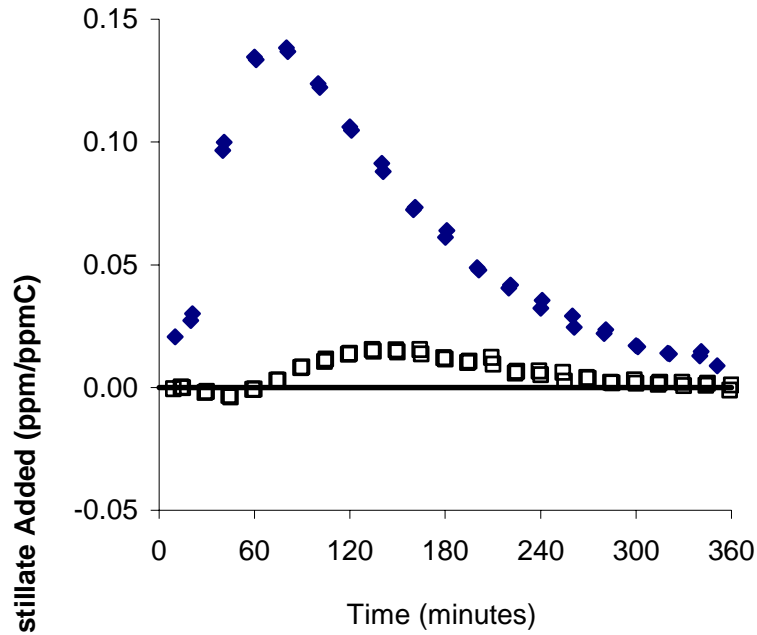


Low NOx / VOC Base Case

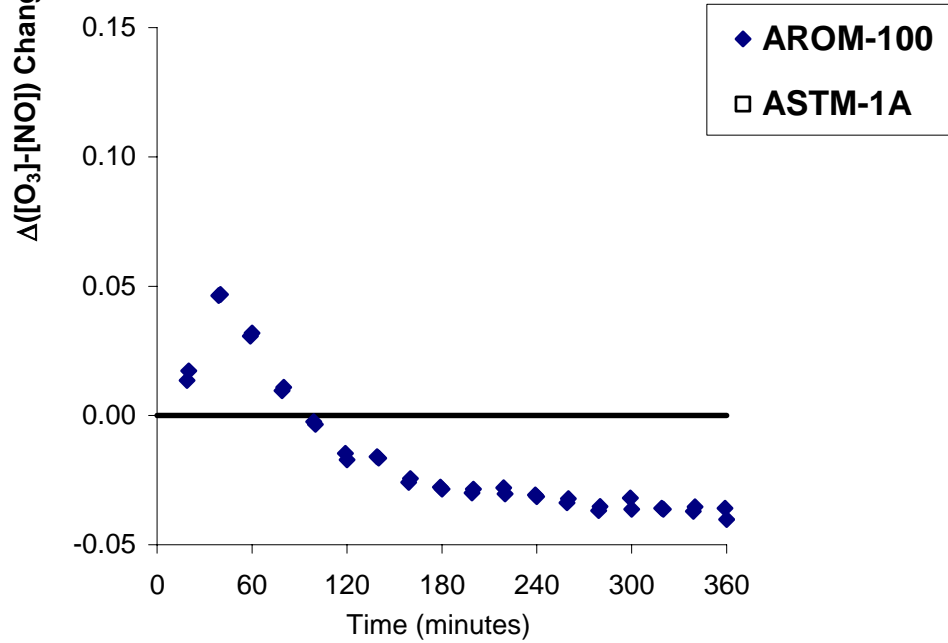


EXAMPLE OF REACTIVITY RESULTS

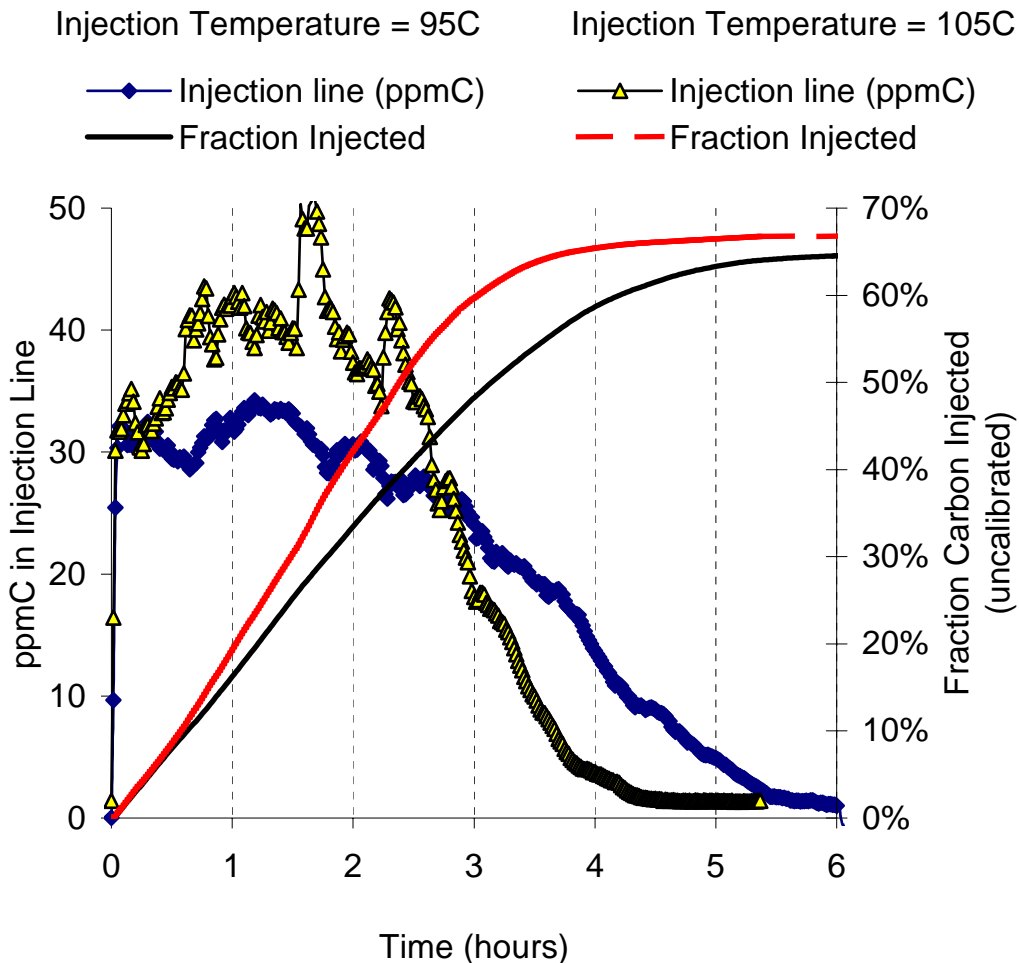
MIR Base Case



Low NOx / VOC Base Case



TEXANOL® INJECTION TESTS



Injection lines heated to $\sim 120^{\circ}\text{C}$ to prevent condensation

Injection time ≤ 5 hours if liquid sample being injected heated to $\geq 100^{\circ}\text{C}$

Need to calibrate gas-phase measurements to determine true recovery.

MEASUREMENT OF DIRECT REACTIVITY

Background

Direct reactivity measures the O₃ formed directly from the VOC's reactions. Such measurements could reduce mechanism evaluation ambiguities

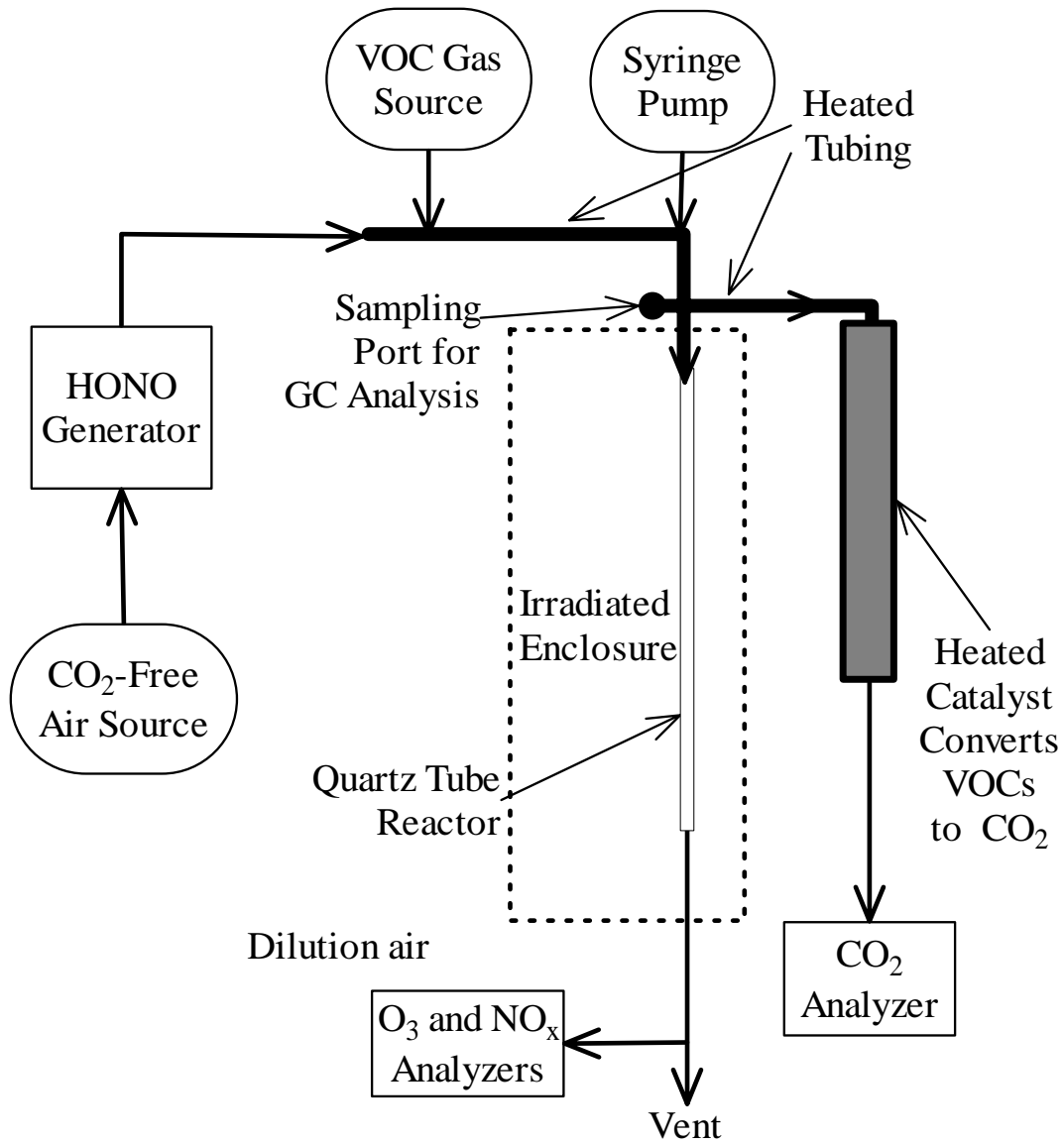
A plug flow HONO photolysis system worked well for volatile compounds analyzable by GC.

The system was interfaced with a total carbon analyzer to eliminate need for GC, Problem with memory effects with low volatility compounds.

Current Status

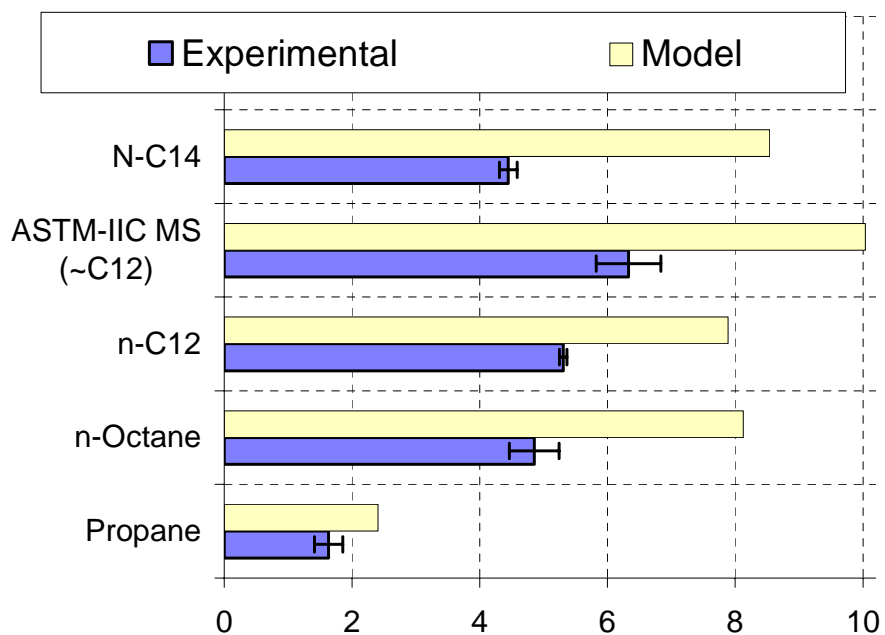
- Memory effects problem solved by improving combustion catalyst with total carbon analyzer
- System tested with propane, n-octane, n-C12, n-C14, and Mineral Spirits (ASTM-2C, ~12Cs)
- Good reproducibility and relative reactivities for C_{≤12} materials are consistent with model
- However, absolute reactivity measures are consistently lower than model predictions.
- **Resources allocated for this task in this project have been expended.**

DIAGRAM OF PLUG FLOW SYSTEM MODIFIED FOR TOTAL CARBON ANALYSIS

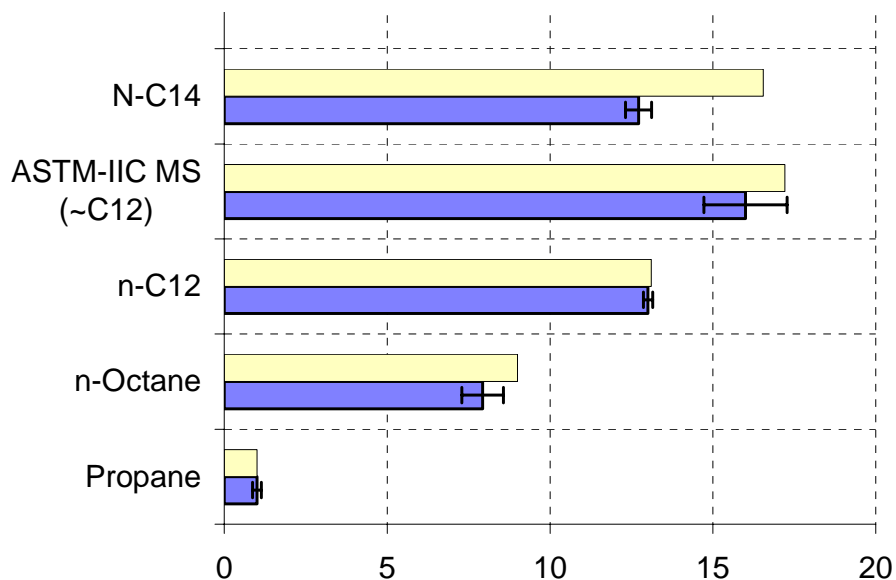


- Combustion catalyst is heated to $\sim 550^{\circ}\text{C}$.
- Sub-ppm sensitivity CO₂ analyzer funded by ACC gift

DIRECT REACTIVITY RESULTS USING CURRENT CONFIGURATION



Direct Reactivity Measure per Carbon



Direct Reactivity Normalized to Propane

REMAINING WORK

Chamber Experiments

Complete development of analysis and injection methods for Texanol®

Conduct experiments with Texanol®

Complete data processing and modeling analysis of petroleum distillate experiments

Conduct petroleum distillate experiments for another set of base case conditions to be determined based on the modeling analysis.

Direct Reactivity Measurement

Project resources are not sufficient for additional development of this method.

Current system may give useful *relative* direct reactivity data for the $C_{\leq 12}$ petroleum distillates

Reactivity Evaluation of Pet. Distillates

Develop standard spreadsheet format and reactivity and uncertainty analysis procedures

DEVELOPMENT AND EVALUATION OF A GAS-PHASE ATMOSPHERIC REACTION MECHANISM FOR LOW NO_x CONDITIONS

CARB Contract Number 01-305

William P. L. Carter
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Summary of Progress through
November, 2003

Outline of Presentation

- Objectives and Current Status
- Evaluation using TVA Chamber Data
- Low NO_x UCR EPA Chamber Experiments
- Current Status of Mechanism Evaluation
- Ongoing Work

OBJECTIVES

Complete the development of the “Low NO_x” version of the SAPRC-99 mechanism

Evaluate the SAPRC-99 mechanisms against available low NO_x chamber data

Conduct experiments in the UCR EPA most needed for low NO_x mechanism evaluation

Update or modify the mechanism as appropriate

CURRENT STATUS

Low NO_x mechanism prepared but implementation work still underway

Current mechanism satisfactorily simulate most TVA chamber data

Mechanism satisfactorily simulates most new low NO_x experiments in UCR EPA chamber

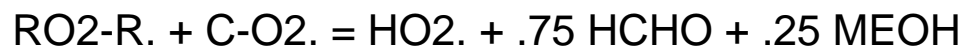
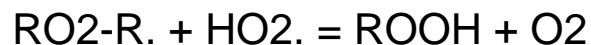
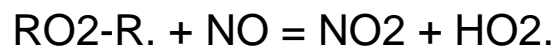
But new data suggest mechanism problems:

- Underprediction of O₃ in high NO_x/ROG surrogate runs (MIR or higher NO_x levels)
- Current aromatic mechanisms probably have compensating errors

LOW NO_x VERSION OF SAPRC-99

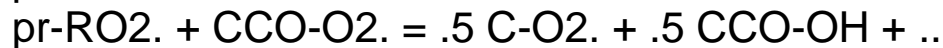
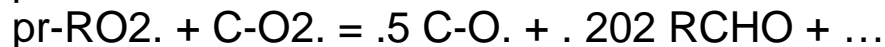
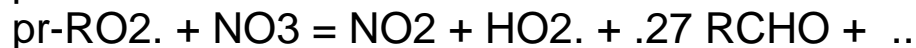
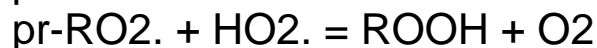
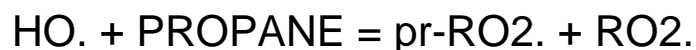
More detailed treatment of peroxy reactions, to permit predictions of different products under low NO_x conditions. For example, for PROPANE:

Standard Representation: Use general radical “operators” to represent peroxy reactions, e.g.,



(etc)

Low NO_x Representation: Use separate radical model species for each compound in model, e.g.,



SUMMARY OF RESULTS OF SIMULATIONS OF THE TVA CHAMBER DATA

Run Type	Runs	NO _x Range (ppb)	Average $\Delta(\text{O}_3\text{-NO})$ Bias
HCHO - NO _x	4	39-42	-4%
Isopentane - NO _x	1	18	-28%
Ethylene - NO _x	3	25-52	4%
Propylene - NO _x	4	22-54	13%
trans-2-Butene - NO _x	3	20-41	14%
Toluene - NO _x	3	54-266	1%
m-Xylene - NO _x	2	98-100	4%
Par - Ole Mix 2 - NO _x	3	49-51	12%
Par - Ole Mix 3 - NO _x	3	50-100	9%
Par - Ole - Aro Mix 1	3	50-101	7%
Par - Ole - Aro Mix 2	7	50-54	8%
SynUrban94 - NO _x	12	25-169	-8%

Characterization runs excluded

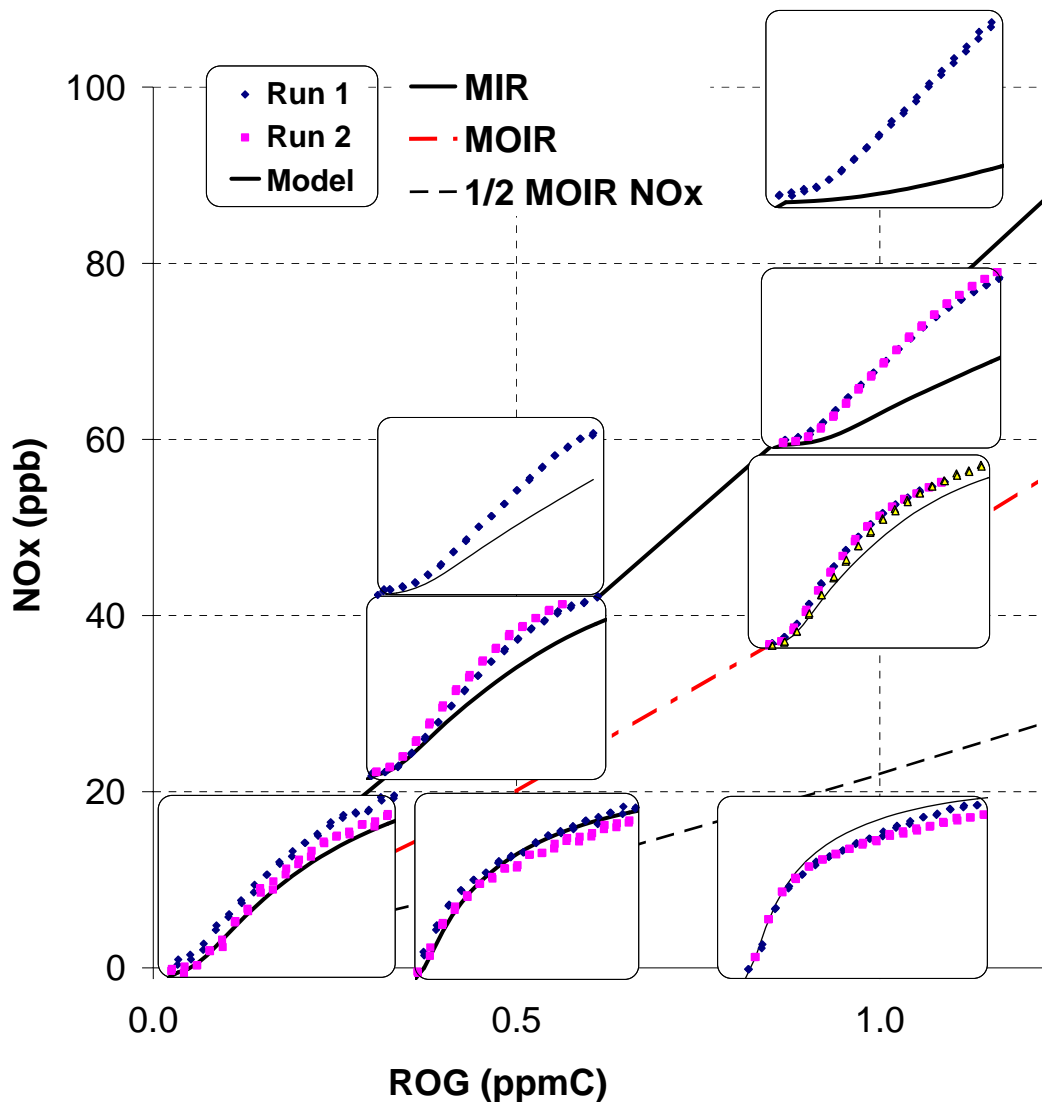
Bias is (model - experiment) / experiment

SUMMARY OF MECHANISM EVALUATION EXPERIMENTS IN THE UCR-EPA CHAMBER

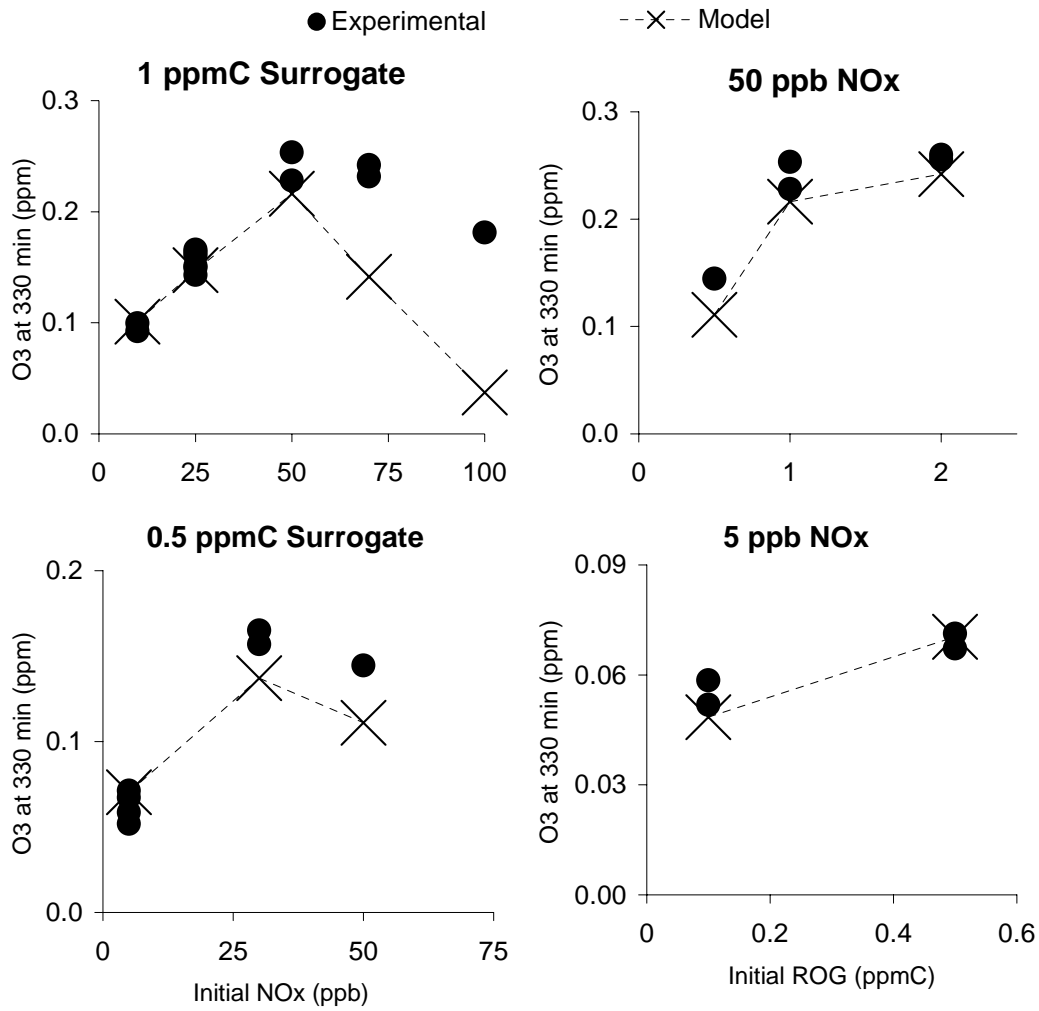
(Excluding characterization, petroleum distillate reactivity, OBM study, and aerosol yield runs)

Experiment Type	Runs	NO _x Range (ppb)
Formaldehyde – NO _x (with & w/o added CO)	4	8 - 25
Acetaldehyde – NO _x (with & w/o added CO)	2	10
Ethene – NO _x	2	10 - 25
Propene – NO _x	2	5 - 25
Toluene – NO _x (with & w/o added CO)	8	5 - 30
m-Xylene – NO _x (with & w/o added CO)	2	5
Surrogate – NO _x (Various ROG and NO _x)	12	2 - 110

MODEL PERFORMANCE SIMULATING O₃ AT DIFFERENT ROG AND NO_x LEVELS

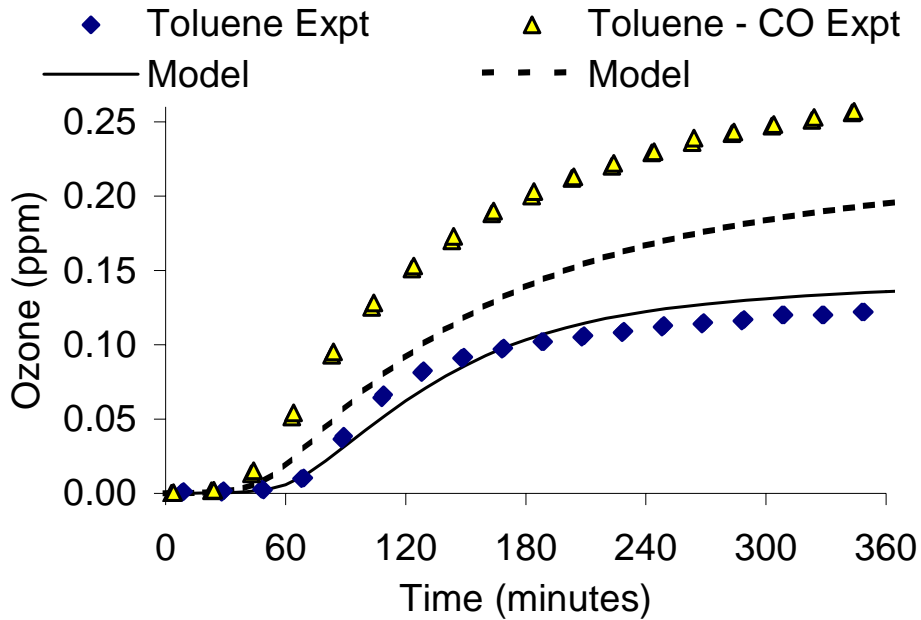


EXPERIMENTAL AND CALCULATED FINAL O₃ IN AMBIENT SURROGATE EVALUATION EXPERIMENTS

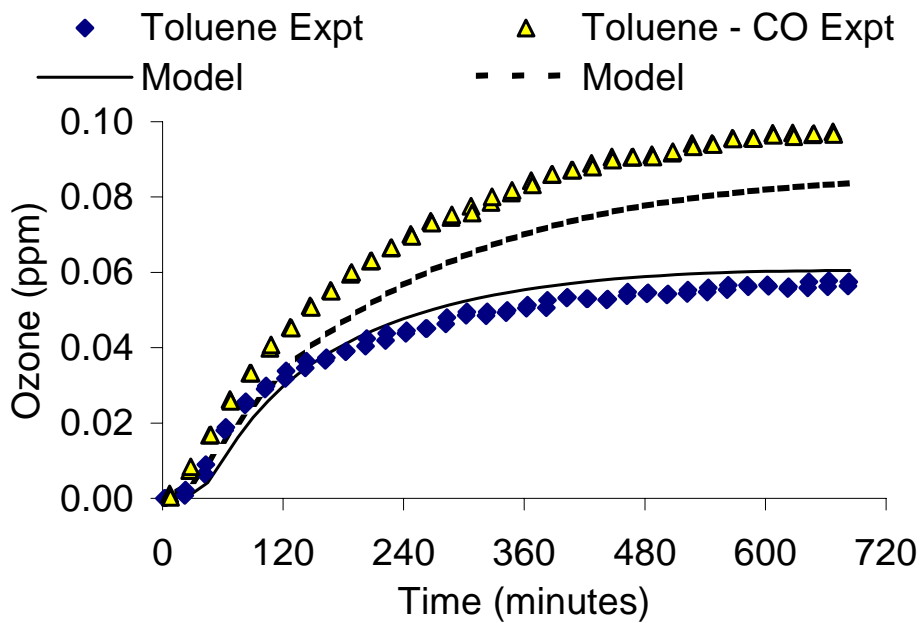


TOLUENE & TOLUENE – CO - NO_x RUNS

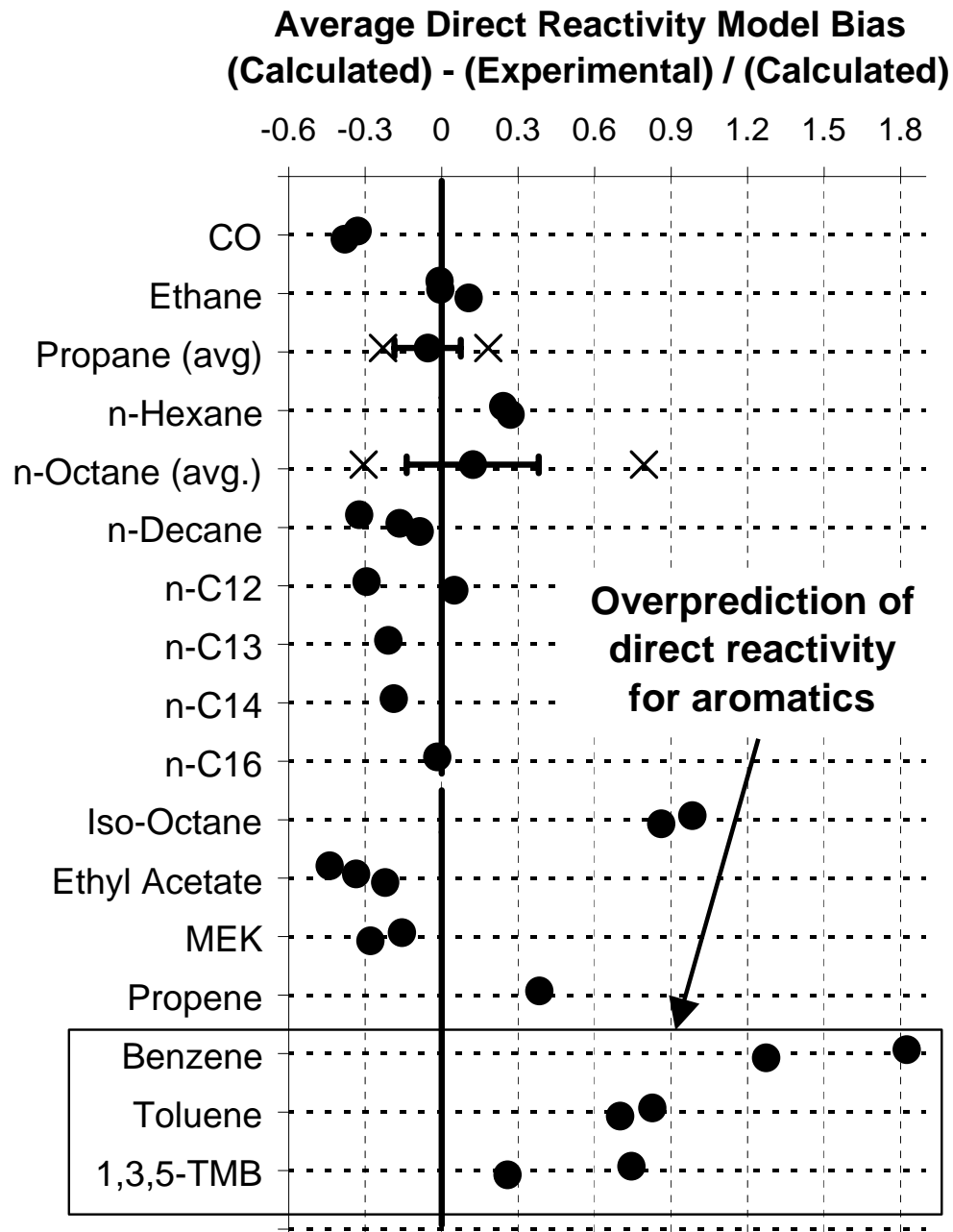
25 ppb NO_x, 150 ppb Toluene, 45 ppm CO



5 ppb NO_x, 60 ppb Toluene, 25 ppm CO



MODEL PERFORMANCE IN SIMULATING DIRECT REACTIVITY DATA (HONO +VOC FLOW TUBE EXPERIMENTS)



REMAINING WORK

Complete implementation of Low NO_x version of SAPRC-99, compare predictions to standard version, and prepare documentation

Finalize data for low NO_x experiments and model simulations of those runs

Summarize existing model discrepancies and evaluate where further work needed

Prepare final report.

Note: Fixing the problems with the aromatics and high NO_x mechanisms will be objective of follow-on project.