Shock Tube Studies of RP Series Fuel Surrogates and RP Fuel Thermal Stability

Fuel Summit at USC, September, 15-17, 2009

R. K. Hanson, M. E. MacDonald, D. F. Davidson
High Temperature Gasdynamics Laboratory
Mechanical Engineering Department
Stanford University, Stanford CA

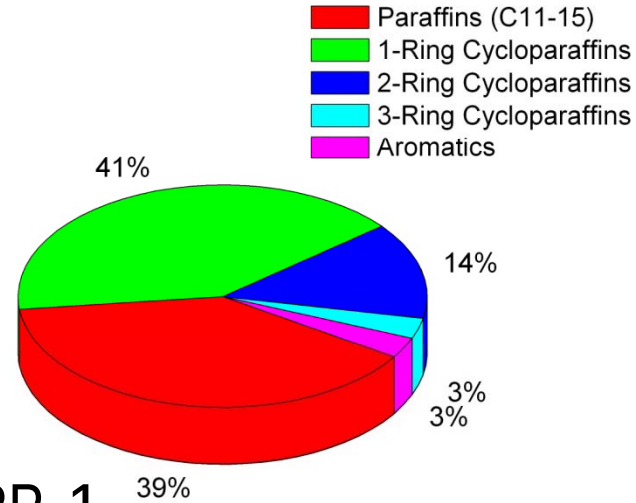
- Background & Experimental Approach
- Fuel Stability Studies
- RP-Fuel Surrogate Studies

This work sponsored by ERC, Inc. at the Air Force Research Laboratory, Edwards AFB, Matthew Billingsley, contract monitor.

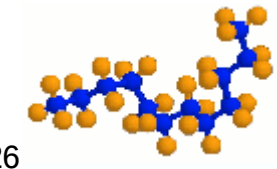
Approved for Public Release; Distribution is Unlimited

Motivation: Improving High Temperature Thermal Stability of RP fuels

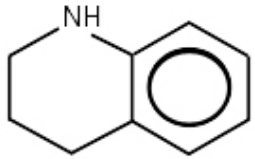
- Future jet/rocket engine designs will likely involve higher fuel temperatures, however this may promote fuel decomposition and **coking** in fuel lines
- To reduce fuel decomposition (and coking) improved understanding of the kinetics of jet fuels (and surrogates) are needed
  - RP fuels: RP-1/-2 (narrow distillation cut fuels)
  - n-dodecane (single component RP-1 surrogate)
  - Methylcyclohexane (2nd RP surrogate component)
- Do existing thermal stability additives (i.e. hydrogen donors such as THQ) work at higher temperatures (i.e. above 800 K)?



RP-1



$C_{12}H_{26}$

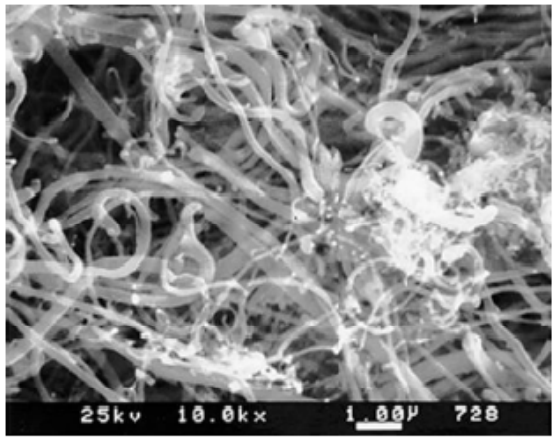


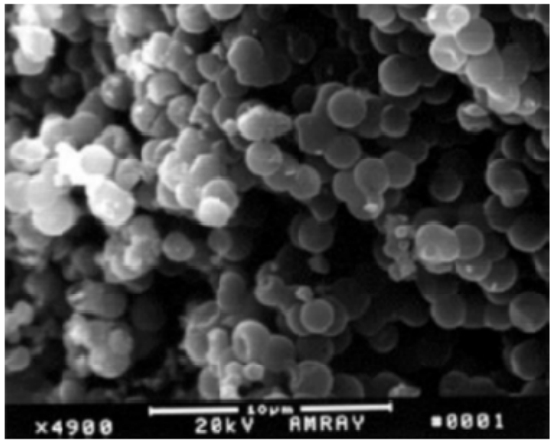
1,2,3,4-Tetrahydroquinoline
THQ

Approved for Public Release; Distribution is Unlimited

Overview: Coke formation processes and fuel decomposition

- Different coke formation mechanisms at different T
  - Oxidation (T < 600 K)
    - Fuel reaction with trace impurities
  - Catalytic or Filament (650 K < T < 1750 K)
    - Fuel reaction with heat exchanger walls
    - Filamental carbon deposits on walls
  - Condensation or Dehydrogenation (T > 850 K)
    - Fuel decomposition
    - Amorphous particles formation in the flow
    - Similar to sooting, formation of PAHs





- This study addresses first step of high temperature coke formation: **fuel decomposition and role of additives to slow this process**

Approved for Public Release; Distribution is Unlimited

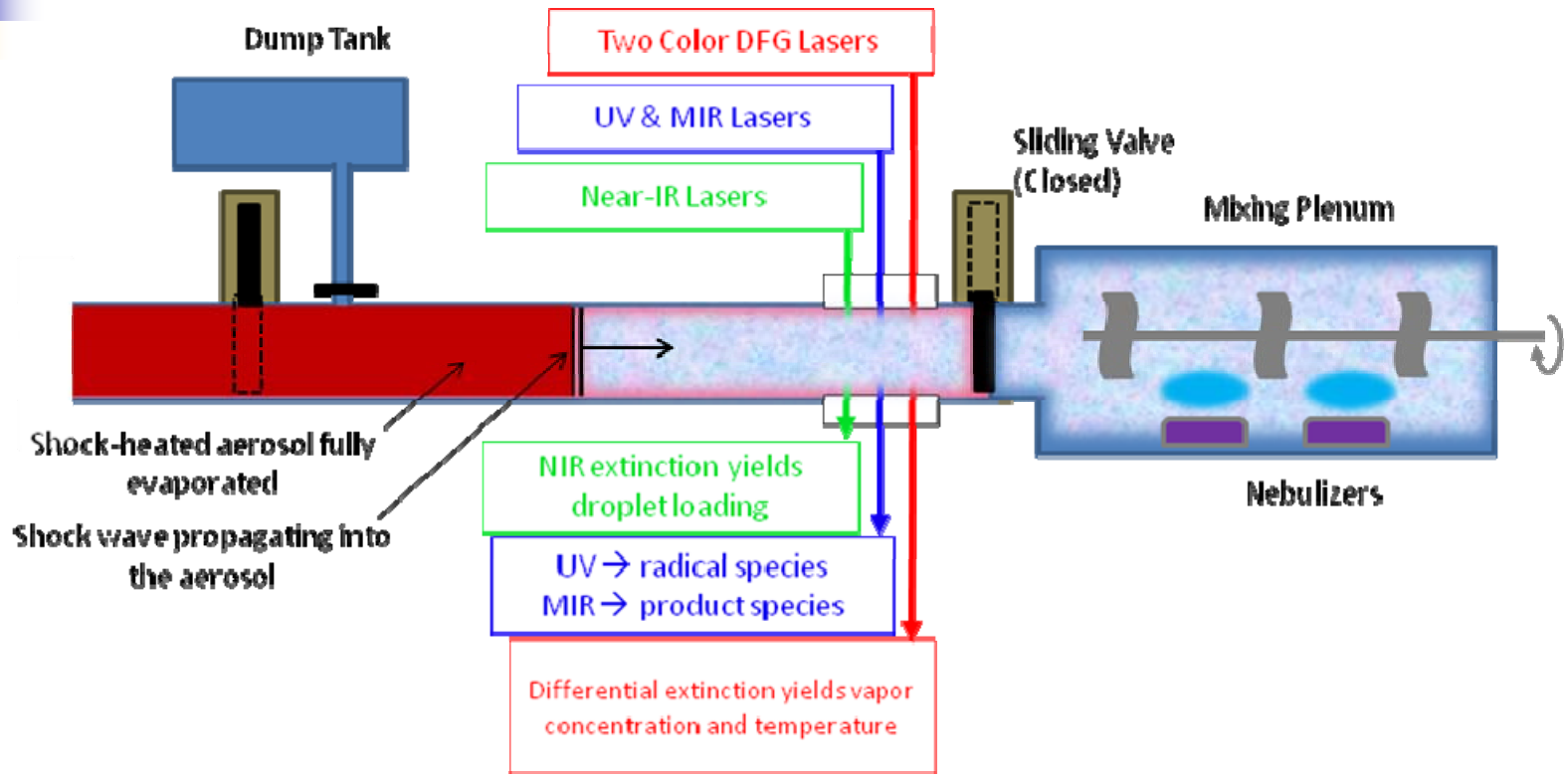
RP Fuels Stability Studies Strategy:

Measure decomposition rates with shock tubes/laser absorption

- Pyrolysis via Reflected Shock Wave Heating:
  - conventional (gas phase) and aerosol shock tubes
- Laser Absorption Diagnostics:
  - 3.39 μm mid-IR: Fuel concentration
  - 10.57 μm mid-IR: ethylene, alkenes
  - 650 nm visible: droplet extinction
- Fuels & Additives:
  - RP-1, RP-2, n-dodecane, MCH, THQ
    (RP-1 Cetane No. = 38.6: high cyclo-alkane content)
- Experimental Conditions:
  - 1050-1300 K, 2-8 atm, 0.05-0.5% fuel/Argon
- Measurement Targets:
  - Fuel half-lives
  - Species concentration time-histories: fuel, C_2H_4

Approved for Public Release; Distribution is Unlimited

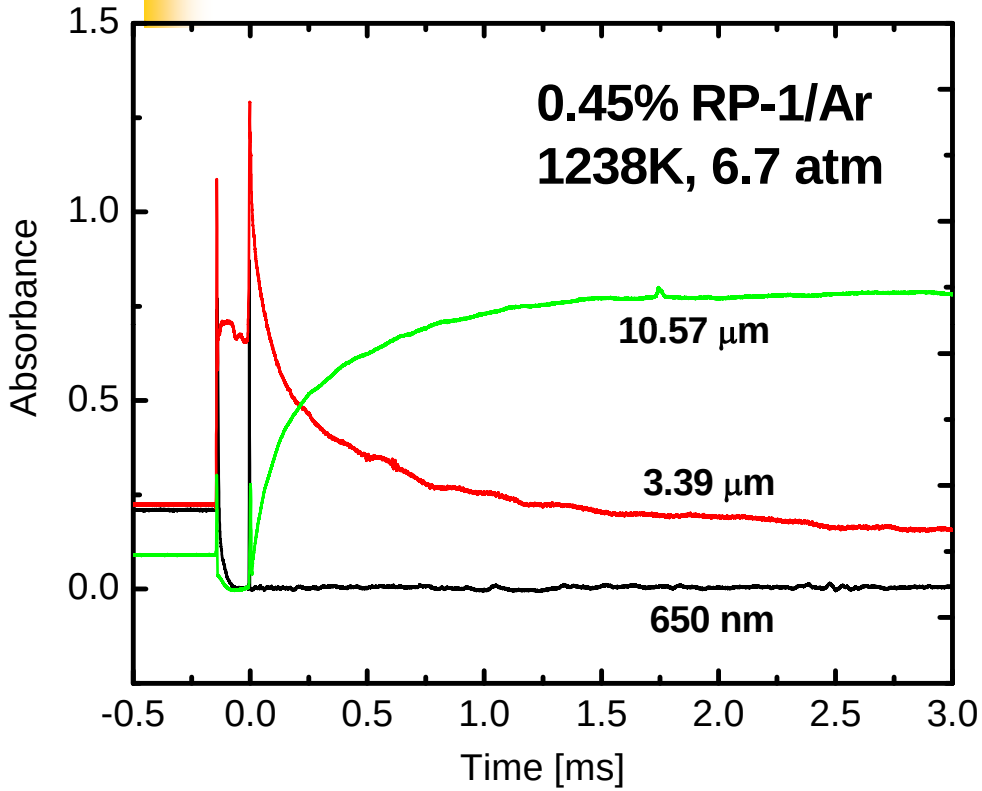
Experimental Setup: Aerosol shock tube (AST) with laser diagnostics



- AST enables study of low-vapor-pressure fuels
  - Load aerosols pre-shock
  - Full evaporation after incident shock
  - High T test conditions after reflected shock

Approved for Public Release; Distribution is Unlimited

Example AST/Laser Absorption Experiment: RP-1 Pyrolysis

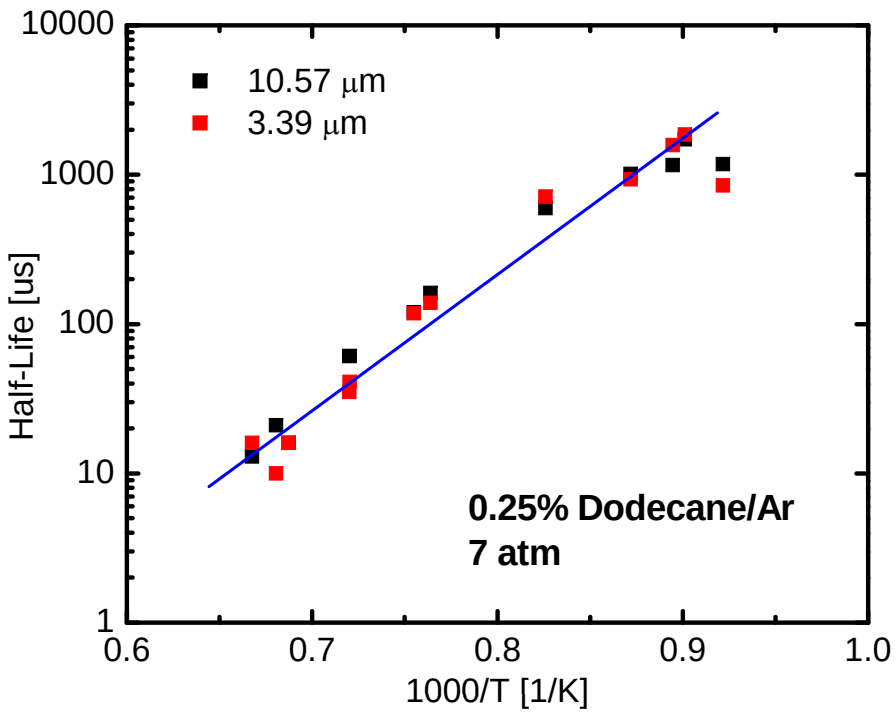


- Three wavelengths
- Excellent SNR

- 10.57 μm: absorption by ethylene and other alkenes
- 3.39 μm: absorption by fuel
- 650 nm: extinction by droplets

- Complete evaporation of RP-1 droplets behind incident shock wave
- Strong evidence of conversion of RP-1 fuel components to ethylene and higher alkenes

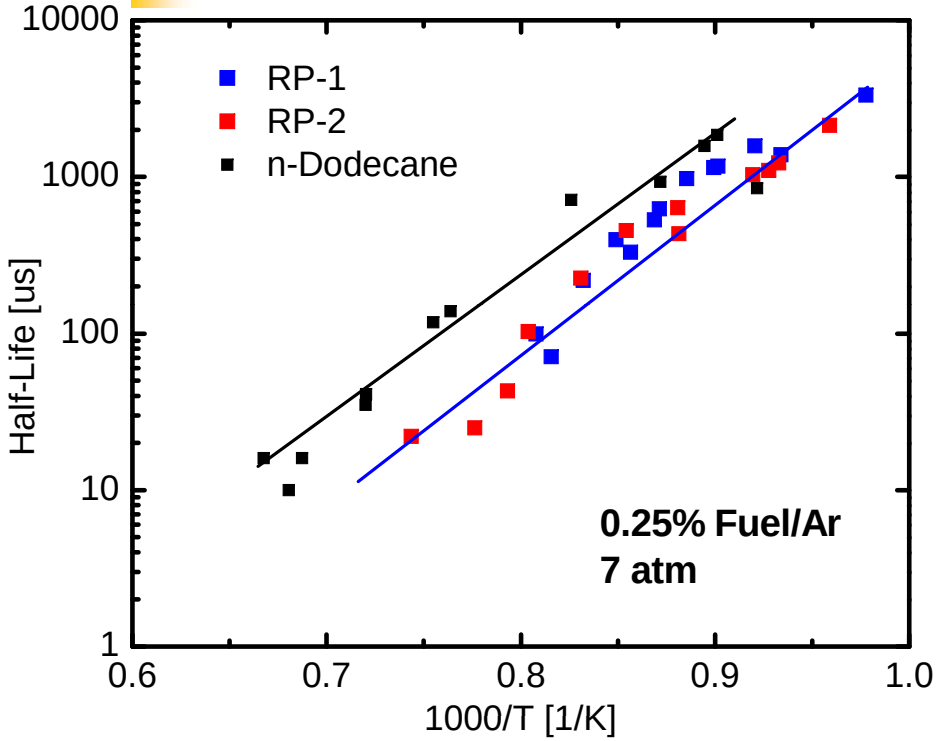
Example Half-Life Measurements: n-Dodecane Pyrolysis



- Strong temperature dependence to fuel decomposition rate as expected
- Close agreement between 10.57 μm absorption (by ethylene) and 3.39 μm: absorption (by fuel)

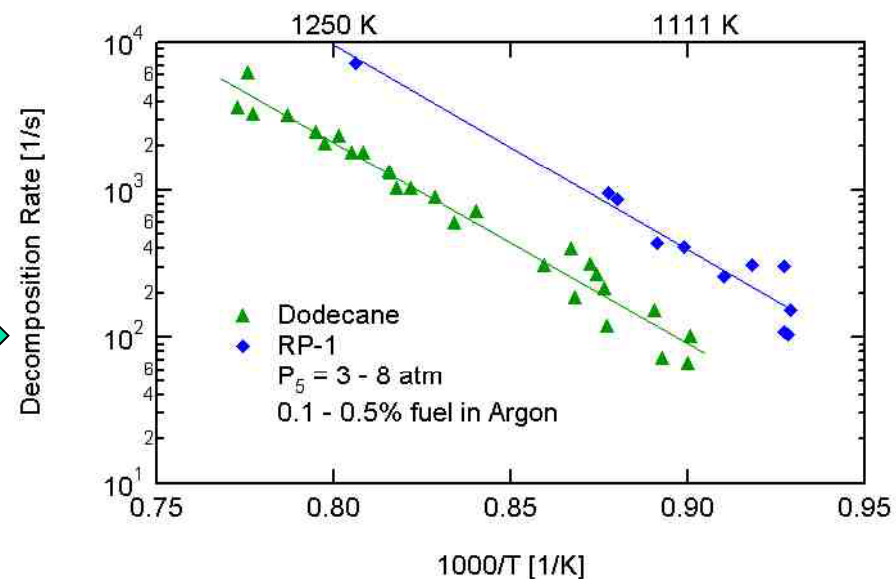
- Direct comparison of RP fuels and surrogate half-life measurements possible with and without thermal stablility additives

Comparison of Fuel Half-Life Measurements: RP-1, RP-2 and n-Dodecane Pyrolysis



- RP-1 and RP-2 have similar pyrolysis half-lives
- N-dodecane half-life ~3x RP-fuel half life

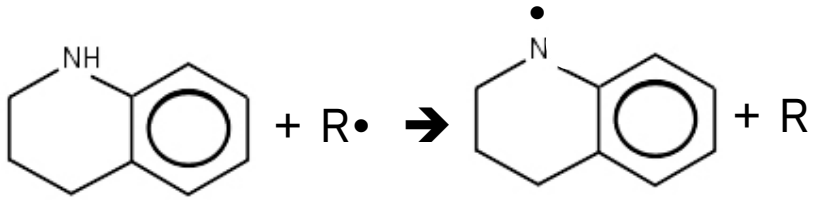
- Measurements consistent with earlier decomposition rate study (2008)
- faster decomposition rate, shorter half-life



Thermal Stability Additives: Hydrogen donors - THQ

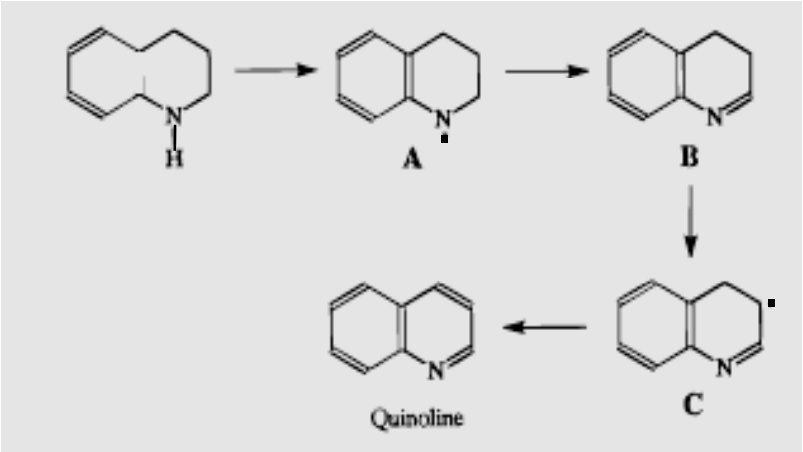
- THQ: proposed hydrogen donor additive for high temperature fuel stabilization

- Fuel Stabilization Process: Simple H-abstraction from hydrogen donor (i.e. THQ) by alkyl radicals (i.e. dodecyl $C_{12}H_{25}$•) should stabilize early fuel decomposition products and slow overall fuel decomposition rate



1,2,3,4-Tetrahydroquinoline

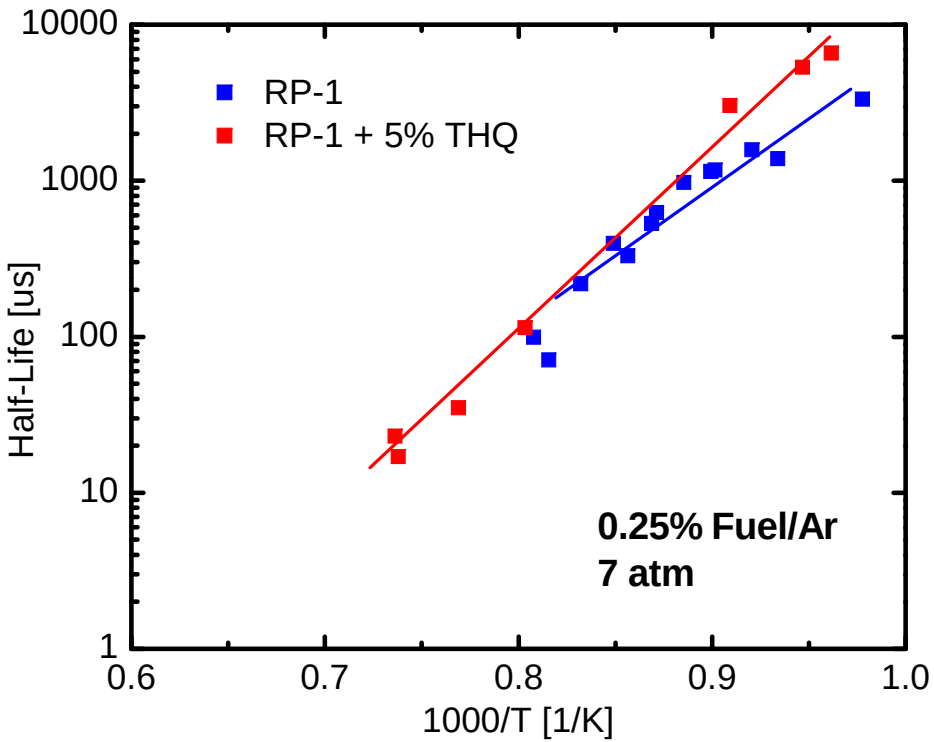
Sequential hydrogen donation to alkyl radicals by THQ (adapted from Yoon et al.)



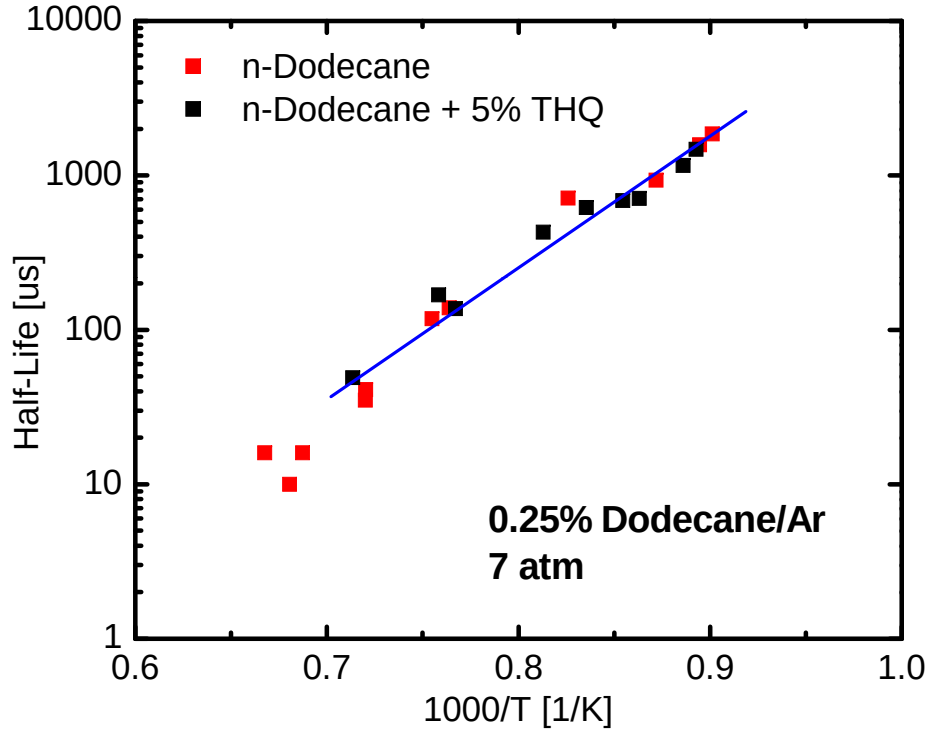
Approved for Public Release; Distribution is Unlimited

Comparison of Fuel Half-Life Measurements: Effect of Thermal Stability Additive THQ

RP-1 + THQ



N-Dodecane + THQ



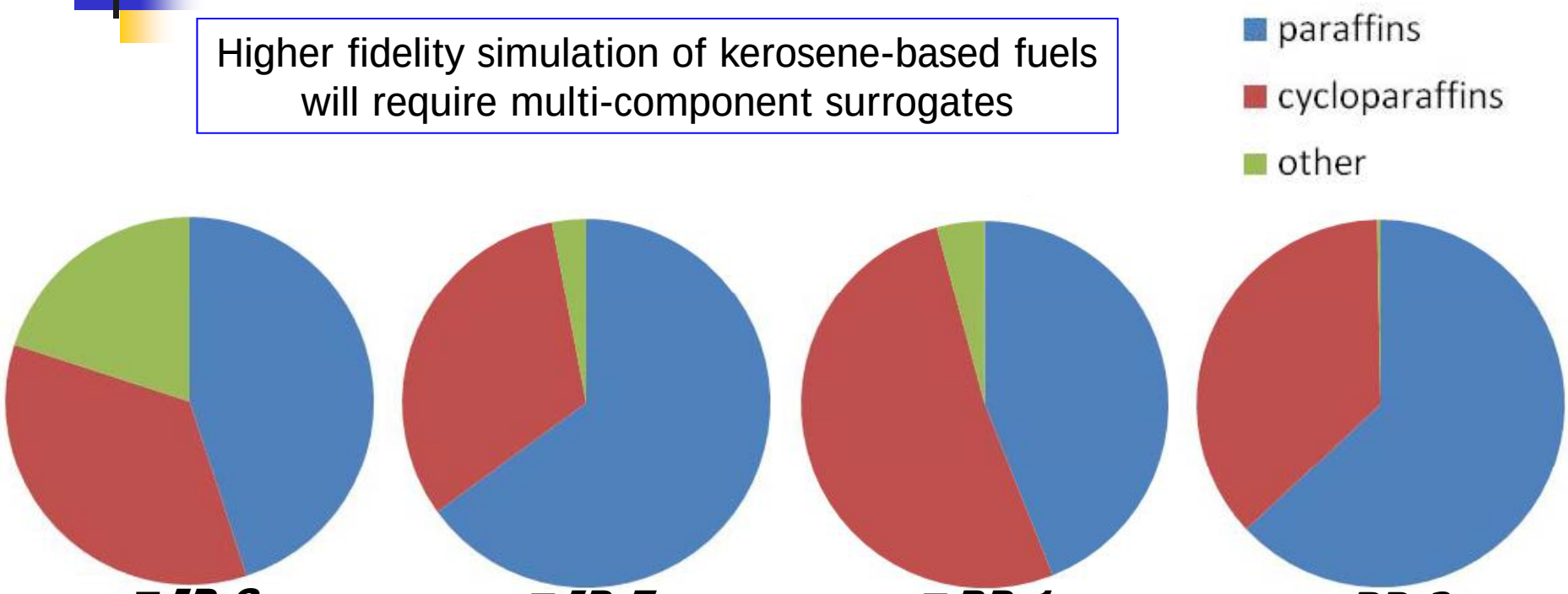
- Preliminary measurement show evidence of THQ slowing RP-1 decomposition
- Stabilizing effect not seen in n-dodecane (down to 1100 K)
- Yoon et al. (1996) sees effect with dodecane/10%THQ at 660-740K

RP Fuel Thermal Stability Studies: Status

- Pyrolysis half-life measurements provide simple test of fuel stability
  - Good agreement between ethylene formation and fuel decomposition half-lives
- Pyrolysis half-lives measured for:
  - RP-1, RP-2, n-dodecane
  - RP-1 and n-dodecane + THQ
- Further low temperature studies needed to confirm effect of THQ addition

Multi-Component RP-Fuel Surrogates and Composition of Various Aviation Fuels

Higher fidelity simulation of kerosene-based fuels will require multi-component surrogates



JP-8

- **"other" is aromatics/olefins (18/2 vol%)**
- **500 ppm total sulfur**

JP-7

- **"other" is aromatics**
- **60 ppm total sulfur**

RP-1

- **"other" is aromatics**
- **30 ppm total sulfur (max)**

RP-2

- **"other" is mostly aromatics**
- **0.1 ppm total sulfur (max)**

Testing and Validation of RP-Fuel Surrogate Pyrolysis Mechanisms

Problem:

- Intermediate temperature (600-1200K) pyrolysis mechanisms needed to describe first steps of RP fuel decomposition

Stanford Strategy:

- Multi-species testing of single component RP-fuel surrogate: n-Dodecane
- Multi-species testing of possible second component of RP-fuel surrogate: Methylcyclohexane
- Test JetSurF 1.1: possible RP-fuel surrogate mechanism for pyrolysis

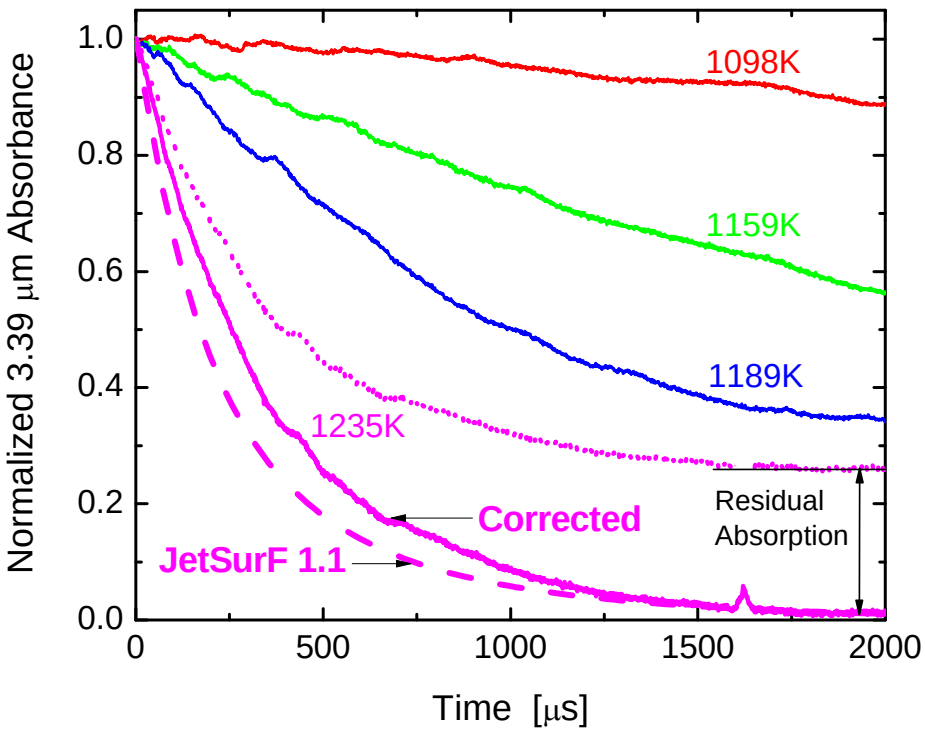
Testing and Development of a Single Component Surrogate for RP Series Fuels: N-Dodecane:

- N-Dodecane oxidation mechanisms are currently being validated
- This work focuses on pyrolysis chemistry
- Multi-species laser absorption studies of n-dodecane pyrolysis : 3.39 μm (dodecane), 10.57 μm (ethylene)

- Dodecane (and ethylene) measurements provide test of overall fuel decomposition rate
- Ethylene measurements provide test of fuel decomposition branching ratios

N-Dodecane Pyrolysis: Laser Absorption Time-Histories

400 ppm n-Dodecane/Ar, 2.4 atm

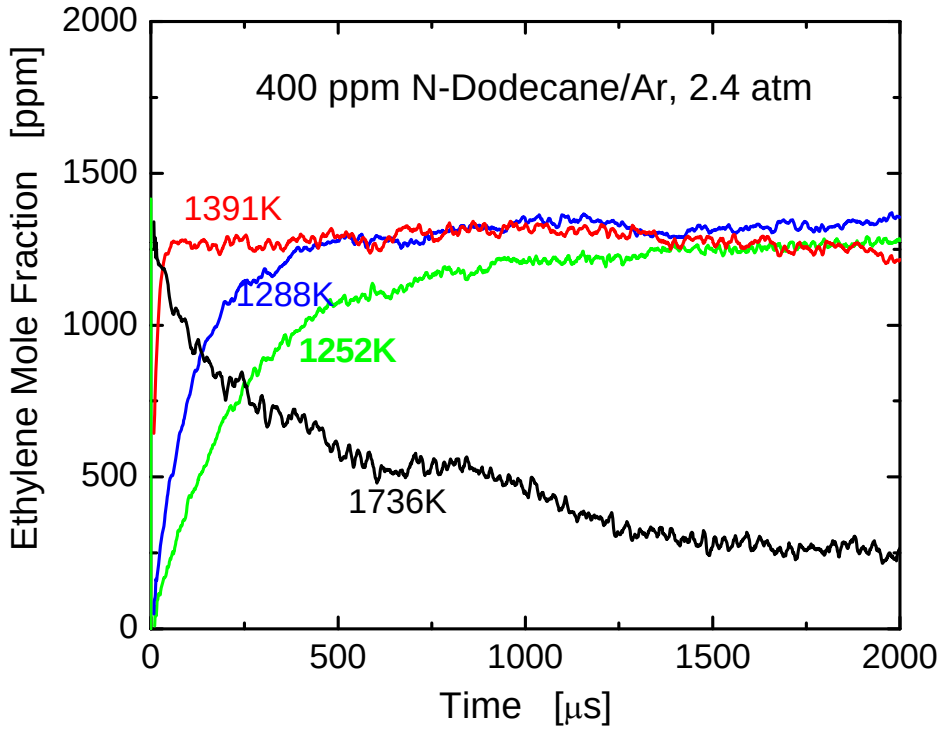


- High SNR measurement
- Strong variation of decomposition rate with temperature
- Residual absorption at long time from product species (large alkenes)

- JetSurF 1.1 model may slightly overpredict n-dodecane removal rate

Ethylene Formation during N-Dodecane Pyrolysis: 10.57 μm Laser Absorption

400 ppm n-Dodecane/Ar, 2.4 atm

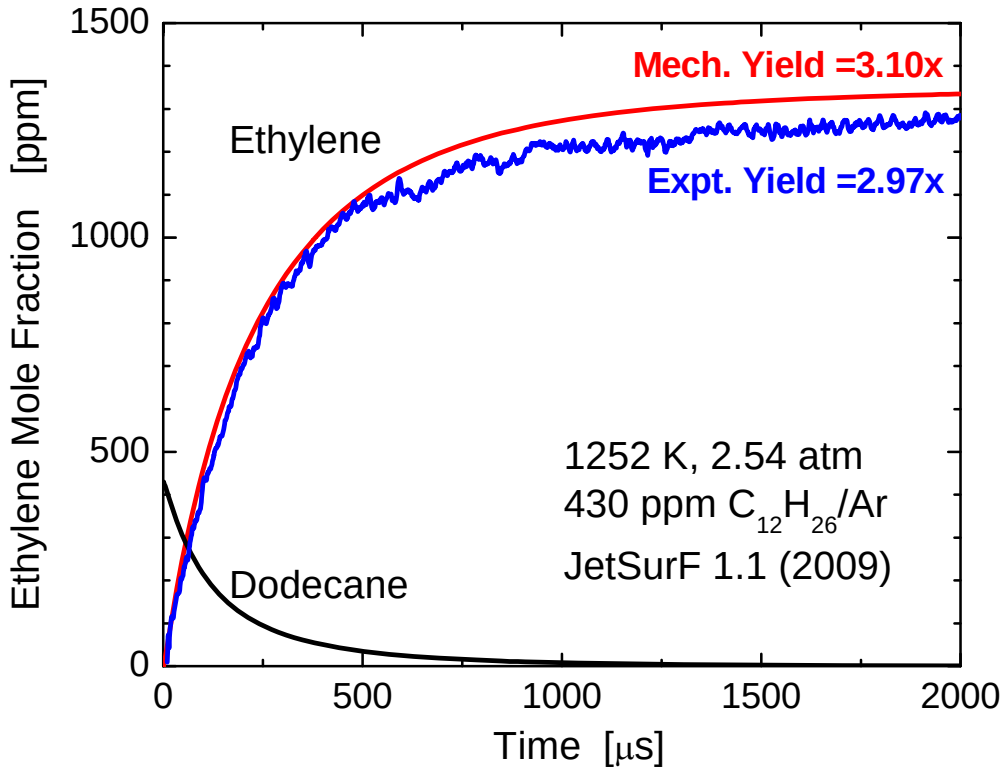


- High signal/noise ratio measurement
- Near constant ethylene yield over 1250-1736K temperature range: (2.98±0.05) C_2H_4 per $C_{12}H_{26}$ molecule

- Direct comparison with JetSurF model predictions provides check on branching ratios of decomposition pathways

Ethylene Formation during N-Dodecane Pyrolysis: Comparison with Model

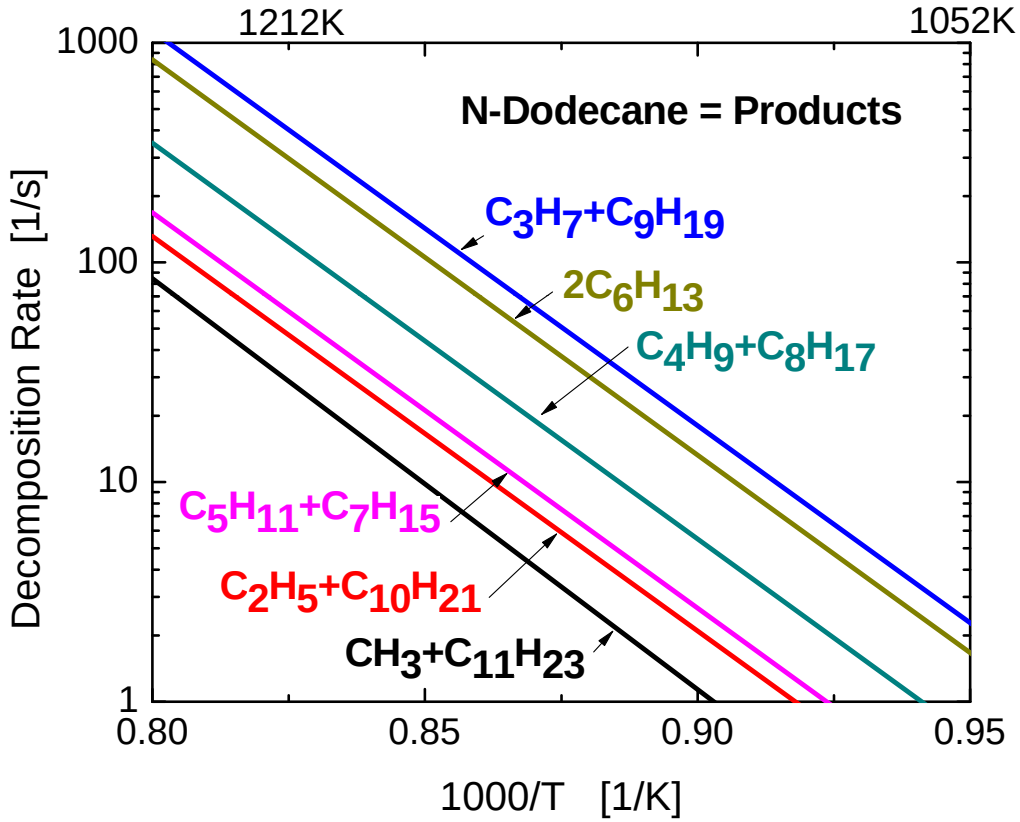
Experiment vs. JetSurF Mech.



- Constant ethylene yield (2.98±0.05) with T (1250-1736K)
- JetSurF mechanism predicts gradual rise in ethylene yield (3.1x-3.4x)
- Good agreement with product formation time scales

- Current n-dodecane decomposition rates and pathways (JetSurF) sufficiently accurate to predict major product (C_2H_4) formation rates

N-Dodecane Decomposition Channels



- JetSurF mechanism uses effectively constant branching ratios (1050-1250K) for $C_{12}H_{26}$ decomposition
- JetSurF branching ratios consistent with current experiments

Next Steps: 1) investigate higher alkane/alkene product yields in $C_{12}H_{26}$

2) Extend investigations to multi-component surrogates

Conclusions and Future Work

- Thermal Stability Studies
  - Measurements of RP-1/RP-2 decomposition in AST
  - Possible evidence of RP-1 thermal stabilization by THQ at high T
  - ➔ Kinetic model needed for THQ chemistry

- RP fuel surrogate pyrolysis mechanism development
  - Multi-species studies of n-dodecane pyrolysis
  - Initial multi-species studies of MCH pyrolysis
  - ➔ Development/refinement of RP-fuel surrogate mechanism

Approved for Public Release; Distribution is Unlimited