Incorporation of a Detailed Gas-Phase Furan Mechanism into a Young Biomass Burning Plume Box Model

Thursday, November 12, 2020
Fundamental Oxidation Chemistry (Part 3)
8:00 a.m. – 11:15 a.m. PT

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UCDAVIS
Atmospheric Chemical Mechanisms Conference
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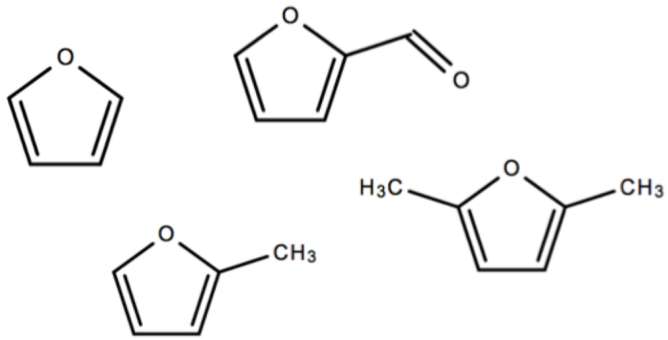
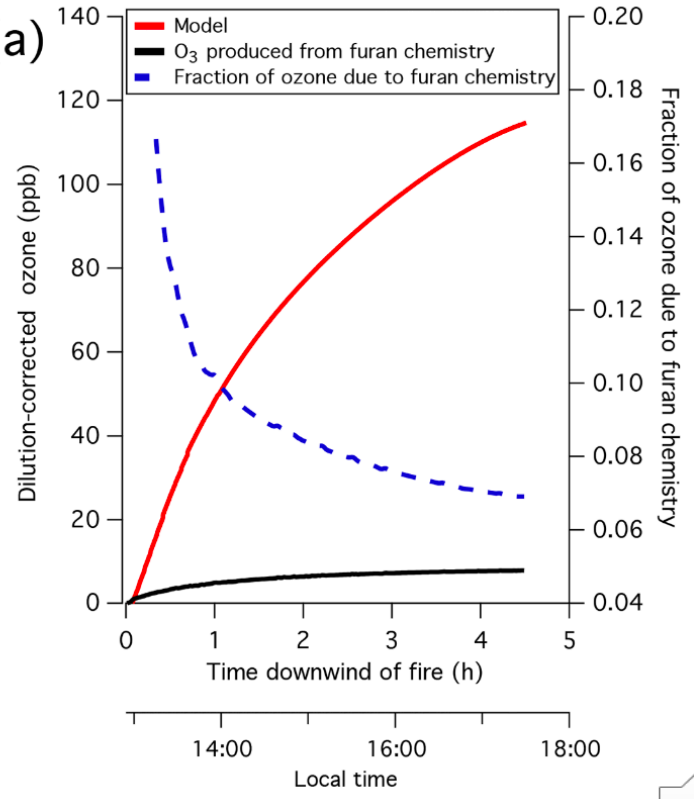
Agenda

- Why furans?
- Why ASP?
- Why SAPRC-18?
- Detailing the “Engine” Swap
- Initial*** Results
- Immediate Next Steps
- Eventual Next Steps

Why furans?



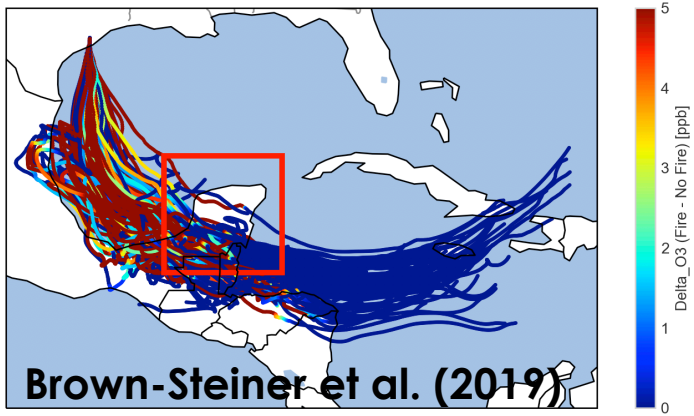
- Furans
  - 2-methylfuran
  - 3-methylfuran
  - 2,5-dimethylfuran
  - Furfural (furaldehyde)
- Furans can contribute up to 10% of **O_3 production** from biomass burning especially in young smoke (e.g. Coggon et al. 2019),
- Furans also contribute to **SOA formation**, although SOA yields are variable and dependent on plume conditions and furan mixture (e.g. Joo et al., 2019)
- Their chemistry is **complex**
  - 4-carbon 1-oxygen ring with 2 double bonds
  - Reactive to OH, NO_3, O_3
  - 100+ species (Jiang et al., 2020)



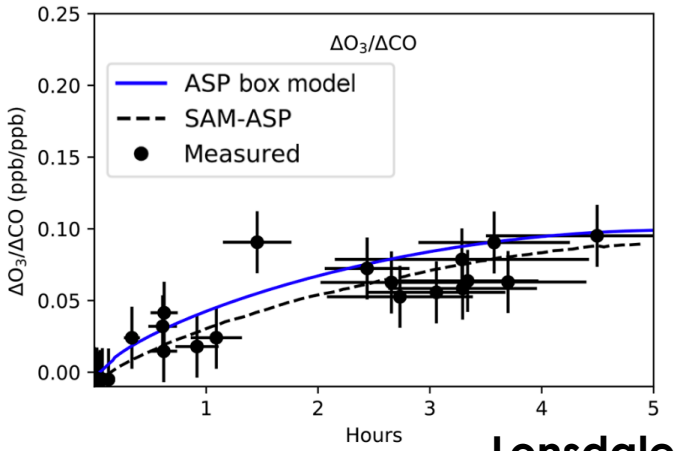
Coggon et al. (2019, ACP)

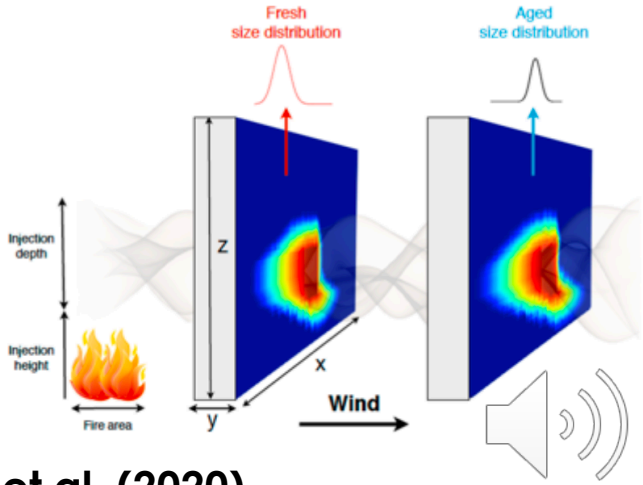
Why ASP?

- Aerosol Simulation Program (ASP v2.1)
  (Alvarado and Prinn, 2009)
- Young (< 24 h) Biomass Burning Box Model
- ASCII formatted input files
- Flexible
  - Box Model (Smoke Plume or Smog Chamber)
  - Semi-Lagrangian (STILT-ASP)
  - 2D Lagrangian (SAM-ASP)
- Mechanism "Ancestry":
  - CACM/RACM
  - MCM



Brown-Steiner et al. (2019)

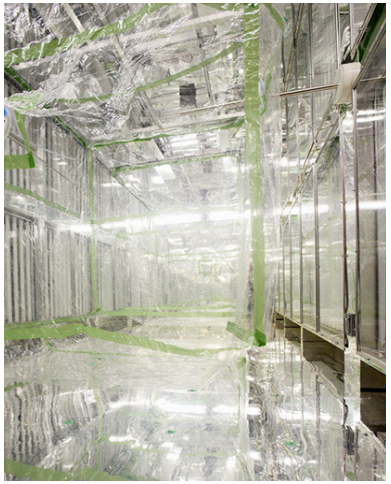


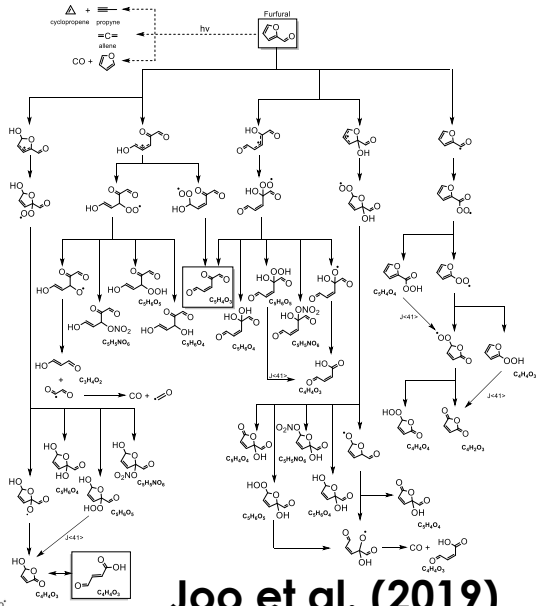


Lonsdale et al. (2020)

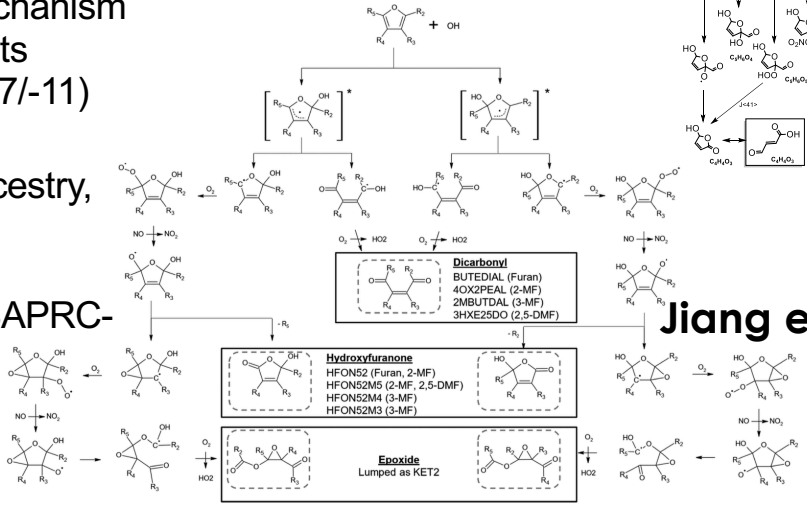
Why SAPRC?

- Current collaboration (NSF) with Nga Lee (Sally) Ng and Taekyu Joo at Georgia Tech to develop furan oxidation chemistry and SOA formation in smog chamber (Joo et al., 2019)
  - 2-MF, 3-MF, 2,5-DMF, Furfural via OH, O_3, NO_3
- Kelley Barsanti and Jia Jiang (UC Riverside) developed a detailed gas-phase mechanism for furan and major oxidation products (Jiang et al., 2020) in SAPRC (-18, -7/-11)
- ASP-SAPRC!
- Since ASP doesn't have SAPRC ancestry, dropping in Jia's SAPRC-18 furan mechanism would be a "fresh" start
- **SPOILER**: We're dropping in all of SAPRC-18, not just the furan mechanism





Joo et al. (2019)



Jiang et al. (2020)

How to Swap Engines (Chemical Mechanisms)

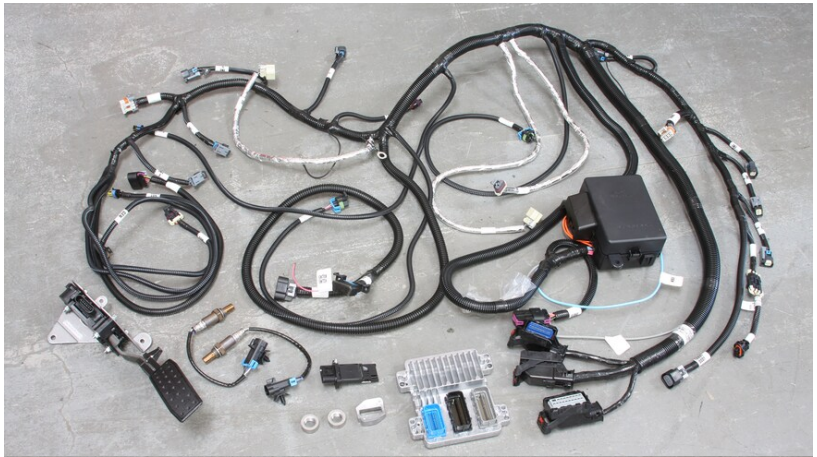
- Branch a new version of ASP
- Start Deleting Things…But Not Everything!
  - Parts of ASP code expect certain species
  - Easier (at this point) to leave them in the mechanism, but not allow them to do anything.
  - Code changes would be undesirable
- Reformat SAPRC-18 mechanism to fit into ASP
  - Jia Jiang was the primary mechanic here
- "Drop" SAPRC-18 into the ASP Chassis
  - Ctrl+V

Oh No What Have We Done

- Glance around at shop floor and see:
  - Duplicate Species?
  - Different forms of RO2 and RCO3 tracking
  - Tracer Species
  - HV? FALLOFF? N-C6F14?
  - 1,500 lines of “Matrix” Style numbers and letters

```
AR01 + OH          => 0.693 AR01_P1 + 0.288 HO2 + 0.137 XYNL + 0.08 OLEA1 + 0.07 OLEA2 + 0.027 RO2C + 0.019 HCHO + 0.013 BALD + 0.012 OH
 + 0.007 RO2XC + 0.006 zRHNO3 + 0.006 MECHO + 0.001 CROOH + 0.31 XC + 0.727 SumRO2  ; 6.67e-12 ; 0. ; 0. ; 1. ;
AR01_P1 + NO       => 0.713 NO2 + 0.36 HO2 + 0.212 AR01_P2 + 0.178 GLY + 0.177 MGLY + 0.177 BUDAL + 0.164 RPNO3 + 0.159 AFG2A + 0.123 RA
NO3 + 0.106 BALD + 0.092 ACET + 0.08 MECHO + 0.075 ETO2 + 0.072 AR01 + 0.067 MEO2 + 0.019 AFG1 + 0.009 HCHO + 0.895 XC + 0.354 SumRO2  ;
 9.13e-12 ; 0. ; 0. ; 1. ;
AR01_P1 + NO3      => NO2 + 0.525 HO2 + 0.286 AR01_P2 + 0.26 GLY + 0.258 MGLY + 0.258 BUDAL + 0.232 AFG2A + 0.142 BALD + 0.125 ACET + 0.
106 MECHO + 0.1 ETO2 + 0.096 AR01 + 0.089 MEO2 + 0.028 AFG1 + 0.012 HCHO + 0.912 XC + 0.475 SumRO2  ; 2.30e-12 ; 0. ; 0. ; 1. ;
AR01_P1 + HO2      => 0.518 RAOOH + 0.482 ROOH +2.964 XC  ; 2.11e-11 ; 0. ; 0. ; 1. ;
AR01_P1 + SumRO2   => SumRO2 + 0.286 AR01 + 0.263 HO2 + 0.259 OLEP + 0.143 AR01_P2 + 0.13 GLY + 0.129 MGLY + 0.129 BUDAL + 0.116 AFG2A +
 0.071 BALD + 0.063 ACET + 0.053 MECHO + 0.05 ETO2 + 0.044 MEO2 + 0.014 AFG1 + 0.006 HCHO + 0.003 RCHO + 0.211 XC + 0.237 SumRO2  ; 1.95
e-12 ; 0. ; 0. ; 1. ;
AR01_P1 + SumRCO3  => SumRCO3 + 0.423 HO2 + 0.254 AR01_P2 + 0.211 GLY + 0.207 MGLY + 0.207 BUDAL + 0.188 AFG2A + 0.145 AR01 + 0.125 ACET
 + 0.114 BALD + 0.101 OLEP + 0.089 MEO2 + 0.085 MECHO + 0.08 ETO2 + 0.022 AFG1 + 0.01 HCHO + 0.002 RCHO + 0.63 XC + 0.423 SumRO2  ; 1.37
e-11 ; 0. ; 0. ; 1. ;
GasChemicalMechanism.in                                                575,1         36%
```

  - Photolysis reactions which are conceptually similar but differing in formats and details
  - Code that will except MWs, BCs, ICs for hundreds of new species



Square Pegs and Round Holes

- Photolysis
  - SAPRC
  - ASP
- ASP cannot handle product-less reactions
  - Use H2O
- Typos and Tweaks
  - Need to convert “E” to “e” for ASP formatting
  - Strange decimal places…
  - A number of reactions didn’t seem to convert the reaction rates cleanly from the SAPRC format
    - Temporary solution: comment them out

Photolysis Mapping

- COOH (MEOOH, ETOOH, RUOOH, RAOOH, ROOH, RPNO3) **CH3OOH (31)**
- HCHOR-13 (HCHO) **HCHO (17, 18)**
- HCHOM-13 (HCHO) **HCHO (17, 18)**
- CCHOR-13 (MECHO) **Acetaldehyde (19)**
- C2CHO (ETCHO, RCHO, RTCHO) {saturated aldehydes} *ALD as Butanal (49)*
- GLALD-14 (GLCHO) **HOCH2CHO (23)**
- PAA (PAA) **CH3CO3H (31)**
- GLY-I13R (GLY) **GLY (44,45)**
- GLY-I13M (GLY) **GLY (44,45)**
- ACET-06 (ACET) **Acetone (26)**
- MGLY-13 (MGLY) **MGLY (46)**
- BACL-11 (BACL) **BIACET (47)**
- BALD-11 (BALD) **BALD (25)**
- NO2-06 (NPHE) {nitrophenols} *PAN (40, 41)*
- PAN-11 (PAN) **PAN (40, 41)**
- PPN-11 (HOPAN, PPN, PAN2, PAN2N, PBZN, APAN, MAPAN) *PPN (42, 43)*
- ACROL-16 (ACRO) **ACR (24)**
- MEK-06 (MEK, KET2) **MEK (28)**
- MACR-06 (MACR, OLEA1) **MCR (25)**
- MVK-16 (MVK, LVKS) **MVK (27)**
- AFGS (BUDAL, AFG1, AFG2A, AFG2B) {aldehydes and ketones} *UALD and MCR (25)*
- IC3ONO2 (RANO3, RHNO3, R1NO3, R2NO3) *NOA (38)*
- CRBNIT (RCNO3) {volatile organic carbonyl nitrates} *NOA (38)*
- DIONO2 (RDNO3) {dinitrates} *NOA (38)*
- HPALDS (HPALD, CROOH) {unsat. hydroperoxy carbonyls} *peroxides as CH3OOH (31)*

Turning the Key

- Errors
  - Incorrect Number of Rate Terms
  - Where's the H2O?

- Then:

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Total Execution Time was 35.718
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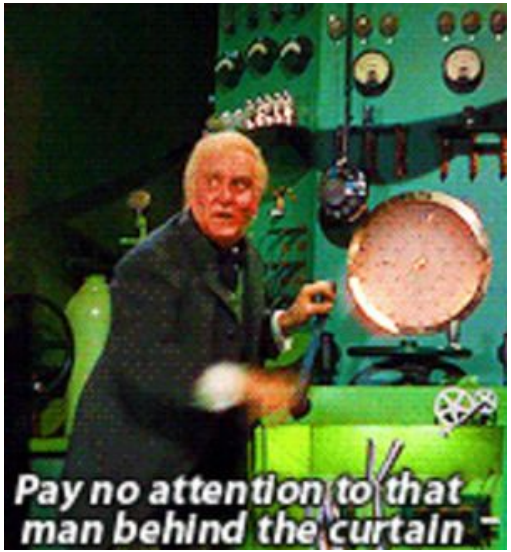
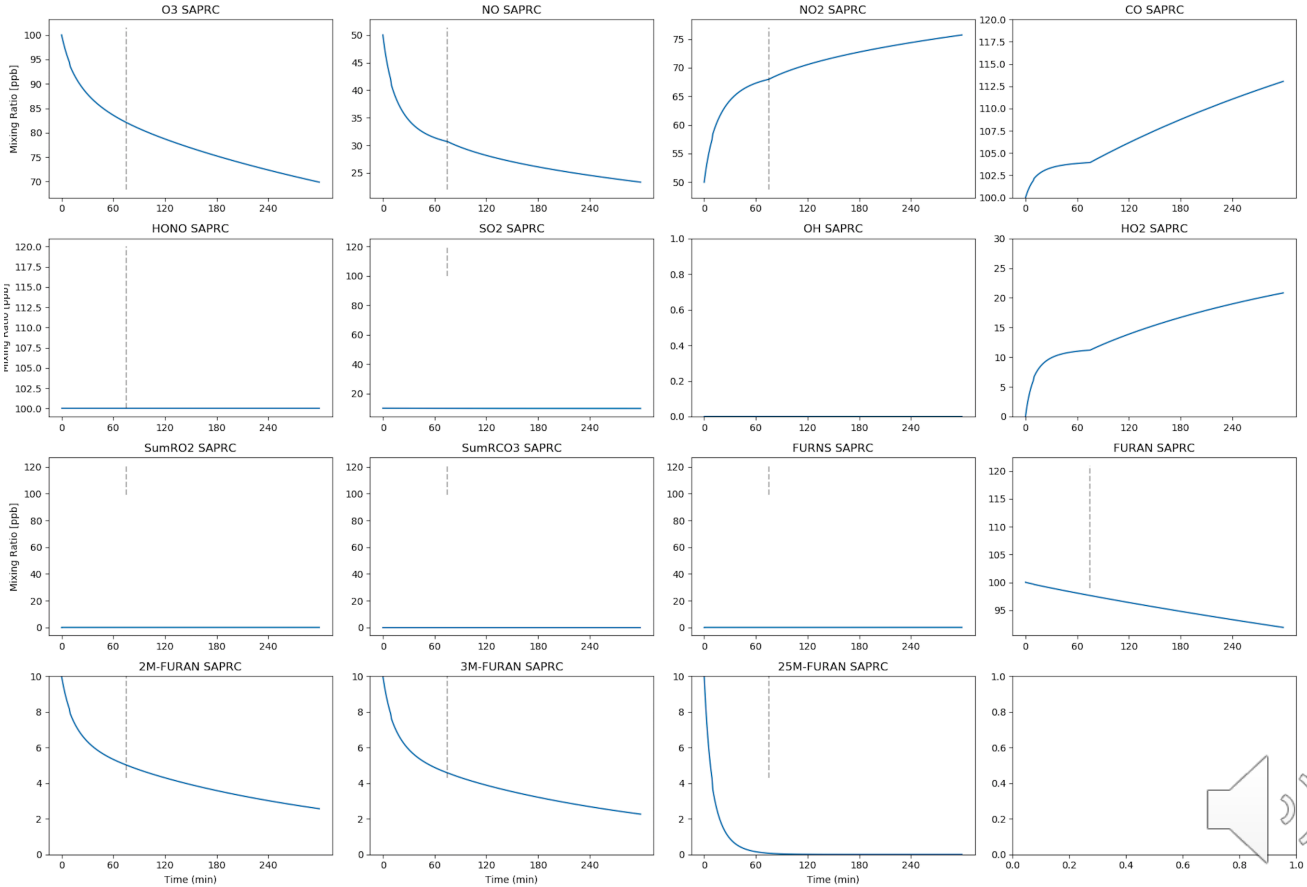
- Success!

- But do we trust it…?

Very Preliminary Results





Immediate Next Steps

- Replicate Chamber Experiments from Jiang et al. (2020)
- Address commented out reactions
- Update/Address Photolysis
- Full audit of gas chemistry
- Connect to SOA

Table 4. List of the Chamber Experiments Used to Evaluate the Model Performance

					initial mixing ratio (ppb)			
group	run ID	light	duration (min)	RH (%)[f]	NO	NO_2	furans	ethylene
furan-1	ITC711	BL[a]	285	50	367	144	423	
	ITC713	BL[a]	360	50	769	206	406	
	ITC715	BL[a]	360	50	391	98	225	
	ITC743	BL[a]	375	50	420	120	389	
furan-2	EPA355A	Arc[b]	312	dry	101	7	40	
	EPA355B	Arc[b]	312	dry	26	~0[g]	41	
	EPA371A	BL[c]	314	dry	90	7	37	
	EPA371B	BL[c]	314	dry	27	1	38	
furan-3	EPA1402A	BL[d]	288	dry	3	10	129	1102
	EPA1403A	BL[d]	289	dry	~0	13	47	981
	EPA1403B	BL[d]	289	dry	~0	14	50	1056
	EPA1448A	BL[d]	469	dry	15	~0[g]	130	878
2-MF	EPA356A	Arc[b]	321	dry	100	~0[g]	51	
	EPA356B	Arc[b]	321	dry	31	2	51	
	EPA996A	BL[e]	509	dry	40	1	50	
	EPA996B	BL[e]	473	dry	40	1	50	
	EPA999A	BL[e]	479	dry	52	~0[g]	600	
	EPA999B	BL[e]	479	dry	50	~0[g]	293	
3-MF	EPA358A	Arc[b]	340	dry	93	7	62	
	EPA358B	Arc[b]	340	dry	28	2	65	
	EPA359A	BL[c]	308	dry	96	4	55	
	EPA359B	BL[c]	308	dry	28	2	55	
	EPA418A	Arc[b]	362	dry	104	7	48	
	EPA418B	Arc[b]	362	dry	26	2	49	
2,5-DMF	EPA357A	Arc[b]	294	dry	96	3	47	
	EPA357B	Arc[b]	294	dry	22	1	50	

[a]Blacklight, light intensity k_1 (NO_2 photolysis rate as measured by actinometry) = 0.35 min^{-1}. [b]Argon arc light, k_1 = 0.26 min^{-1}. [c]Blacklight, k_1 = 0.163 min^{-1}. [d]Blacklight, k_1 = 0.401 min^{-1}. [e]Blacklight, k_1 = 0.131 min^{-1}. [f]Dry condition, RH < 0.1%. [g]below the detection limit (less th ppb).

Eventual Next Steps

- Finalize the SAPRC-ASP Box Model
- Add furfural chemistry of Joo et al.
- Simulate Georgia Tech chamber experiments
- STILT-SAPRC-ASP?
- SAM-SAPRC-ASP?

A Note

- Between ”now” and “now” we’ll have more results
- Please reach out!
  - bbrownst@aer.com
  - @benbrownsteiner

Thank You!