The Properties, Reactivity and Variability of RP-1 and RP-2

MIPR F1SBAA8022G001
MIPR F1SBAA9118G001
MIPR-F4FBEX9205G001

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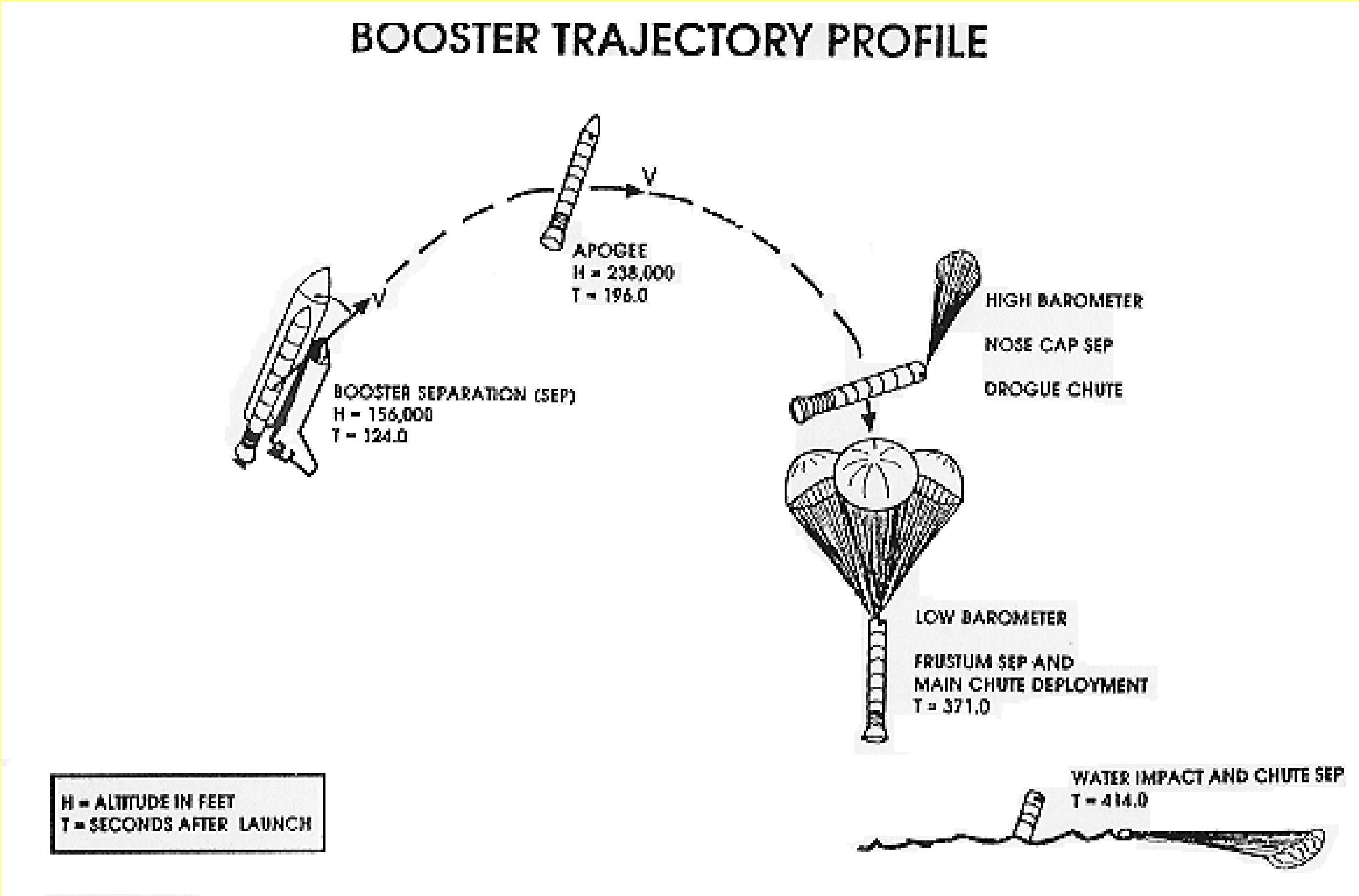
First, a bit of history

RP-1:

- Rocket Propellant 1 (refined petroleum 1)

- Kerosene base, used with LOX in rockets such as the Saturn V
- Density 0.81 - 1.02 g/mL
- Oxidizer to fuel ratio = 2.56
- Temperature of combustion = 3,670 K

Good old days: Fire it , Forget it
Nowadays: Find it, Fix it and Fly it



Fuel Composition Becomes More Critical:

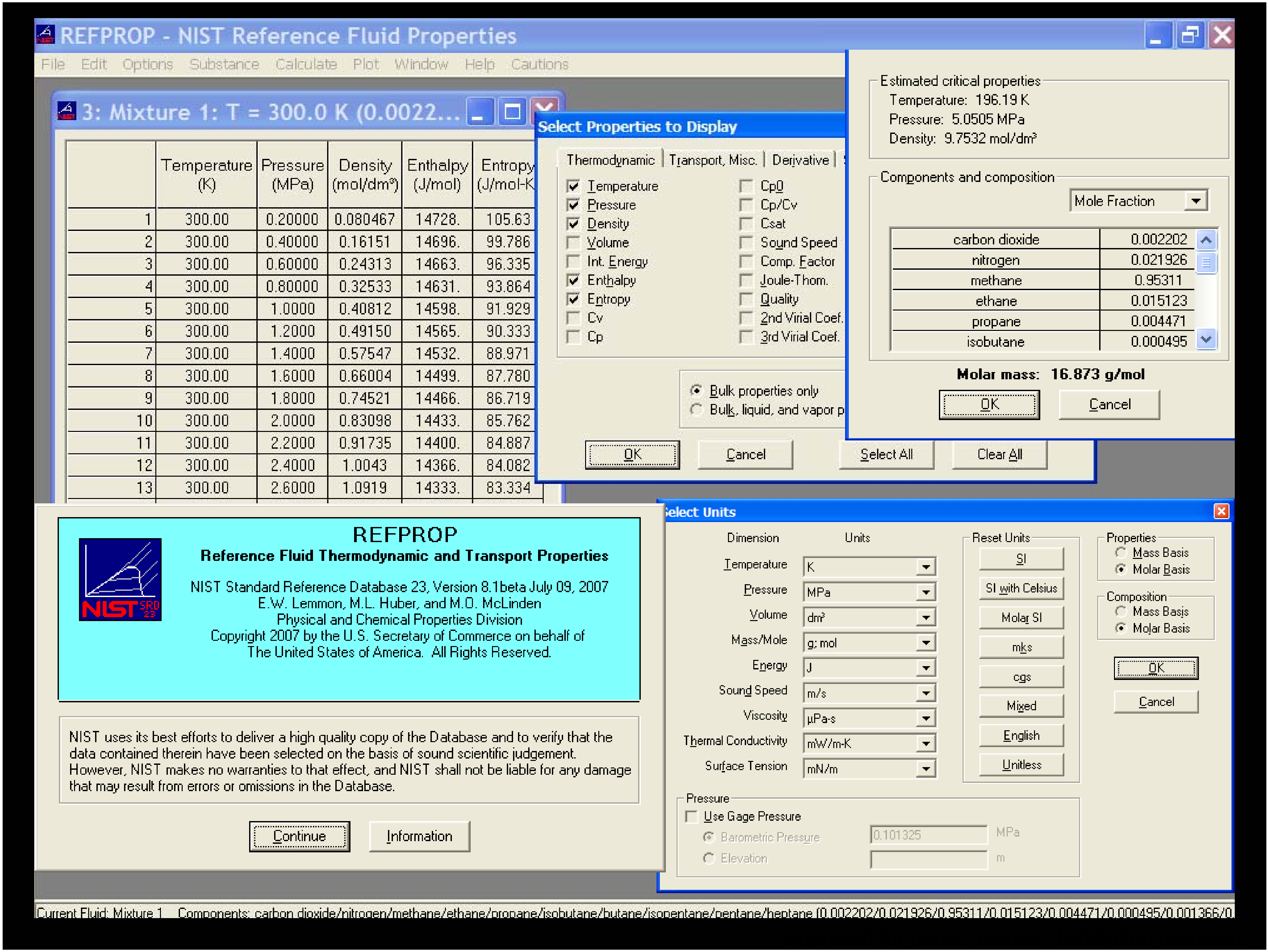
- Sulfur spec. 500 ppm to 30 ppm to 1 ppm
- Ultimately in the ppb level
  - Required remeasuring all thermophysical properties of RP-1
- The debut of “ultra”
  - A very low S kerosene; became RP-2

Executive Summary, Project 1:

AFRL-MIPR F1SBAA8022G001

- Characterization of a real fuel: RP-1/2
  - i.e., chemical analysis, **VLE**, **ρ, μ, λ, ss**
- Complete RefProp fluids files for RP-1 and RP-2
- Perform thermal decomposition studies on RP-2:
  - no additives
  - with THQ, tetralin, +100 package


Measurements go in here
Model comes out here


REFPROP - NIST Reference Fluid Properties
File Edit Options Substance Calculate Plot Window Help Cautions
3: Mixture 1: T = 300.0 K (0.0022...
Temperature (K)
Pressure (MPa)
Density (mol/dm³)
Enthalpy (J/mol)
Entropy (J/mol-K
1 300.00 0.20000 0.080467 14728. 105.63
2 300.00 0.40000 0.16151 14696. 99.786
3 300.00 0.60000 0.24313 14663. 96.335
4 300.00 0.80000 0.32533 14631. 93.864
5 300.00 1.0000 0.40812 14598. 91.929
6 300.00 1.2000 0.49150 14565. 90.333
7 300.00 1.4000 0.57547 14532. 88.971
8 300.00 1.6000 0.66004 14499. 87.780
9 300.00 1.8000 0.74521 14466. 86.719
10 300.00 2.0000 0.83098 14433. 85.762
11 300.00 2.2000 0.91735 14400. 84.887
12 300.00 2.4000 1.0043 14366. 84.082
13 300.00 2.6000 1.0919 14333. 83.334
Select Properties to Display
Thermodynamic
Transport, Misc.
Derivative
Temperature
Pressure
Density
Volume
Int. Energy
Enthalpy
Entropy
Cv
Cp
Cp0
Cp/Cv
Csat
Sound Speed
Comp. Factor
Joule-Thom.
Quality
2nd Virial Coef.
3rd Virial Coef.
Bulk properties only
Bulk, liquid, and vapor p
OK
Cancel
Select All
Clear All
Estimated critical properties
Temperature: 196.19 K
Pressure: 5.0505 MPa
Density: 9.7532 mol/dm³
Components and composition
Mole Fraction
carbon dioxide 0.002202
nitrogen 0.021926
methane 0.95311
ethane 0.015123
propane 0.004471
isobutane 0.000495
Molar mass: 16.873 g/mol
OK
Cancel
REFPROP
Reference Fluid Thermodynamic and Transport Properties
NIST Standard Reference Database 23, Version 8.1beta July 09, 2007
E.W. Lemmon, M.L. Huber, and M.O. McLinden
Physical and Chemical Properties Division
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Continue
Information
elect Units
Dimension
Units
Temperature K
Pressure MPa
Volume dm³
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Energy J
Sound Speed m/s
Viscosity µPa-s
Thermal Conductivity mW/m-K
Surface Tension mN/m
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Current Fluid: Mixture 1 Components: carbon dioxide/nitrogen/methane/ethane/propane/isobutane/butane/isopentane/pentane/heptane (0.002202/0.021926/0.95311/0.015123/0.004471/0.000495/0.001366/0.

Documentation:

- Bruno, T. J., Smith, B.L., Improvements in the measurement of distillation curves - part 2: application to aerospace/aviation fuels RP-1 and S-8. *Ind. Eng. Chem. Res.* 2006, 45, 4381-4388.

- Lovestead, T. M., Bruno, T.J., Comparison of the hypersonic vehicle fuel JP-7 to the rocket propellants RP-1 and RP-2 with the advanced distillation curve method. *Energy & Fuels* 2009, in press.

- Ott, L. S., Hadler, A., Bruno, T.J., Variability of the rocket propellants RP-1, RP-2, and TS-5: application of a composition- and enthalpy-explicit distillation curve method. *Ind. Eng. Chem. Res*. 2008, 47 (23), 9225-9233.

- Widegren, J. A., Bruno, T.J. The Properties of RP-1 and RP-2, Interim Report, MIPR F1SBAA8022G001; March, 2008.

- Magee, J. W., Bruno, T.J., Friend, D. G., Huber, M.L., Laesecke, A., Lemmon, E.W., McLinden, M.O., Perkins, R.A., Baranski, J., Widegren, J.A. Thermophysical Properties Measurements and Models for Rocket Propellant RP-1: Phase I, NIST- IR 6644, National Institute of Standards and Technology (U.S.),; 2006.

- Huber, M. L., Lemmon, E., Ott, L.S., Bruno, T.J., Preliminary surrogate mixture models for rocket propellants RP-1 and RP-2. *Energy & Fuels* 2009, 23, 3083-3088.

- Huber, M. L., Lemmon, E., Bruno, T.J., Effect of RP-1 compositional variability on thermophysical properties. *Energy & Fuels* 2009, in press.

- Perform thermal decomposition studies on RP-2:
  - no additives
  - with THQ, tetralin, +100 package

Last Year, for the third task,

all I had was a teaser!

Executive Summary:

AFRL-MIPR F1SBAA8022G001

Perform thermal decomposition studies on RP-2:

- no additives
- with THQ, tetralin, +100 package

- All measurements have since been completed, and were presented at:
    - Joint NIST/AFRL Workshop on Rocket Propellants and Hypersonic Vehicle Fuels, September 25 and 26, 2008 at the Boulder, Colorado Laboratories of NIST
    - JANNAF 6th Modeling and Simulation / 4th Liquid Propulsion / 3rd Spacecraft Propulsion Joint Subcommittee Meeting, Orlando, Florida, 8-12 December, 2008.

Executive Summary, Project 2:

AFRL-MIPR F1SBAA9118G001

- Study the additive concentration dependence of thermal decomposition for THQ

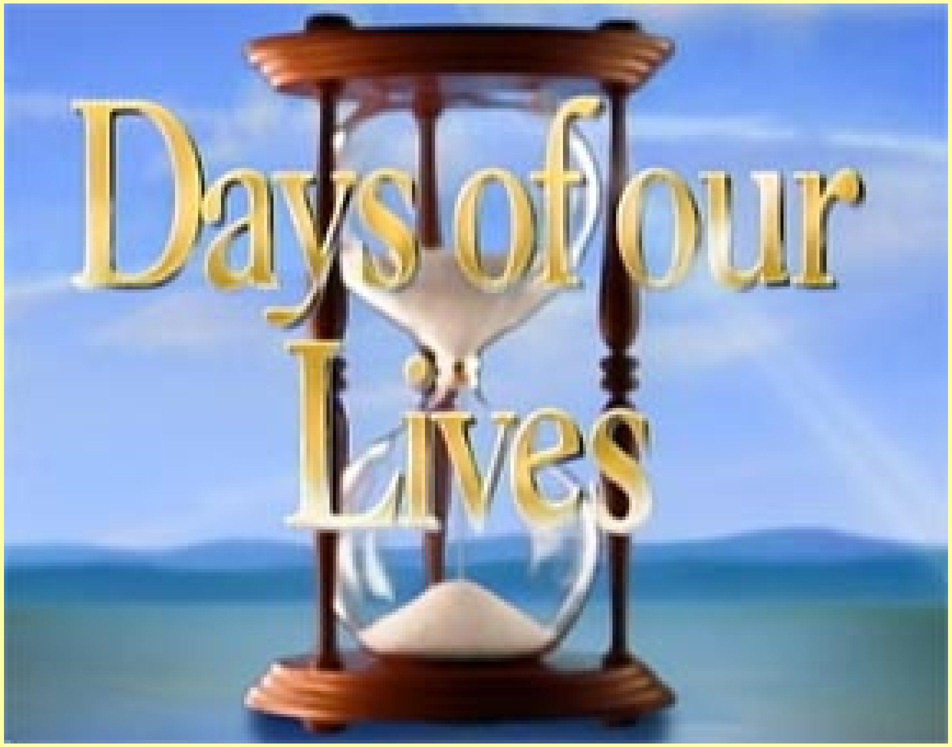
Executive Summary, Project 3:
AFRL-MIPR-F4FBEX9205G001

- Evaluate the variability of RP-1:
  - For a set of orthogonal* samples
    - Measure composition, VLE (ADC), **ρ, μ, ss**
    - Compare with RefProp predictions

*orthogonal means separate batches or different recipes.

- That’s the administrative layout,

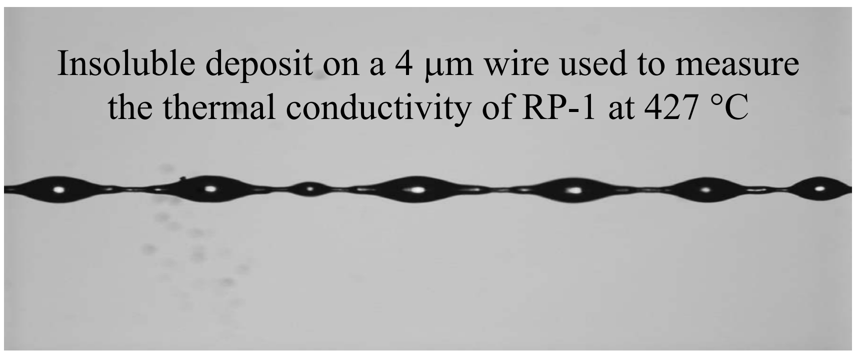
  technical aspects will be presented in soap opera order.

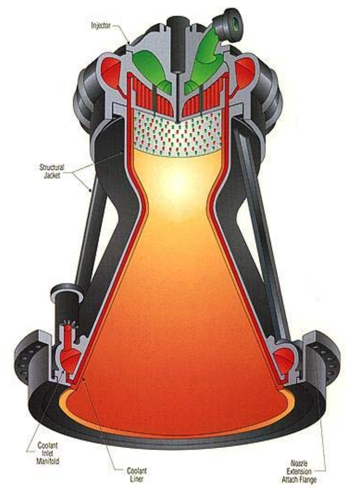


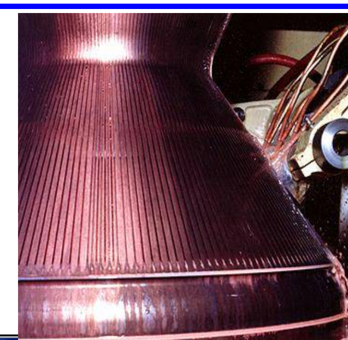
Thermal Decomposition:

NIST-specific:
- Ensure the quality of property data at high *T*
- Protect our expensive instruments from decomposition products

Application:
- The fuel cools the walls of the thrust chamber
- Avoid engine failure caused by fuel decomposition

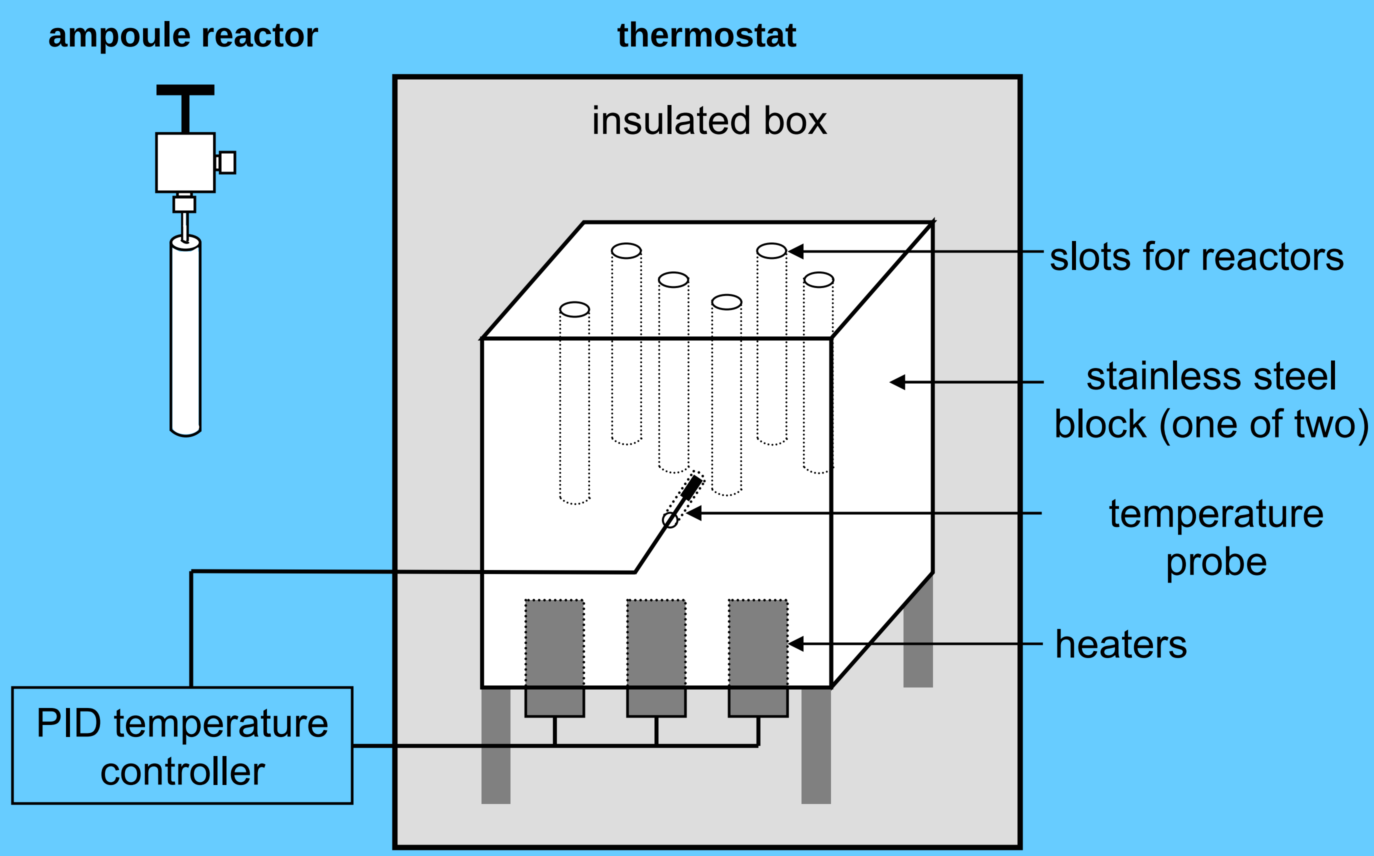

Insoluble deposit on a 4 μm wire used to measure the thermal conductivity of RP-1 at 427 °C





The kinetics of decomposition are important!

Fuels are thermally stressed in stainless steel ampoule reactors



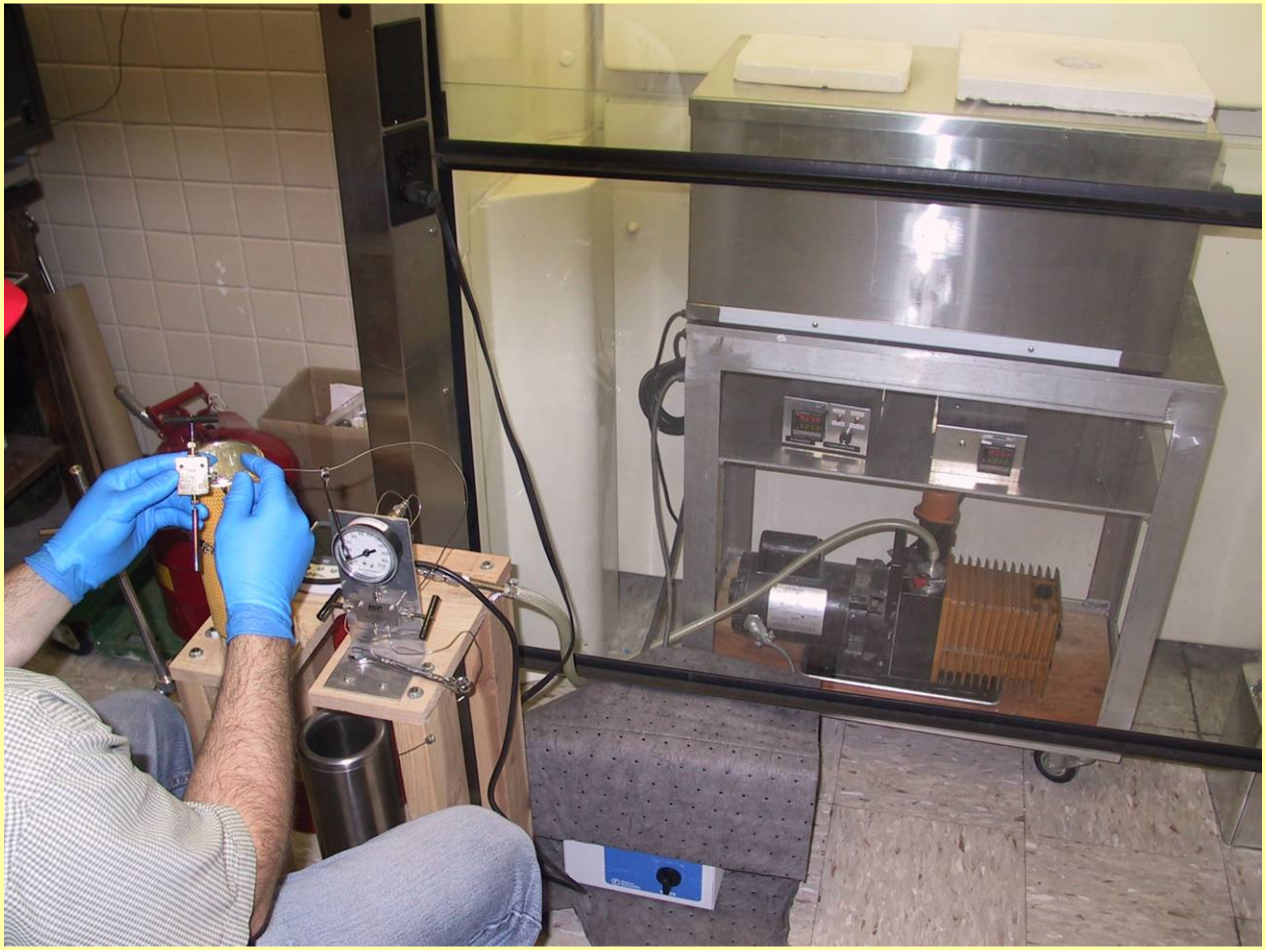
Reactors:

Maximum *T* and *p*:

500 °C / 773 K

15,000 psi / 103 MPa

Thermostat

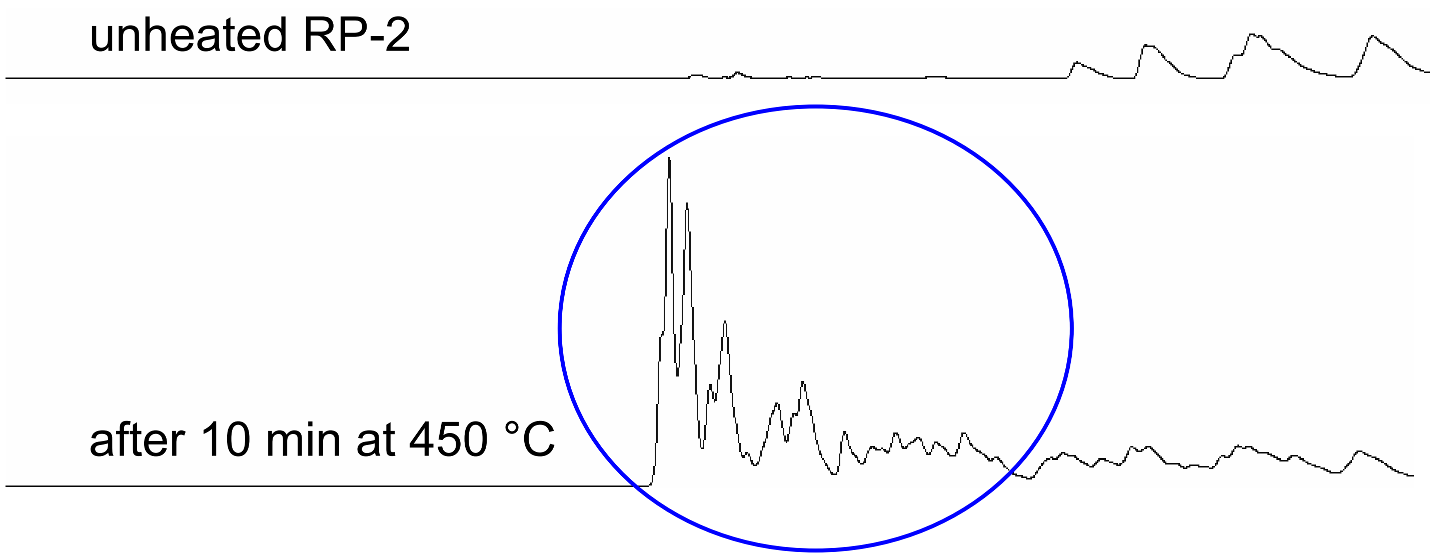


Reaction conditions

- Initial pressure of 5000 psia (34.5 MPa)
- Temperature range: 375, 400, 425, 450 °C
648, 673, 698, 723 K
- Reaction times from 10 min to 24 h
- Thermal equilibration time of ~2 min

Extent of decomposition determined by analysis

Emergent suite of GC-FID chromatograms for RP-2



Light decomposition products are used for the kinetic analysis.

Pseudo-first-order kinetics on the emergent suite of decomposition products

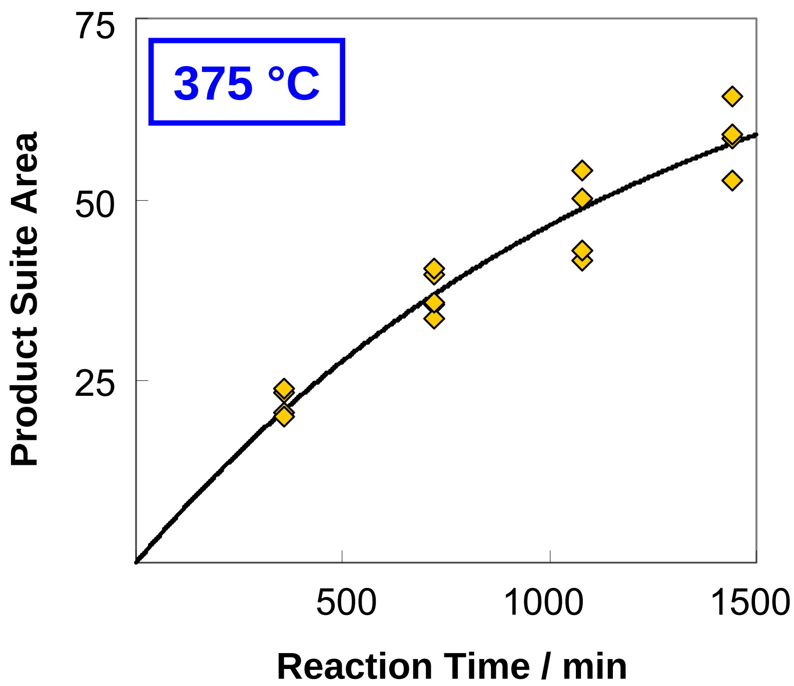
$$\mathrm{A} \xrightarrow{\mathrm{k}'} \mathrm{B}$$

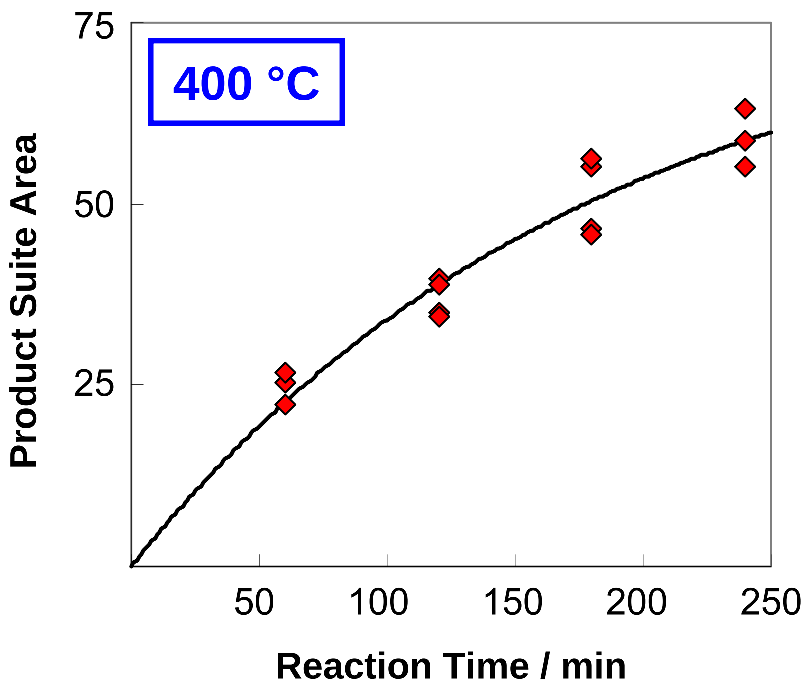
$$-\frac{d[A]}{dt} = \frac{d[B]}{dt} = k'[A]$$

$$t_{1/2} = \frac{\ln 2}{k'}$$

The assumption of first-order kinetics is a necessary approximation for these complex mixtures.

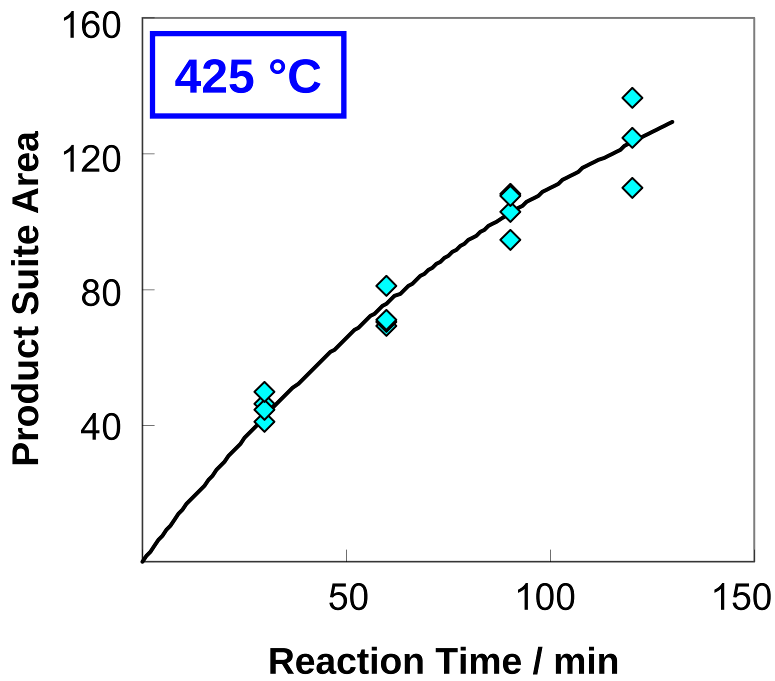
Decomposition kinetics of RP-2

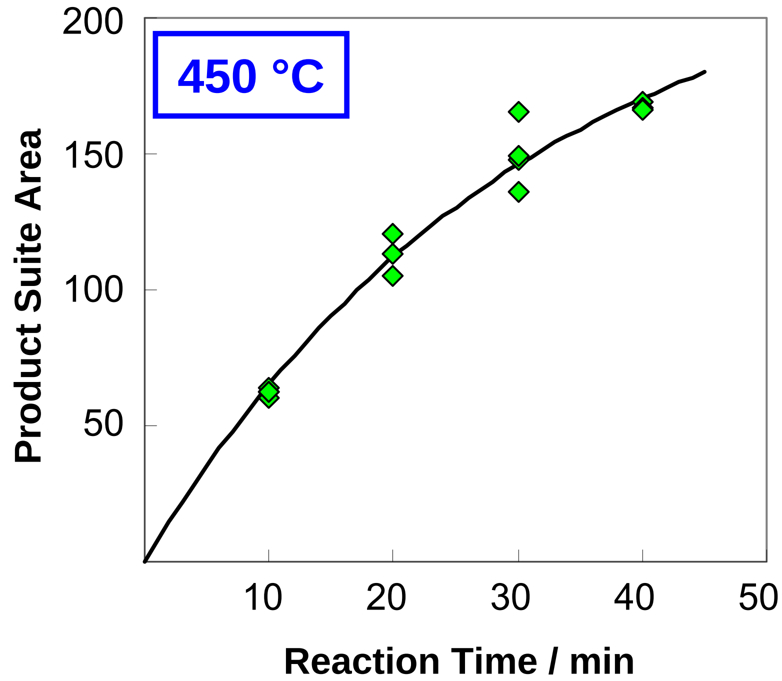




The rate constant for decomposition, *k′*, is obtained from the fit.

Decomposition kinetics of RP-2





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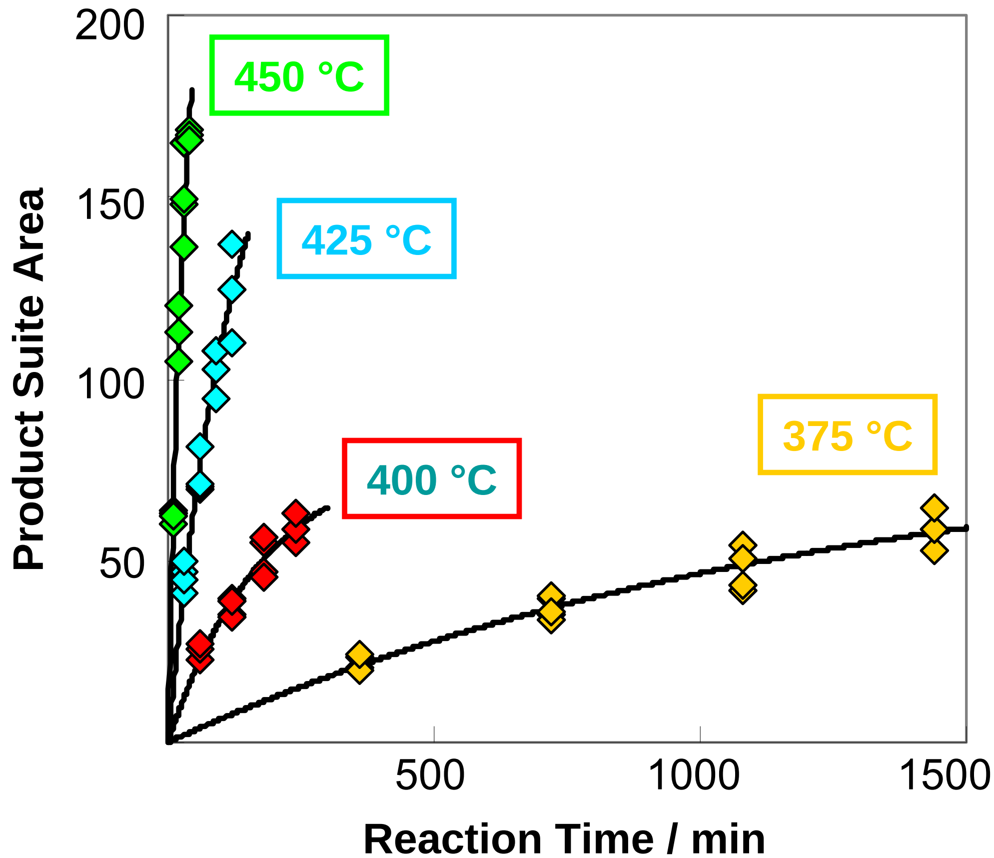
Decomposition kinetics of RP-2



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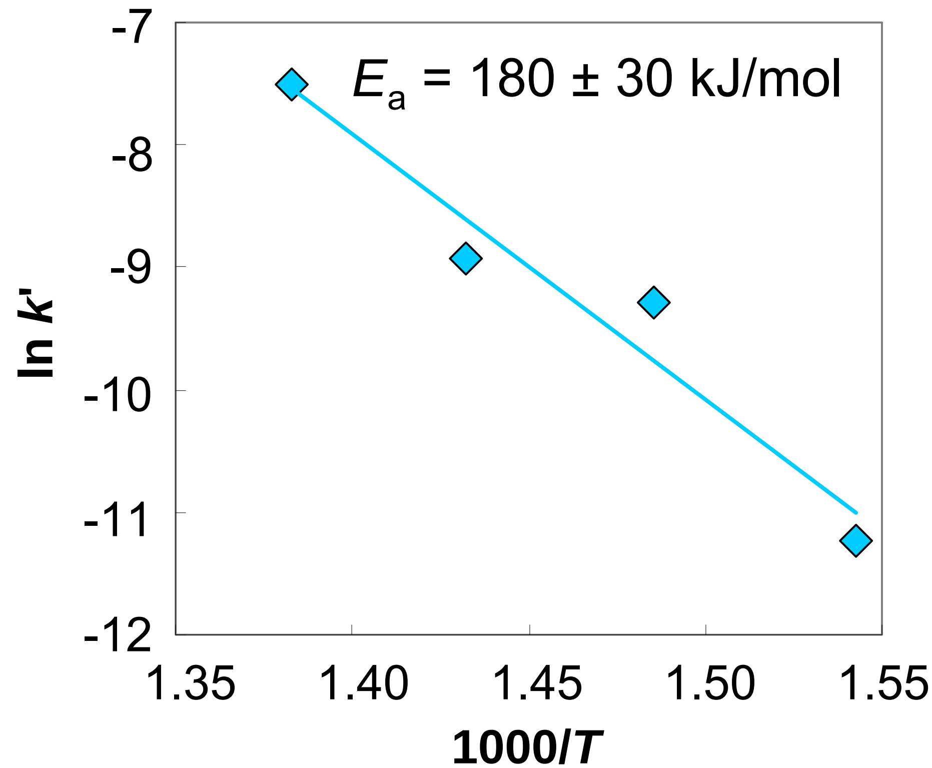
Rate constants for RP-2 decomposition

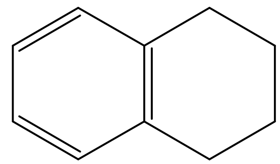
T / °C	$(k' \pm 1\sigma)$ / s^{-1}
375	$(1.33 \pm 0.30)\times10^{-5}$
400	$(9.28 \pm 2.01)\times10^{-5}$
425	$(1.33 \pm 0.33)\times10^{-4}$
450	$(5.47 \pm 0.80)\times10^{-4}$

An Arrhenius plot is useful because it is predictive.

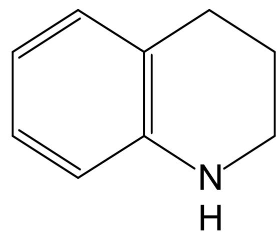


Decomposition of RP-2 with additives

- RP-2 with 5% tetralin



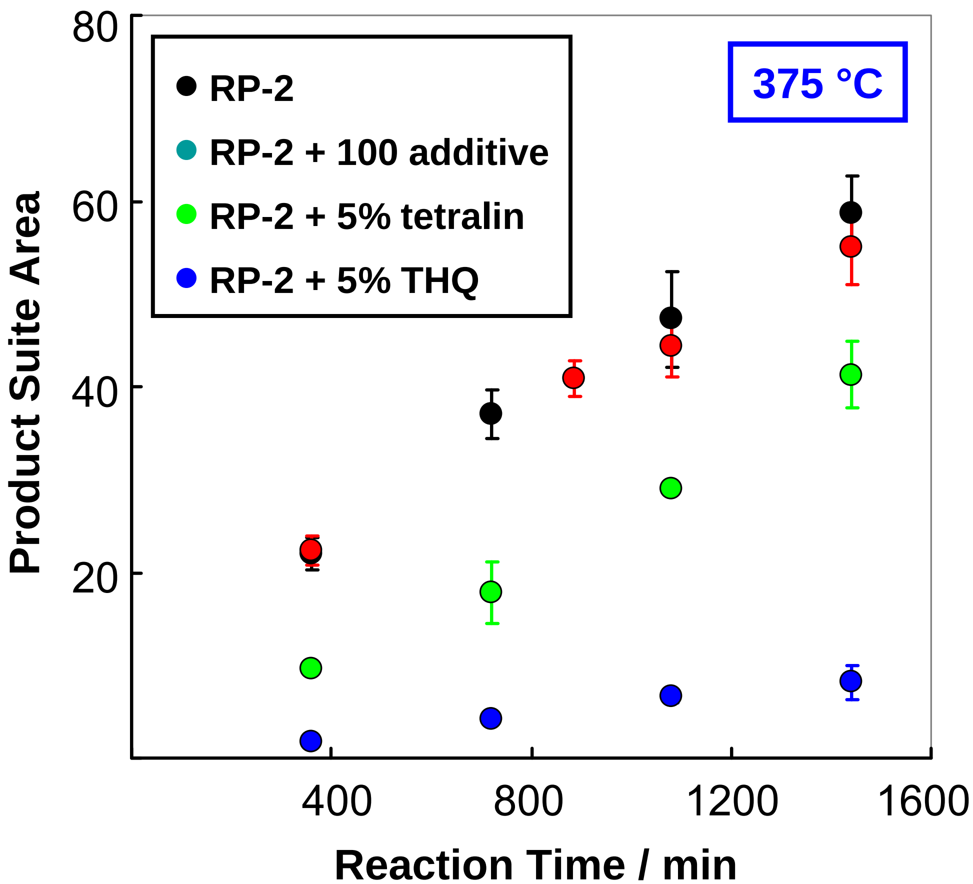
- RP-2 with 5% THQ



Hydrogen donors increase thermal stability by interrupting radical decomposition pathways.

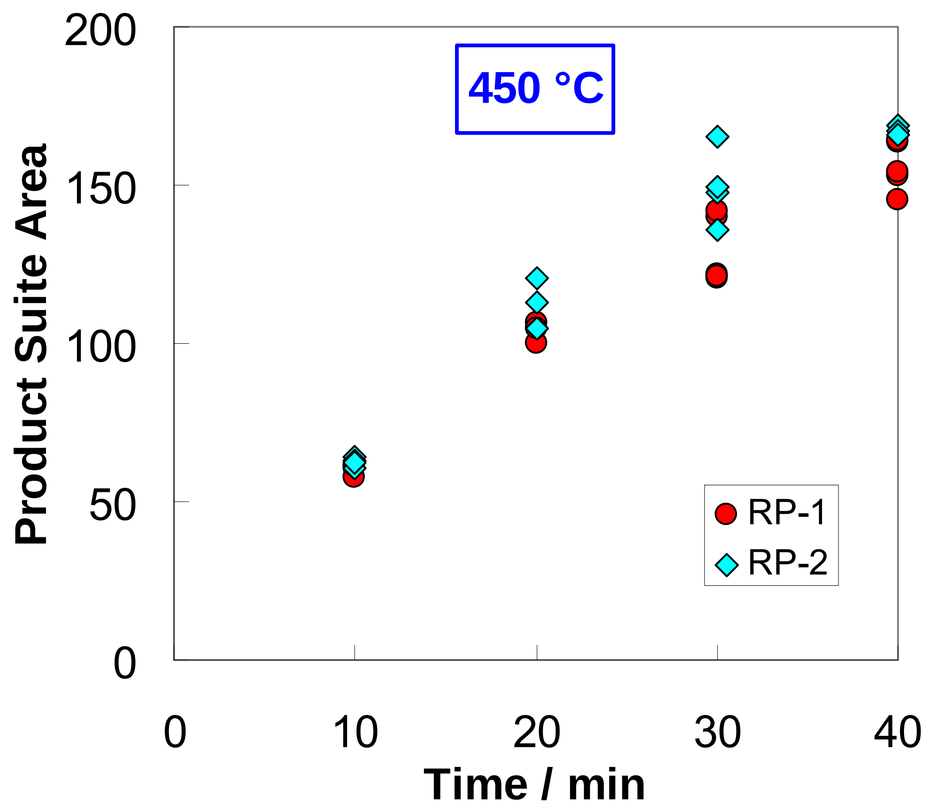
- RP-2 with 256 ppm of the additive mixture in JP-8+100
  - metal deactivator, anti-oxidant, and dispersant

Decomposition of RP-2 with additives



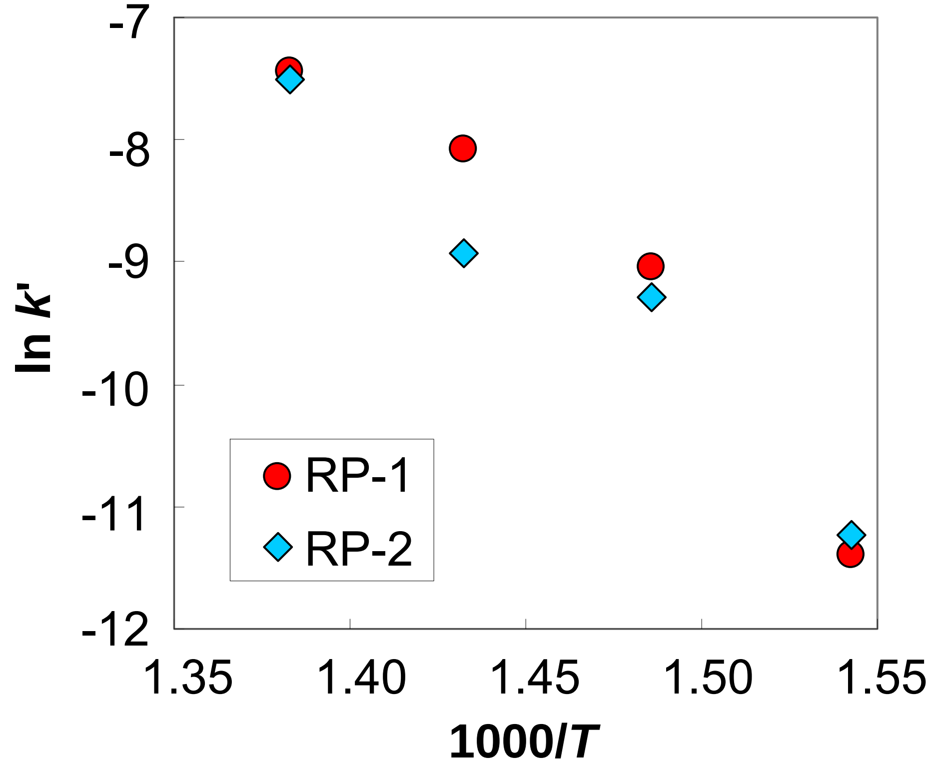
5% THQ lowers the rate of decomposition by about an order of magnitude.

Decomposition kinetics of RP-1



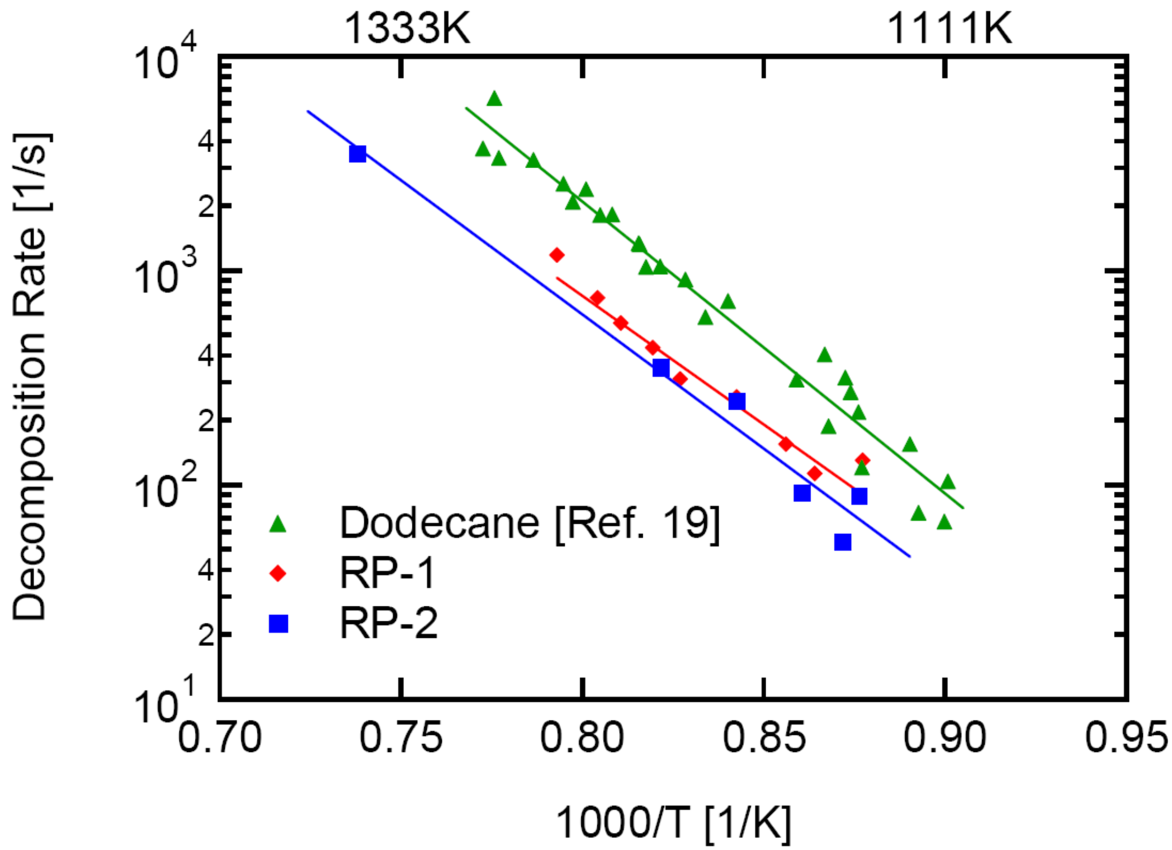
The decomposition of RP-1 and RP-2 is very similar.

Comparison of RP-1 and RP-2 decomposition



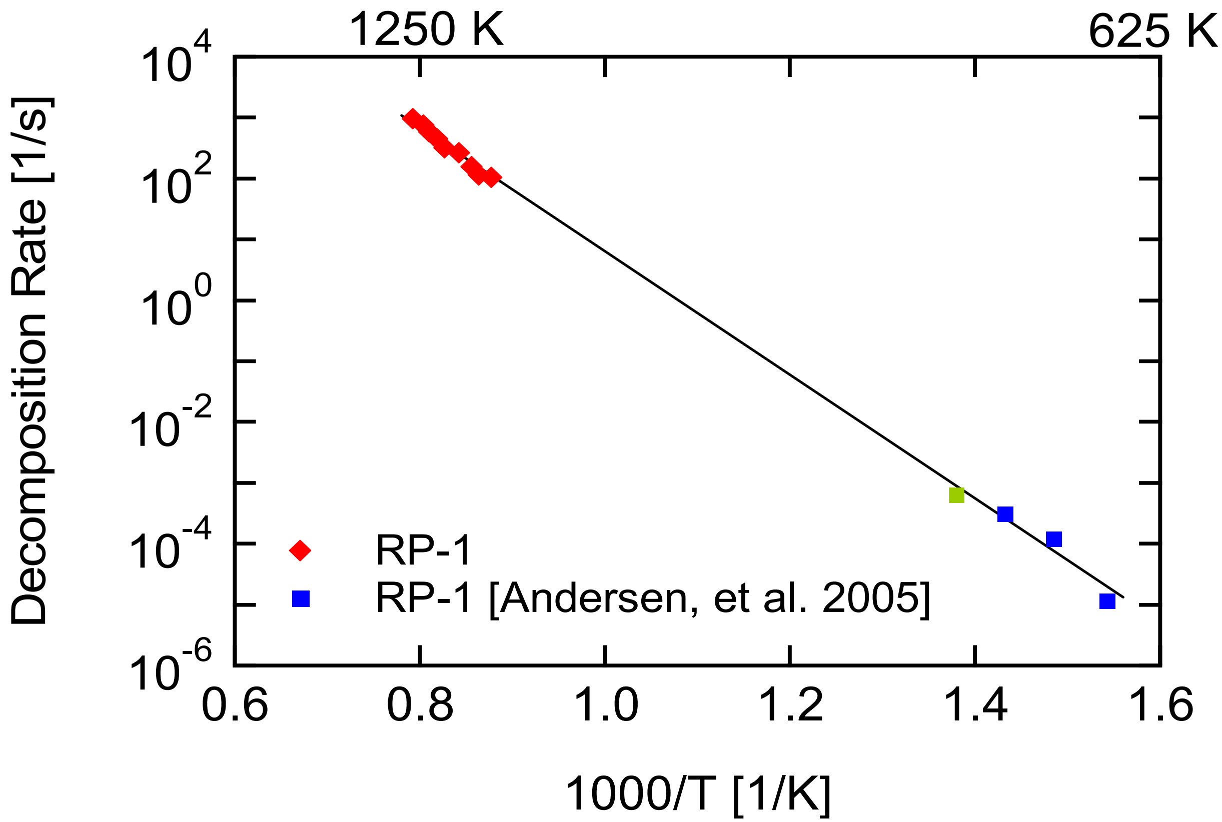
There is no significant difference between RP-1 and RP-2.

High-temperature shock tube data from Stanford



MacDonald, M. E.; Davidson, D. F.; Hanson, R. K. Decomposition Rate Measurements of RP-1, RP-2, n-Dodecane, and RP-1 with Fuel Stabilizers. 44th AIAA/ASME/SAE/ASEE Joint Propulsion Conference & Exhibit, Hartford, CT, 2008; AIAA Paper 2008-4766.

Comparison with high-temperature shock tube data for RP-1 from Stanford



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Andersen, P.C., Bruno, T.J., Thermal decomposition kinetics of RP-1 rocket propellant. *Ind. Eng. Chem. Res.* 2005, 44, (6), 1670-1676.

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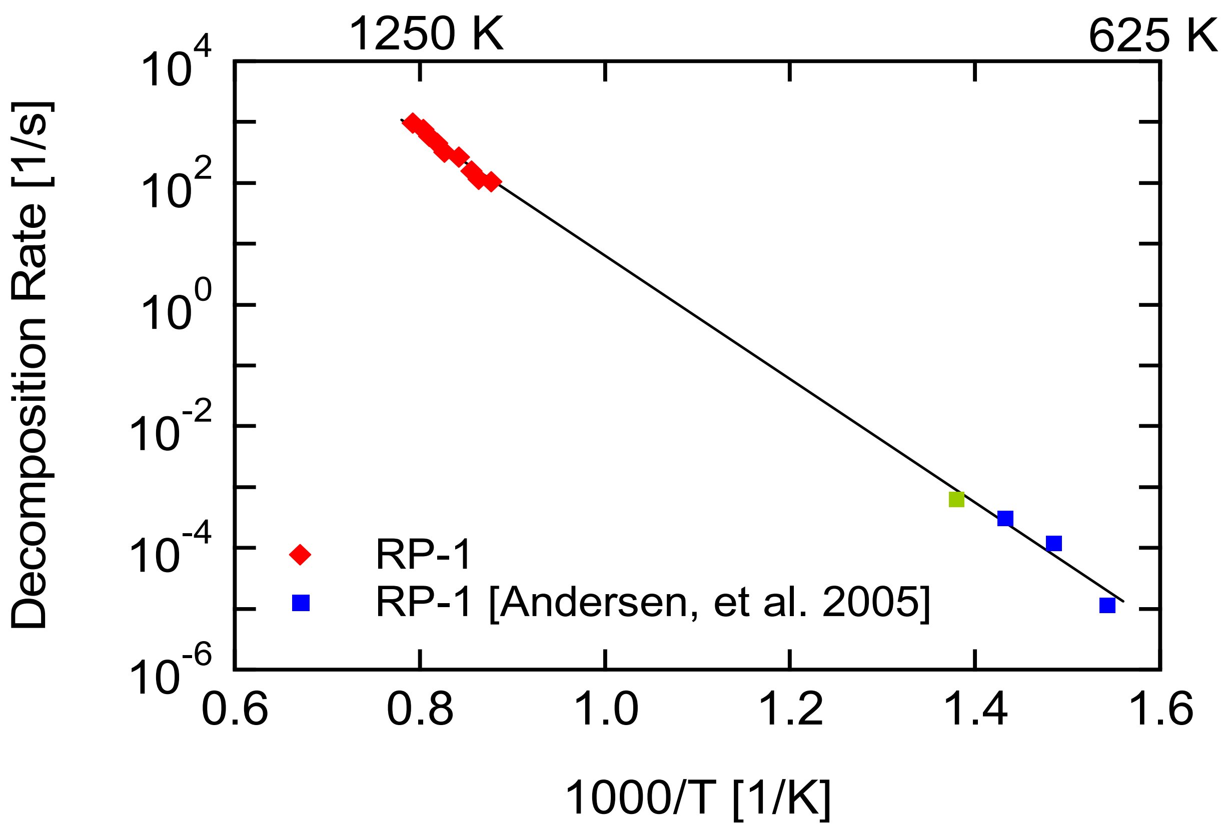
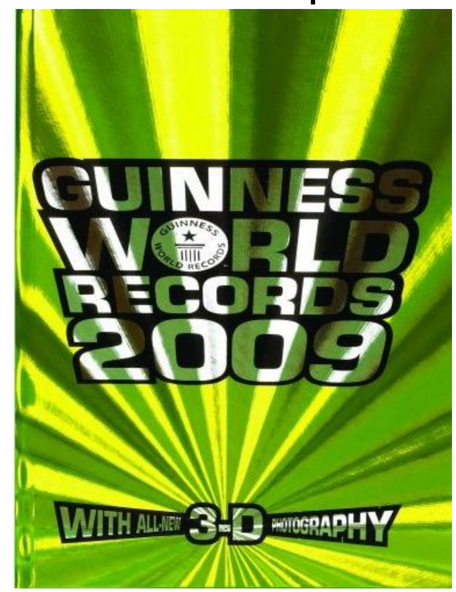


Worlds longest Arrhenius plot



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Documentation:

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- Widegren, J. A., Bruno, T.J. The Properties of RP-1 and RP-2, Interim Report, MIPR F1SBAA8022G001; March, 2008.

- Widegren, J. A., Bruno, T.J., Thermal decomposition kinetics of the kerosene based rocket propellants 2. RP-2 stabilized with three additives. *Energy & Fuels* 2008, in press.

- Widegren, J. A., Bruno, T.J., Thermal decomposition of RP-1 and RP-2, and mixtures of RP-2 with stabilizing additives, December, 2008. *Proc. 4th Liquid Propulsion Subcommittee, JANNAF* 2008, December.

- Widegren, J. A., Bruno, T.J., Thermal decomposition kinetics of kerosene-based rocket propellants. 1. comparison of RP-1 and RP-2. *Energy & Fuels* in press.

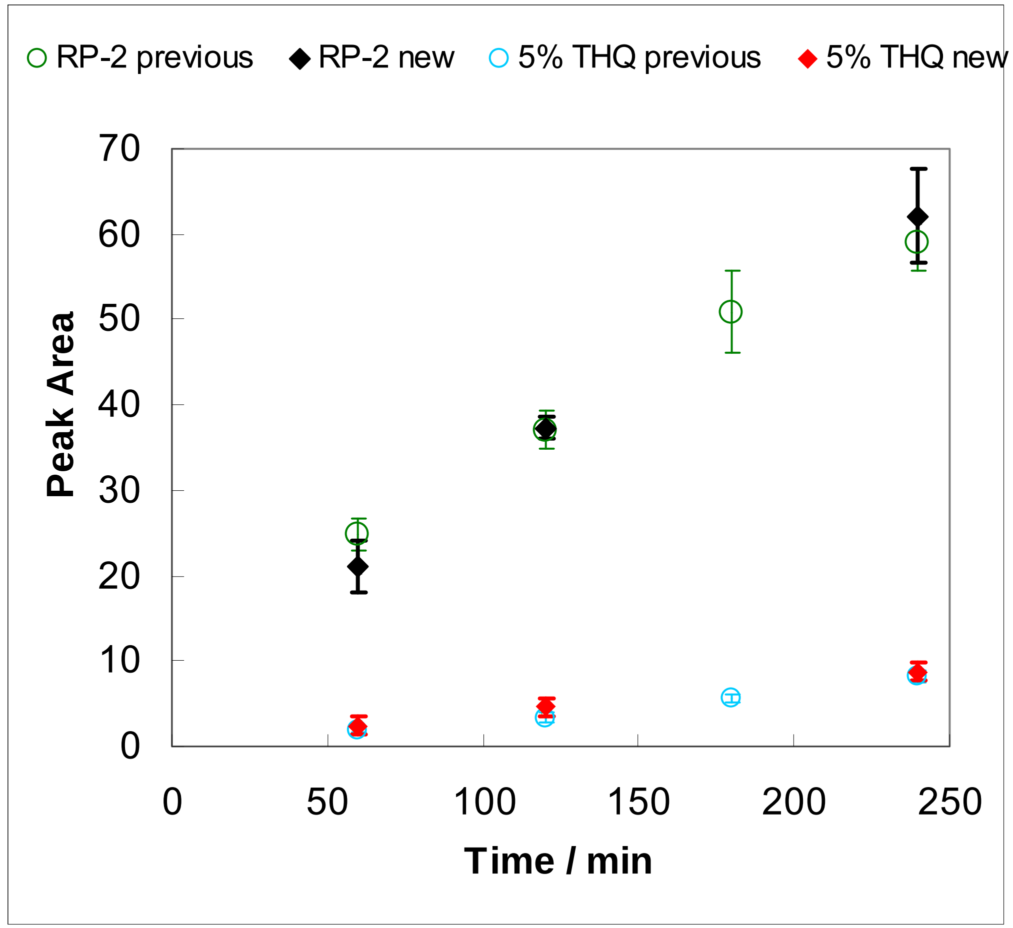
Current Project on Determining the Concentration Dependence of THQ stabilization

Repeatability of RP-2 decomposition measurements taken 12 months apart

To toot our own horn a bit!

Measurements from last year overlay measurements from this year.

Yeah!



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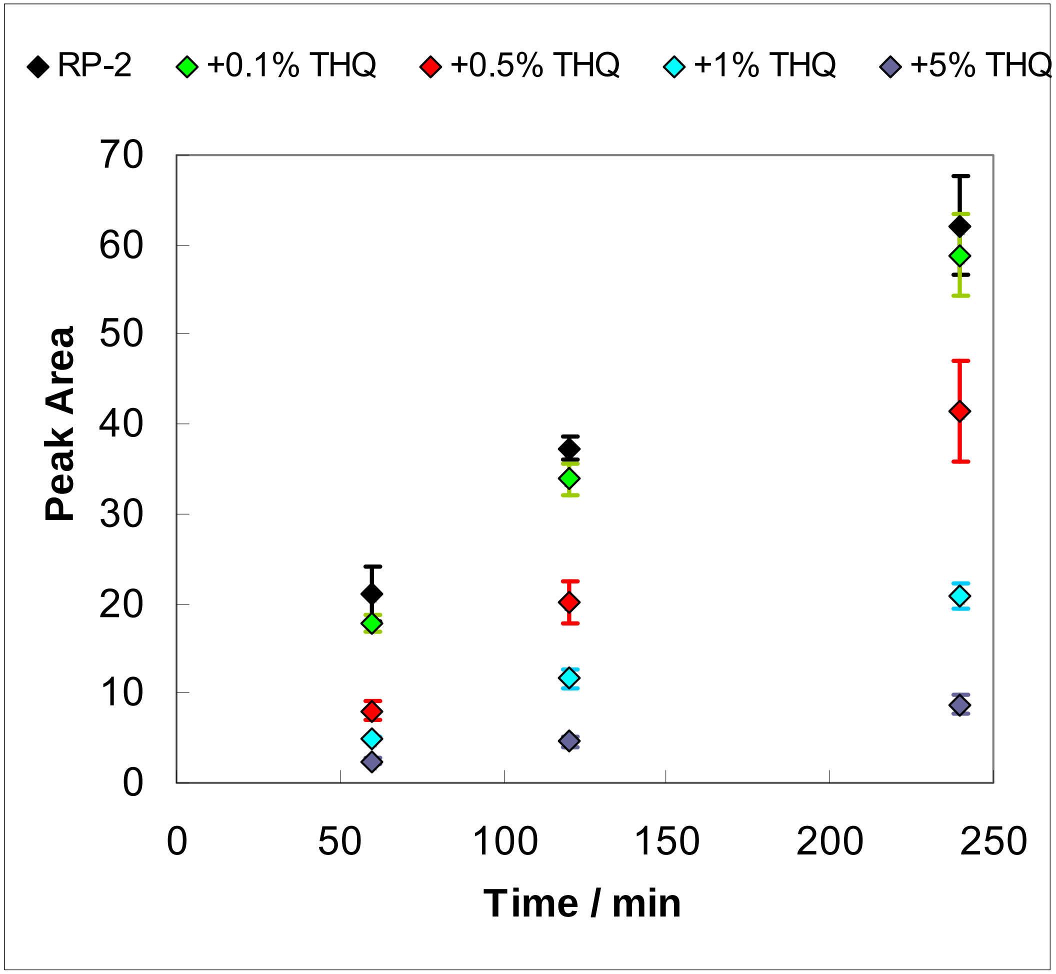
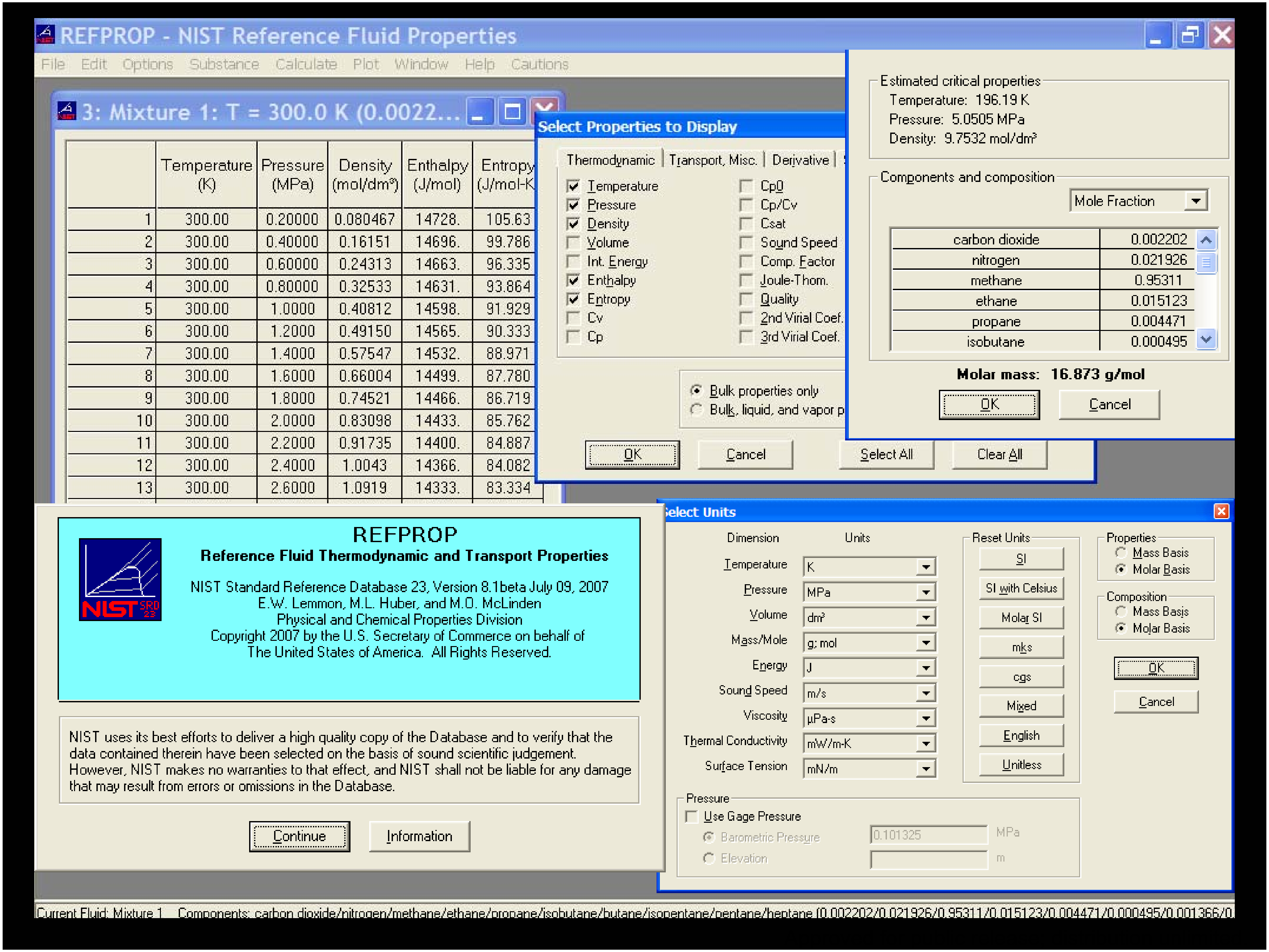
Summary of additive effects of THQ as a function of concentration:



RP-1, RP-2 Compositional Variability

- The RefProp EOS was based on single “reference” samples of RP-1 and RP-2.


REFPROP - NIST Reference Fluid Properties
File Edit Options Substance Calculate Plot Window Help Cautions
3: Mixture 1: T = 300.0 K (0.0022...
Temperature (K) | Pressure (MPa) | Density (mol/dm³) | Enthalpy (J/mol) | Entropy (J/mol-K
1 300.00 0.20000 0.080467 14728. 105.63
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11 300.00 2.2000 0.91735 14400. 84.887
12 300.00 2.4000 1.0043 14366. 84.082
13 300.00 2.6000 1.0919 14333. 83.334
Select Properties to Display
Thermodynamic Transport, Misc. Derivative
Temperature Pressure Density Volume Int. Energy Enthalpy Entropy Cv Cp
Cp0 Cp/Cv Csat Sound Speed Comp. Factor Joule-Thom. Quality 2nd Virial Coef. 3rd Virial Coef.
Bulk properties only
Bulk, liquid, and vapor p
OK Cancel Select All Clear All
Estimated critical properties
Temperature: 196.19 K
Pressure: 5.0505 MPa
Density: 9.7532 mol/dm³
Components and composition
Mole Fraction
carbon dioxide 0.002202
nitrogen 0.021926
methane 0.95311
ethane 0.015123
propane 0.004471
isobutane 0.000495
Molar mass: 16.873 g/mol
OK Cancel
REFPROP
Reference Fluid Thermodynamic and Transport Properties
NIST Standard Reference Database 23, Version 8.1beta July 09, 2007
E.W. Lemmon, M.L. Huber, and M.O. McLinden
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Dimension Units
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Pressure MPa
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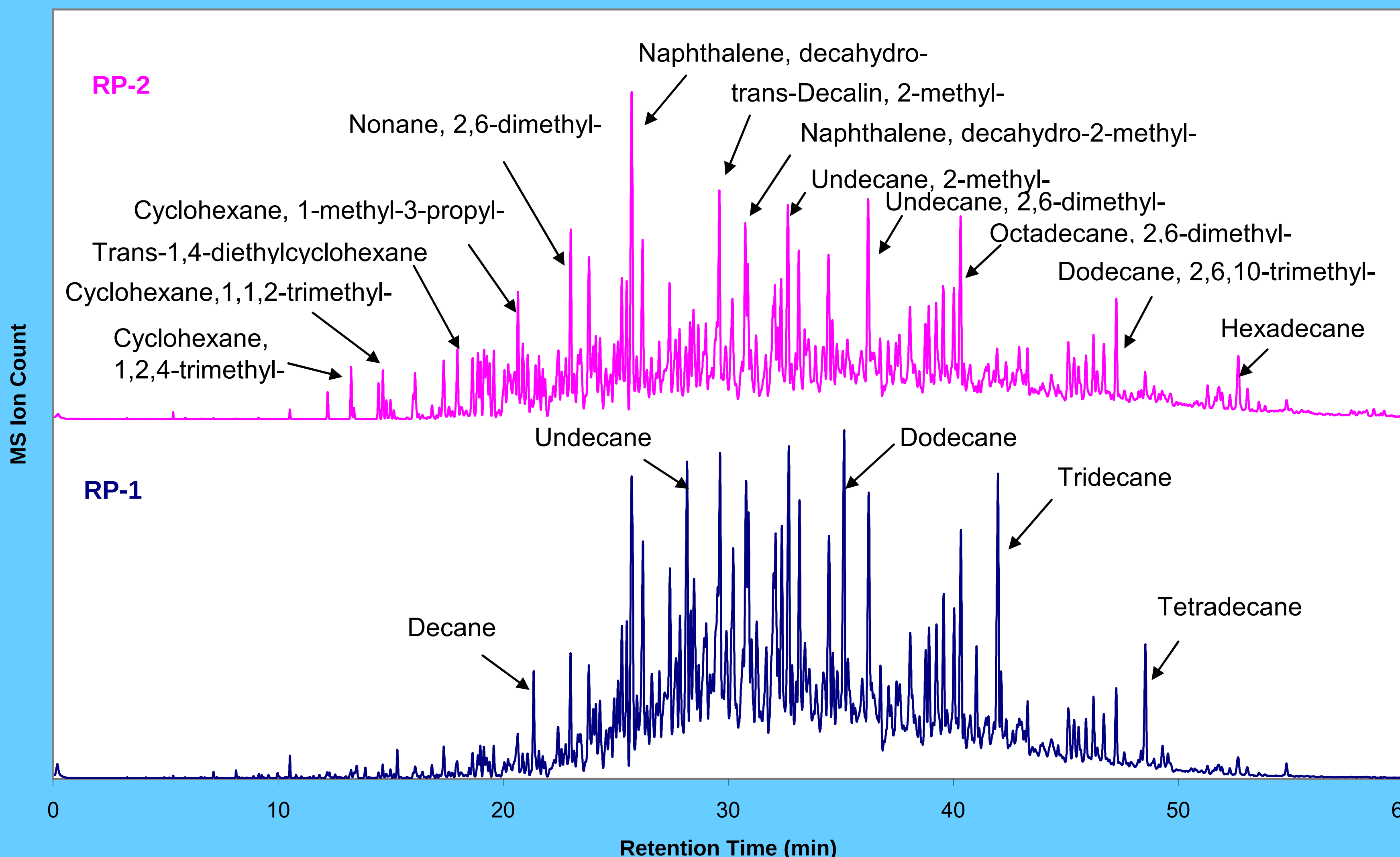
Mass/Mole g; mol
Energy J
Sound Speed m/s
Viscosity µPa-s
Thermal Conductivity mW/m-K
Surface Tension mN/m
Reset Units: SI, SI with Celsius, Molar SI, mks, cgs, Mixed, English, Unitless
Properties: Mass Basis, Molar Basis
Composition: Mass Basis, Molar Basis
OK Cancel
Pressure
Use Gage Pressure
Barometric Pressure 0.101325 MPa
Elevation m
Current Fluid: Mixture 1 Components: carbon dioxide/nitrogen/methane/ethane/propane/isobutane/butane/isopentane/pentane/heptane (0.002202/0.021926/0.95311/0.015123/0.004471/0.000495/0.001366/0.

So what about variability?

- Compositional variability
  - Distribution of paraffins, isoparaffins, aromatics, etc.

GC-MS



RP-2
RP-1
Naphthalene, decahydro-
trans-Decalin, 2-methyl-
Nonane, 2,6-dimethyl-
Naphthalene, decahydro-2-methyl-
Undecane, 2-methyl-
Undecane, 2,6-dimethyl-
Cyclohexane, 1-methyl-3-propyl-
Octadecane, 2,6-dimethyl-
Trans-1,4-diethylcyclohexane
Dodecane, 2,6,10-trimethyl-
Cyclohexane,1,1,2-trimethyl-
Hexadecane
Cyclohexane,
1,2,4-trimethyl-
Undecane
Dodecane
Tridecane
Tetradecane
Decane
MS Ion Count
0
10
20
30
40
50
60
Retention Time (min)

So what about variability?

- Compositional variability
  - Distribution of paraffins, isoparaffins, aromatics, etc.
- Property Variability
  - VLE, ρ, υ, λ, ss, Cp, Cv, …

- One Manufacturer,
- one set of tight specs,
- many years of experience.

Treated as if

“the sample”

has been passed down from on high

So, everything is fine, right?

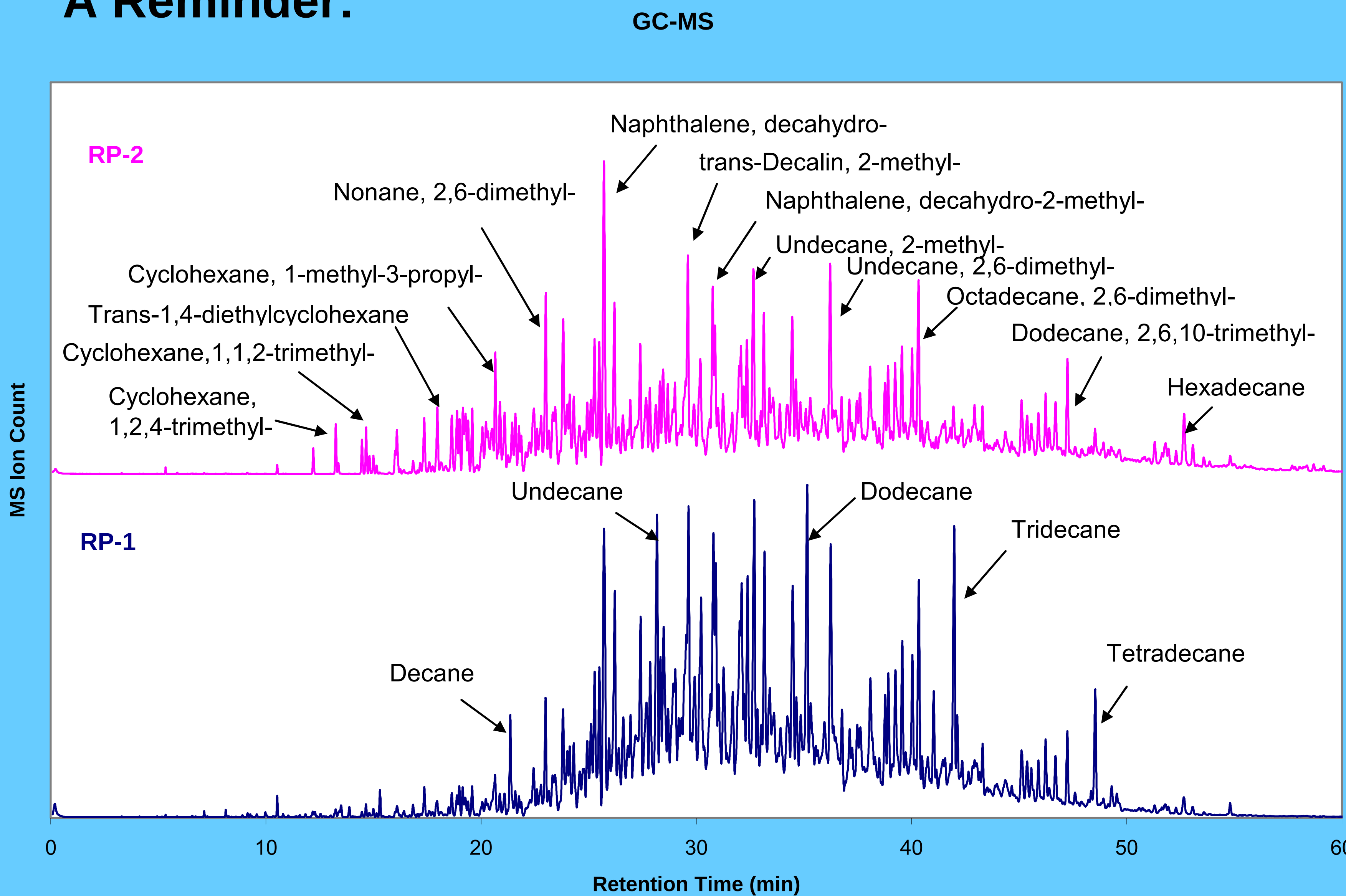
- Questions arise in a Joint USAF, NASA NIST conference:
  - Launch contractors report ρ variations
    - note that ρ is insensitive
  - Rocket OEMs report kinetic variations in coking

So, everything is fine, right?

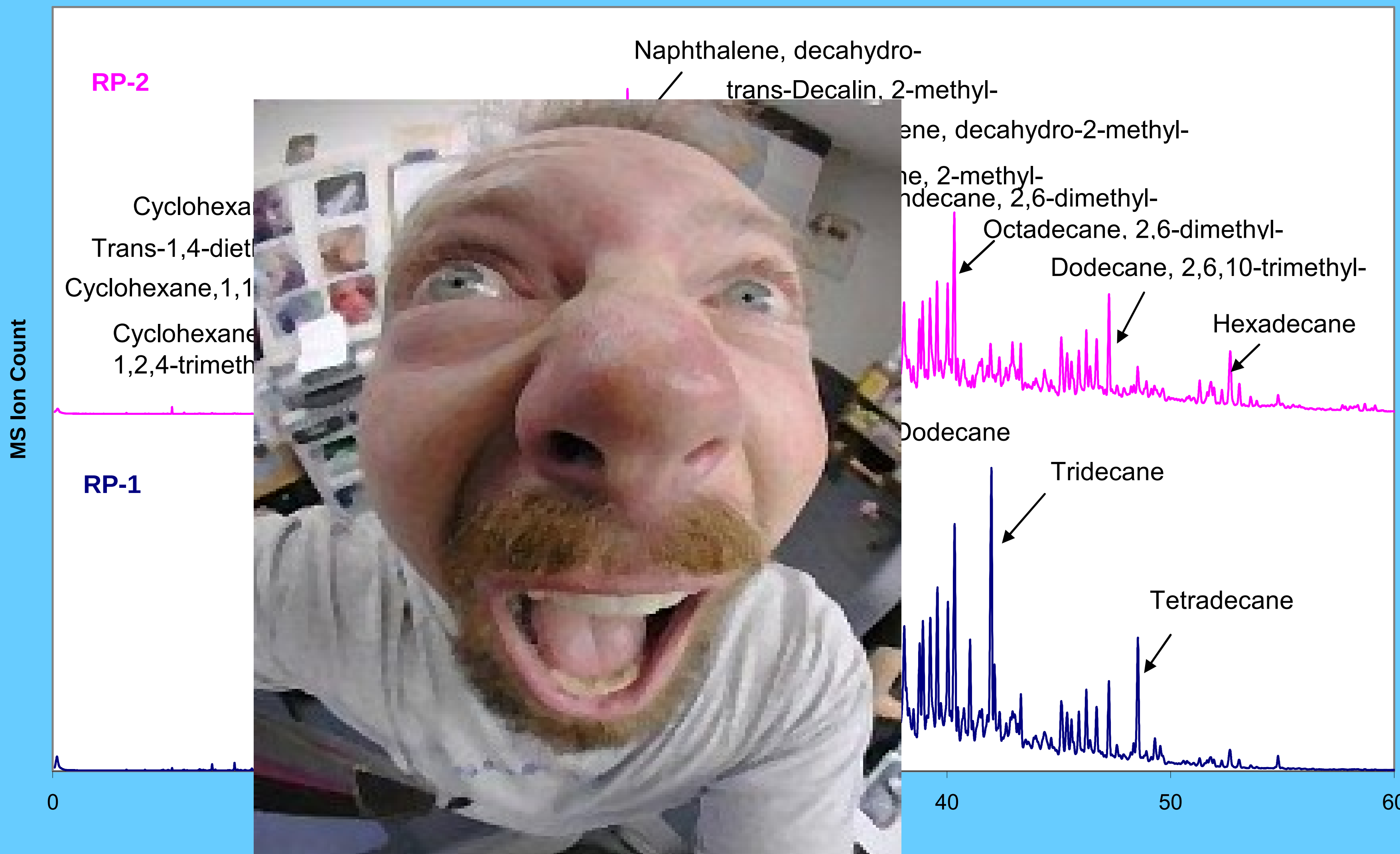
- Questions arise in a Joint USAF, NASA NIST conference:
  - Launch contractors report ρ variations
    - note that ρ is insensitive
  - Rocket OEMs report kinetic variations in coking

<u>Bottom Line:</u> We need to assess the variability of this sacrosanct fluid once and for all!

A Reminder:


GC-MS
RP-2
Naphthalene, decahydro-
trans-Decalin, 2-methyl-
Nonane, 2,6-dimethyl-
Naphthalene, decahydro-2-methyl-
Undecane, 2-methyl-
Undecane, 2,6-dimethyl-
Cyclohexane, 1-methyl-3-propyl-
Octadecane, 2,6-dimethyl-
Trans-1,4-diethylcyclohexane
Dodecane, 2,6,10-trimethyl-
Cyclohexane,1,1,2-trimethyl-
Hexadecane
Cyclohexane,
1,2,4-trimethyl-
MS Ion Count
Undecane
Dodecane
RP-1
Tridecane
Tetradecane
Decane
0
10
20
30
40
50
60
Retention Time (min)

If a peak by peak comparison were needed for every sample, rocket scientists would soon become screaming lunatics



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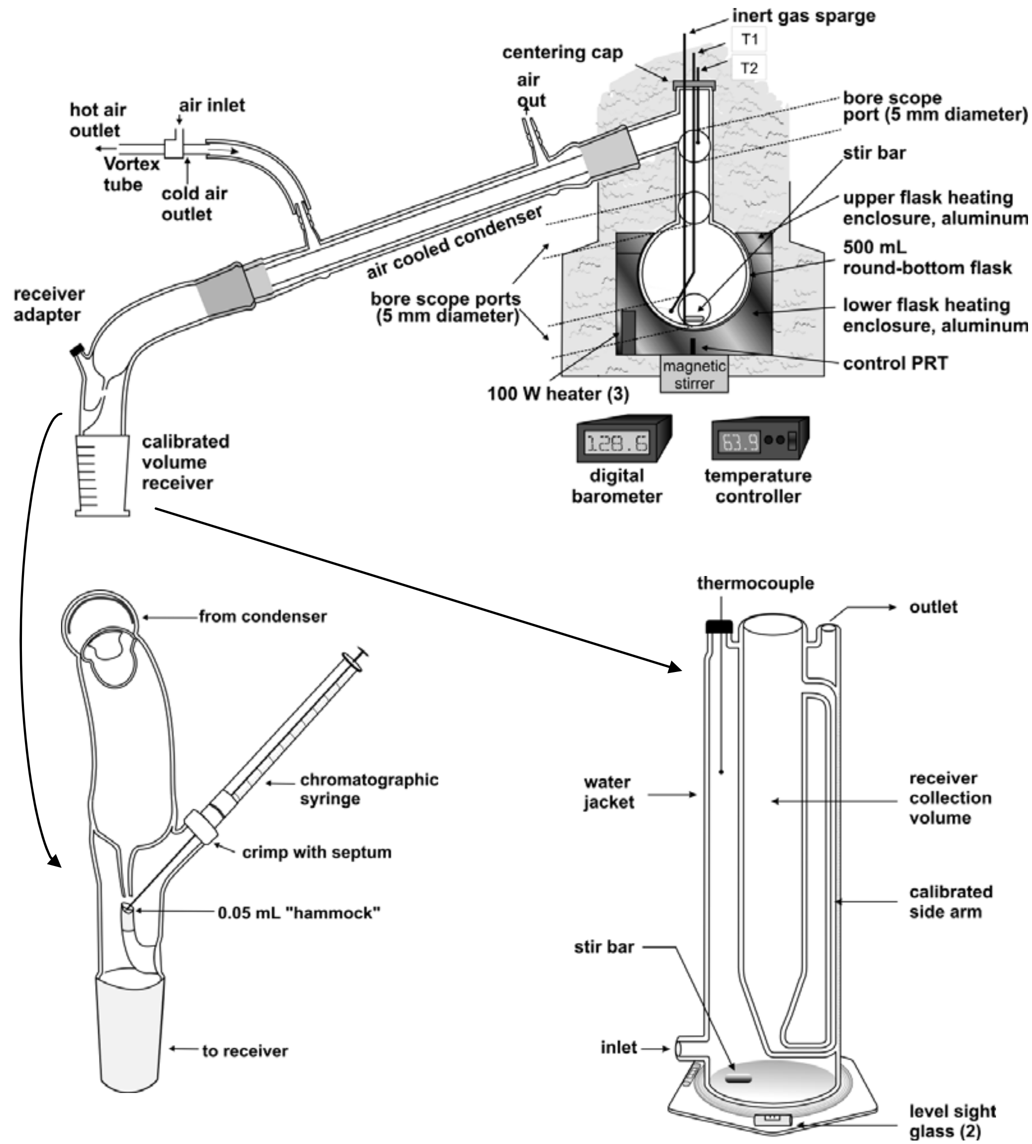
Can we use any of the thermophysical properties for this?

- Density, ρ (PVT surface), for a kerosene
  - write in 0.8 g/mL and you'll be close
- Speed of sound, heat capacities, etc., change by a few %
- viscosity and thermal conductivity change by 4 %
- In contrast, volatility changes appreciably with composition

The ADC:

- –true thermodynamic state points
- –consistent with historical data
- –temperature, volume and pressure measurements of low uncertainty
- –qualitative, quantitative and trace analysis of fractions
- –energy content of each fraction
- –corrosivity of each fraction
- –greenhouse gas output of each fraction
- –thermal and oxidative stability of the fluids



Apparatus for ADC.

Comparison of RP Samples

- Obtain orthogonal batches of RP-1 and RP-2
- Measure ADC:
  - Initial boiling behavior
  - Full curves
- Examine, and model divergence

Initial boiling behavior:

- We measure three parameters:
  - Onset
  - Sustained
  - Vapor rise

Initial boiling behavior:

- We measure three parameters:
  - Onset **(first bubbles appear)**
  - Sustained
  - Vapor rise

Initial boiling behavior:

- We measure three parameters:
  - Onset
  - Sustained **(bubbles continue w/o stirrer)**
  - Vapor rise

Initial boiling behavior:

- We measure three parameters:
  - Onset
  - Sustained
  - Vapor rise **(vapor rises into head)**

Initial boiling behavior:

- We measure three parameters:
  - Onset
  - Sustained
  - Vapor rise **(vapor rises into head)**

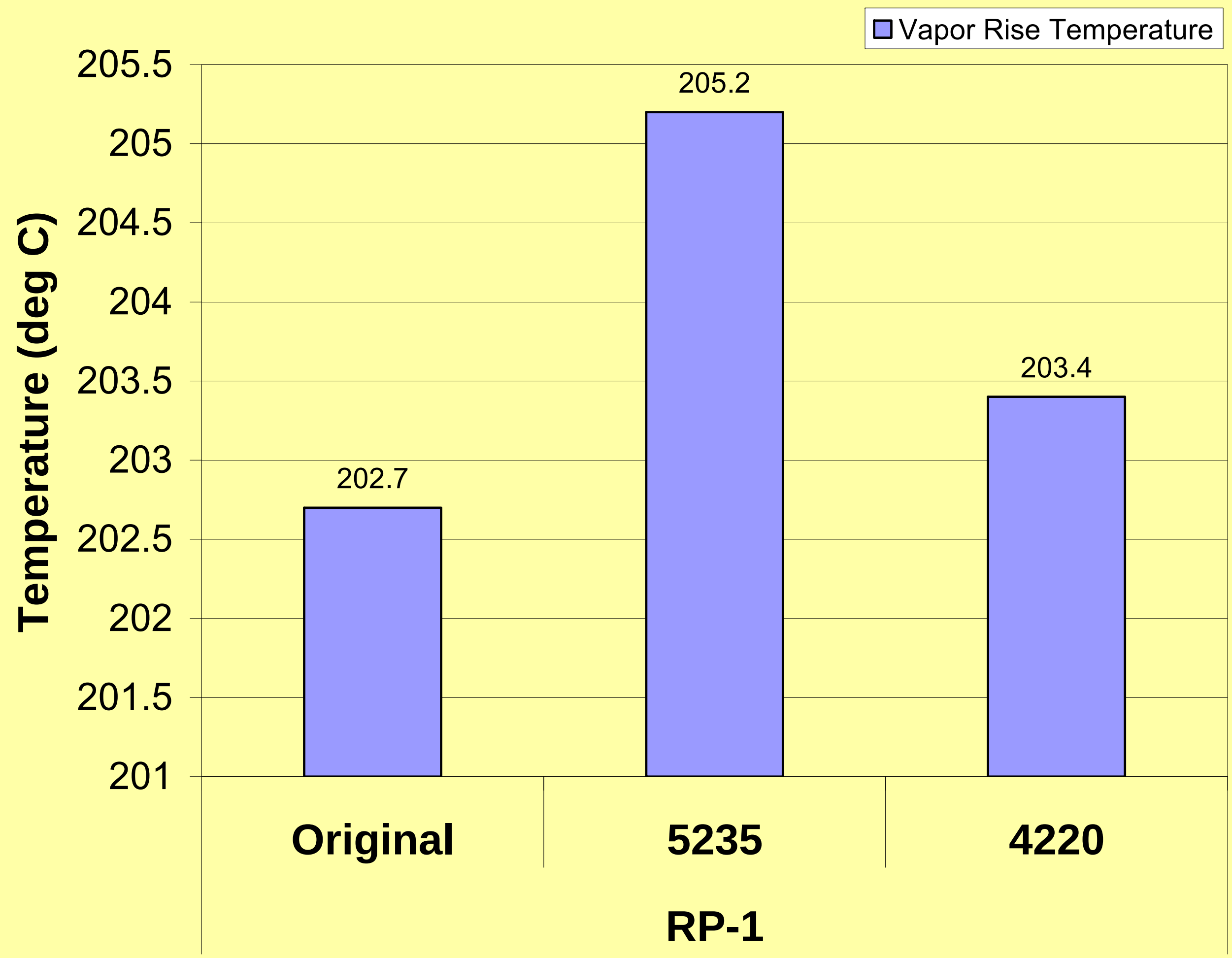
- The vapor rise temperature is the IBT of the fluid, thermodynamically consistent, modeled by EOS.

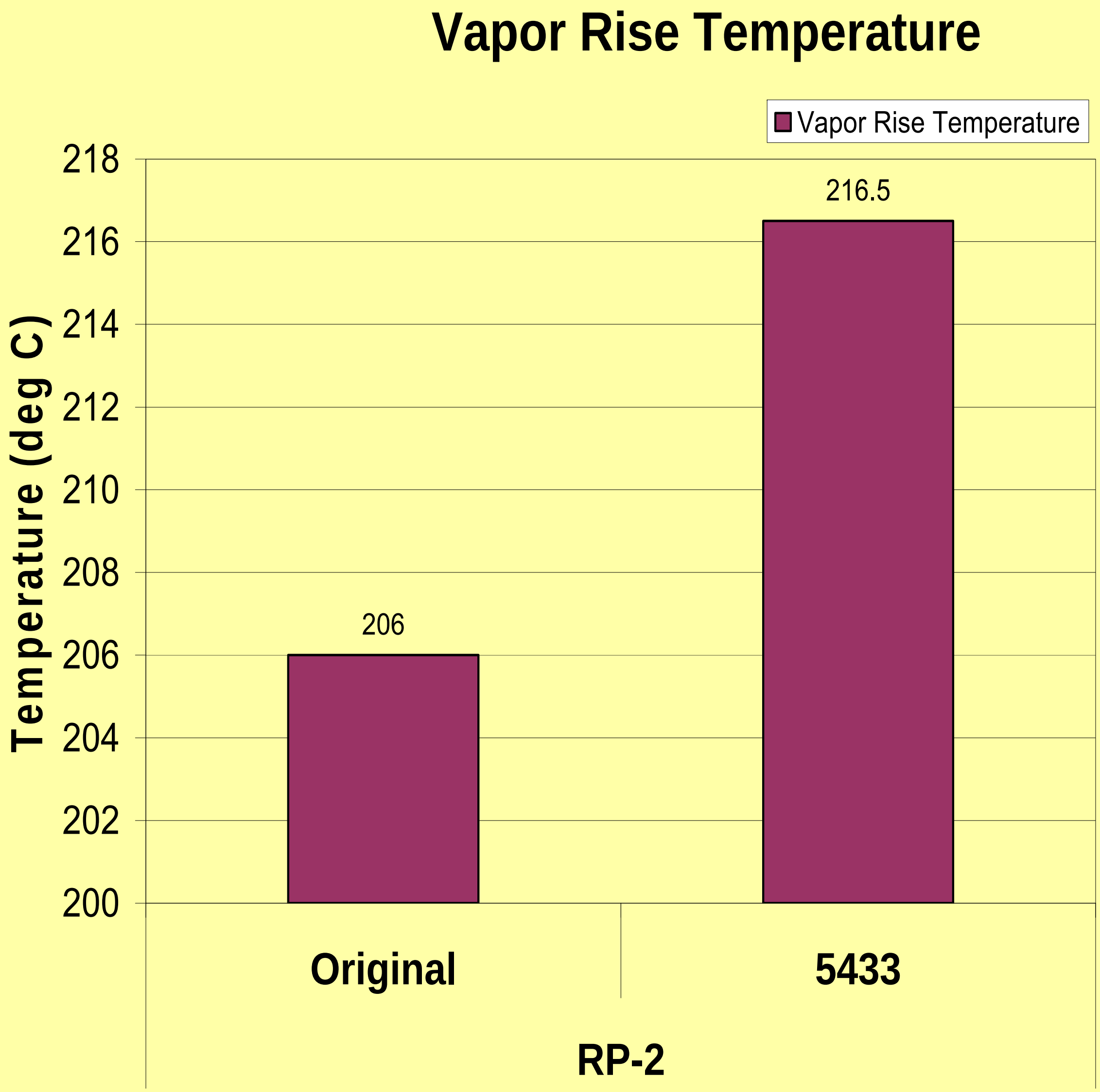
Experiments thus far:

- 3 samples of RP-1
  - We think we can find 3-4 more
    - searching AFRL, NASA, engine makers, launch contractors, etc.

- 2 samples of RP-2
  - The only samples produced as yet

Vapor Rise Temperature





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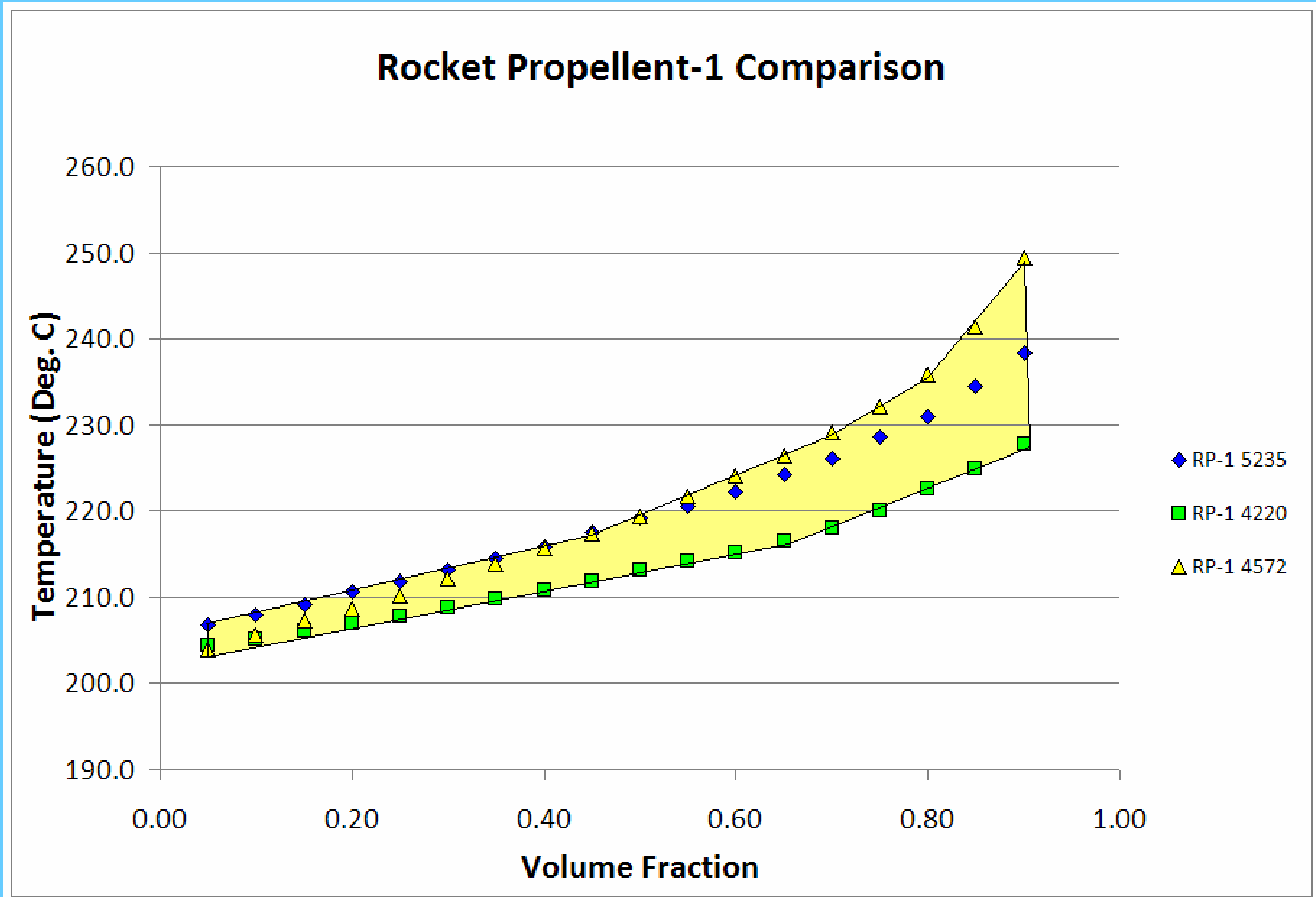
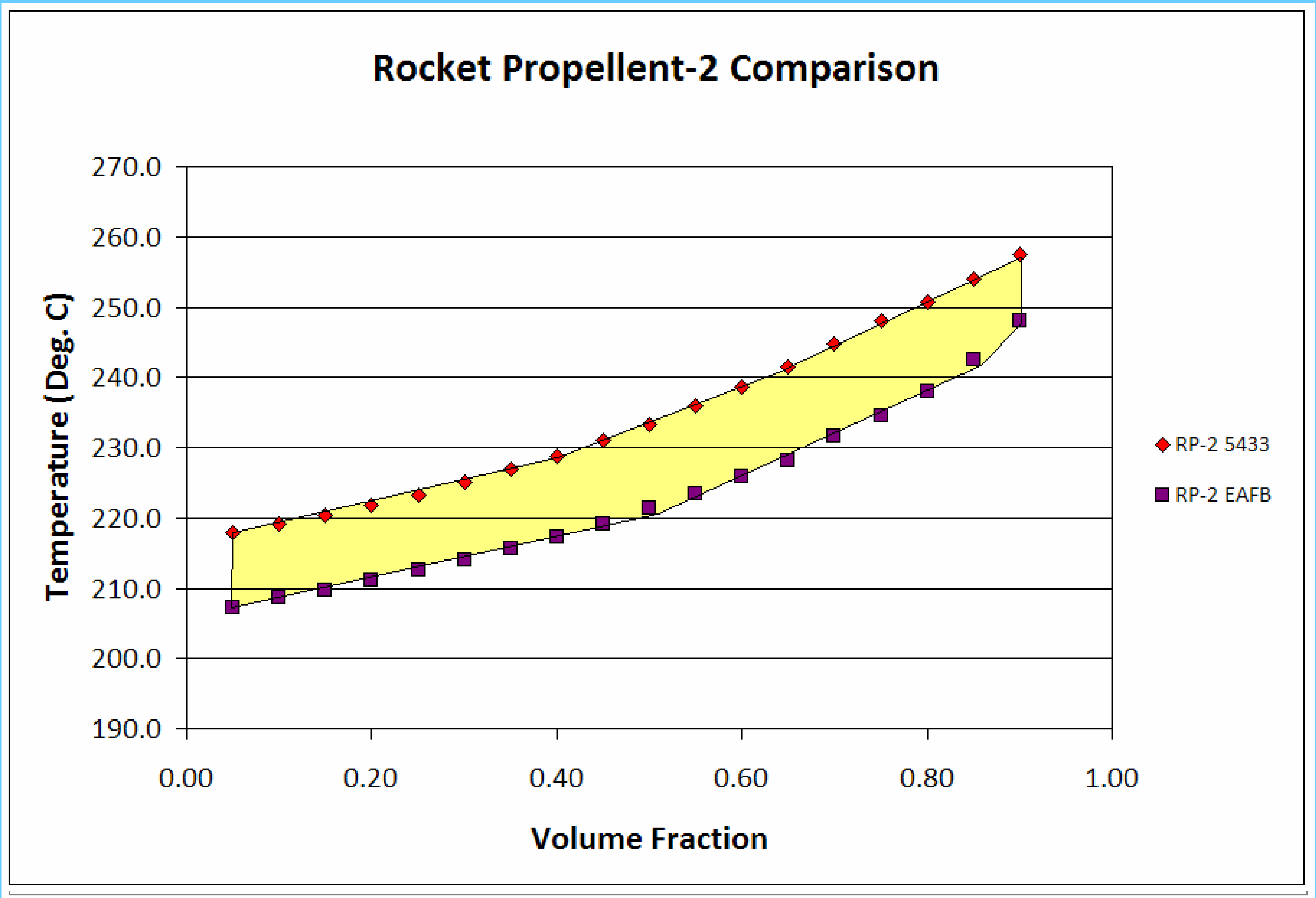

Rocket Propellent-1 Comparison
Temperature (Deg. C)
260.0
250.0
240.0
230.0
220.0
210.0
200.0
190.0
0.00
0.20
0.40
0.60
0.80
1.00
Volume Fraction
RP-1 5235
RP-1 4220
RP-1 4572



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Conclusions:

- The variability of RP-1 is far more significant than previously thought
  - all measurements and modeling done previously must be questioned.

- The variability of RP-2 is extremely large;
  - Only 2 batches have been made; plant upset?
  - regardless, this is disturbing.

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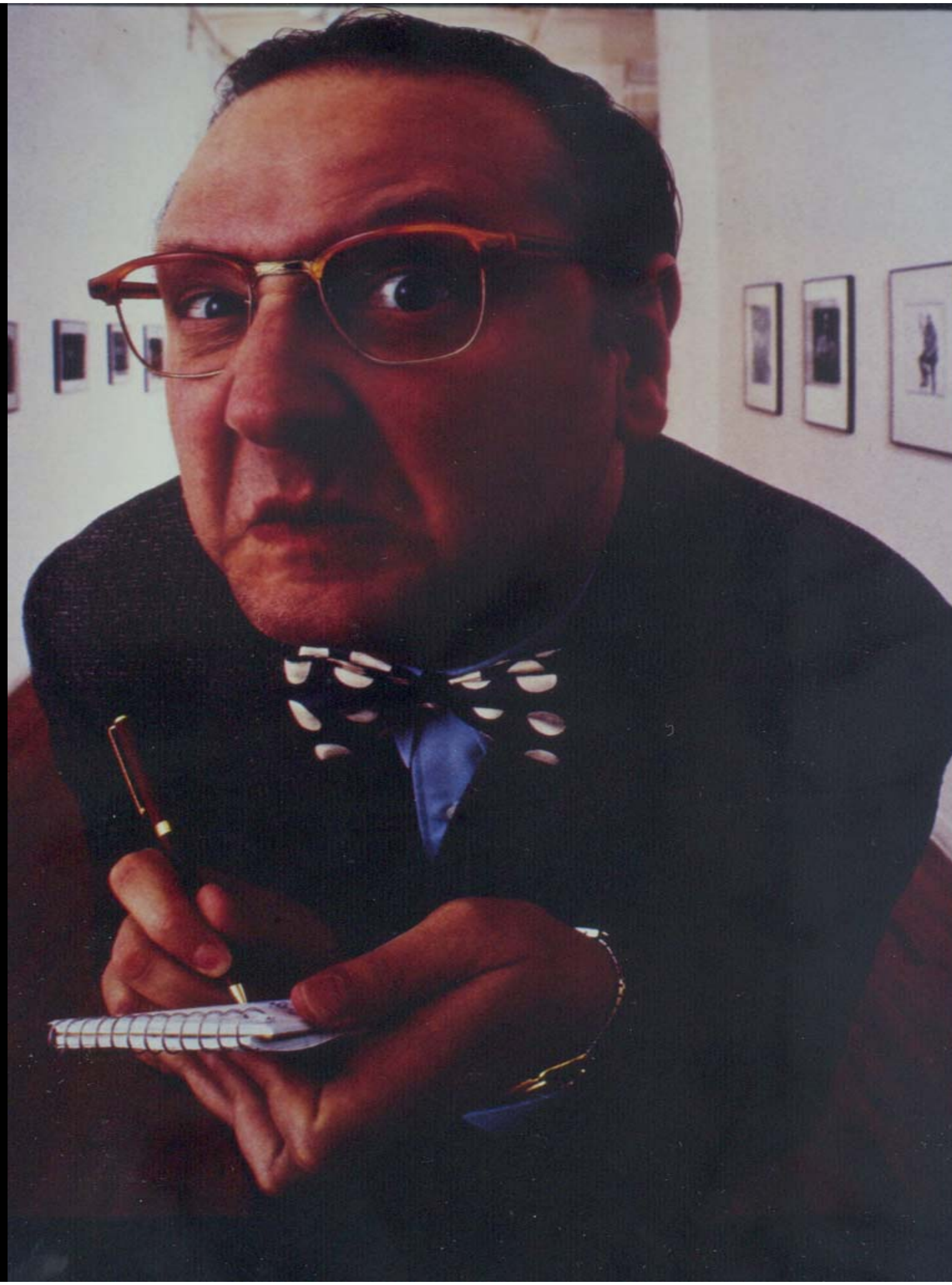

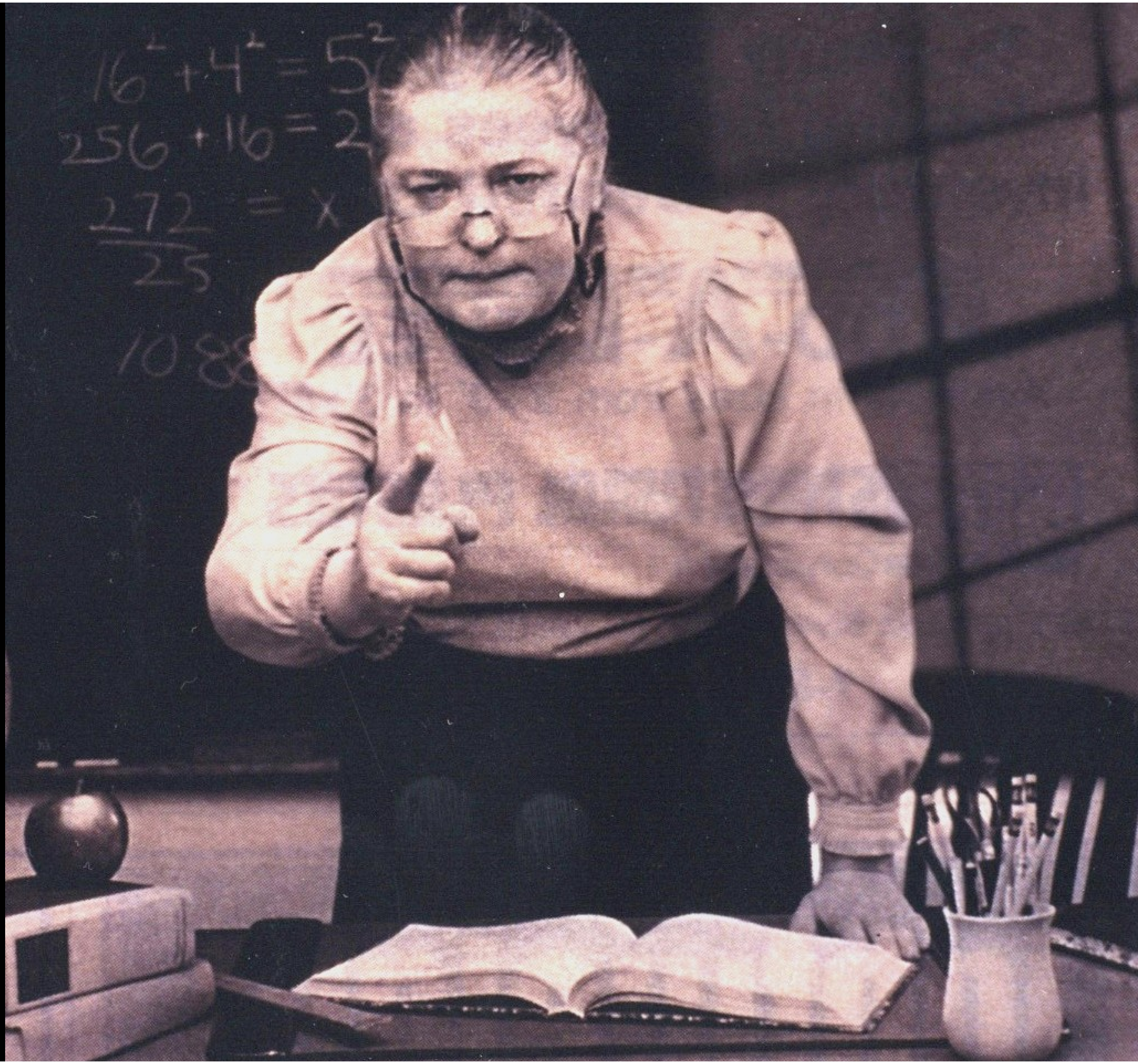
$16^2 + 4^2 = 5^2$
$256 + 16 = 2$
$\frac{272}{25} = x$
10.88