The Properties of RP-1 and RP-2
MIPR F1SBAA8022G001

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Boulder, CO

Executive Summary:

AFOSR-MIPR F1SBAA8022G001

- Characterization of a real fuel: JP-8
  - i.e., chemical analysis, **VLE**, ρ, υ, λ, C_v
- Complete RefProp fluids files for RP-1 and RP-2
- Perform thermal decomposition studies on RP-2:
  - no additives
  - with THQ, tetralin, +100 package

NIST Staff:

- Tom Bruno
- Arno Laesecke
- Stephanie Outcalt
- Richard Perkins
- Jason Widegren
- Marcia Huber
- Eric Lemmon

and Students:

- Beverly Smith
- Lisa Ott
- Kari Brumbeck
- Amelia Hadler
- Tara Lovestead

First, a bit of history

RP-1:

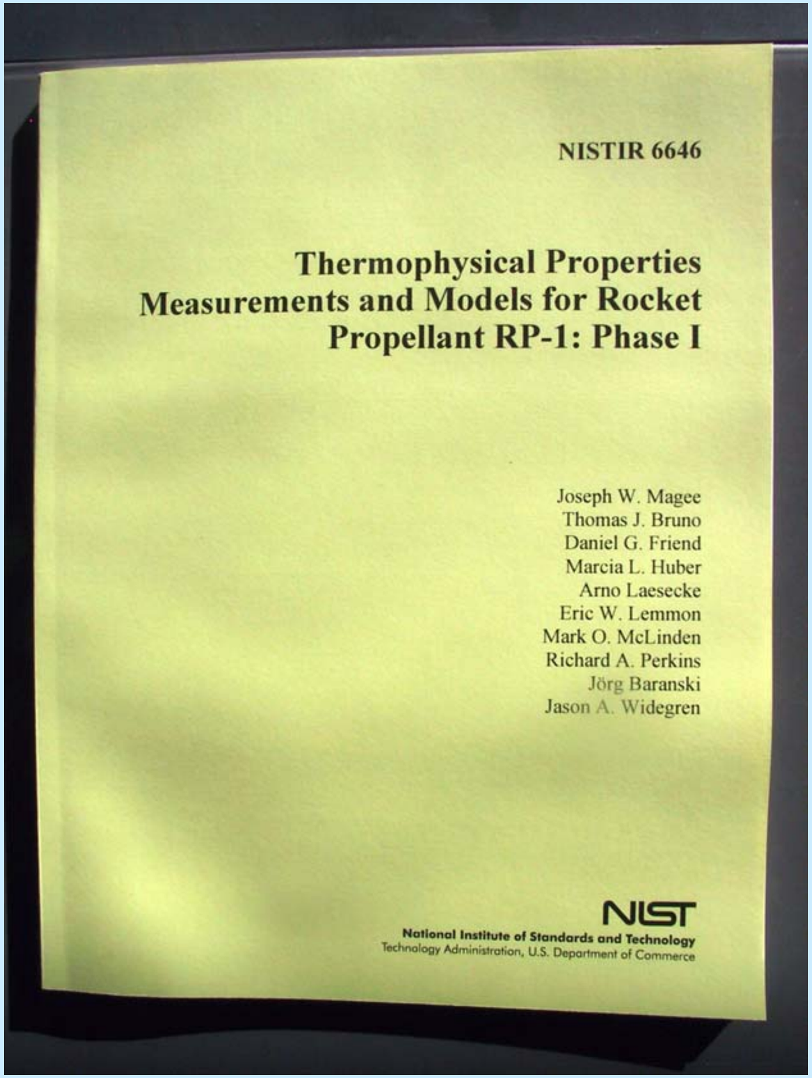
- Rocket Propellant 1 (refined petroleum 1)
- Kerosene base, used with LOX in rockets such as the Saturn V
- Density 0.81 - 1.02 g/mL
- Oxidizer to fuel ratio = 2.56
- Temperature of combustion = 3,670 K

RP-2

- A highly hydrotreated kerosene
- Little or no sulfur
- Few if any aromatics
- Clear at present, no added dye

NASA RP-1 Project

- We obtained a sample of RP-1, 2002:
  - P000016660
  - Chemical analysis revealed presence of many aromatics and alkenes
- An extensive series of measurements and correlations was done.
- At the December ’03 workshop, it was decided that the lot was “unusual”.
- A follow-on project determined compositional variability.

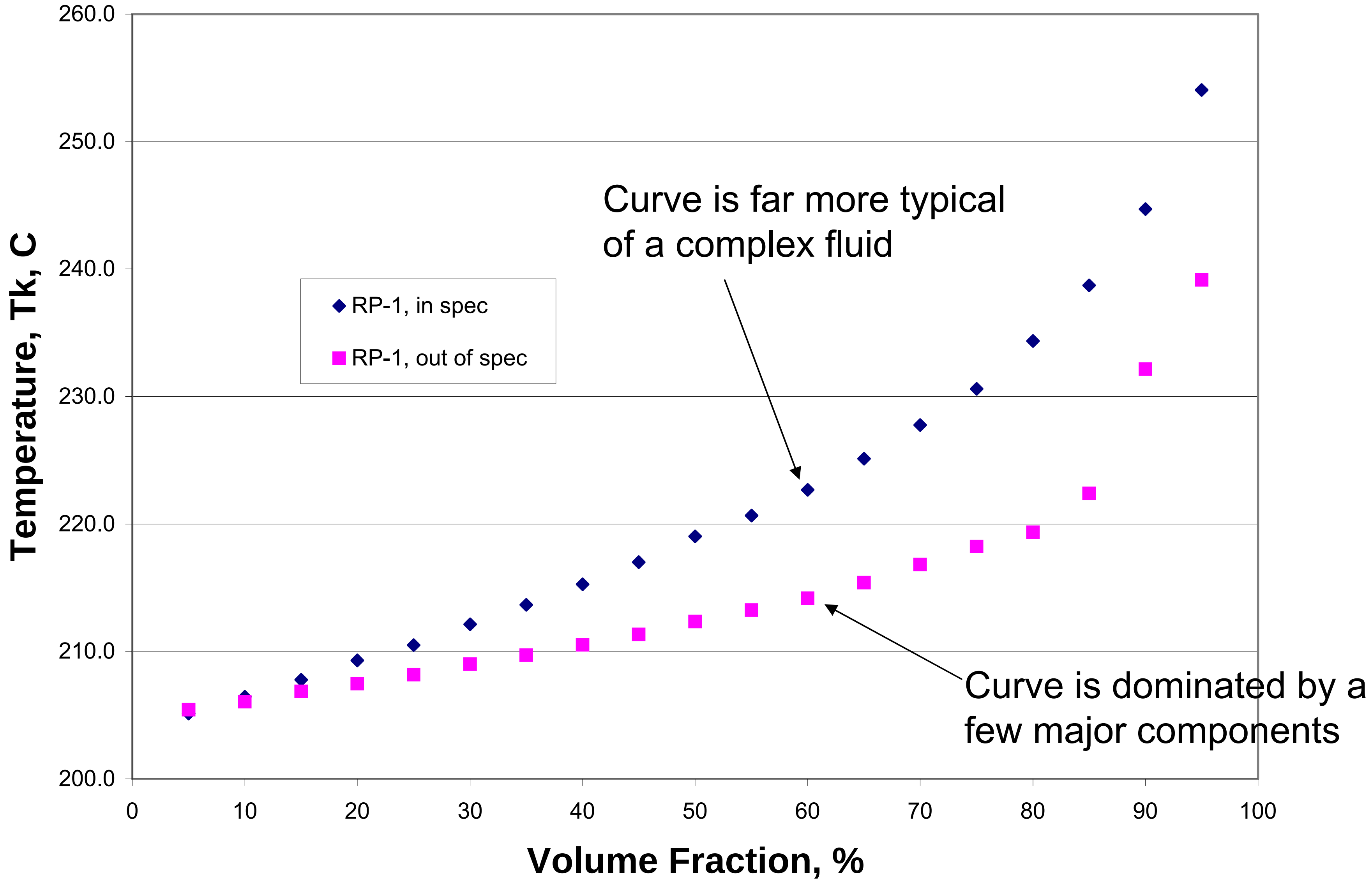


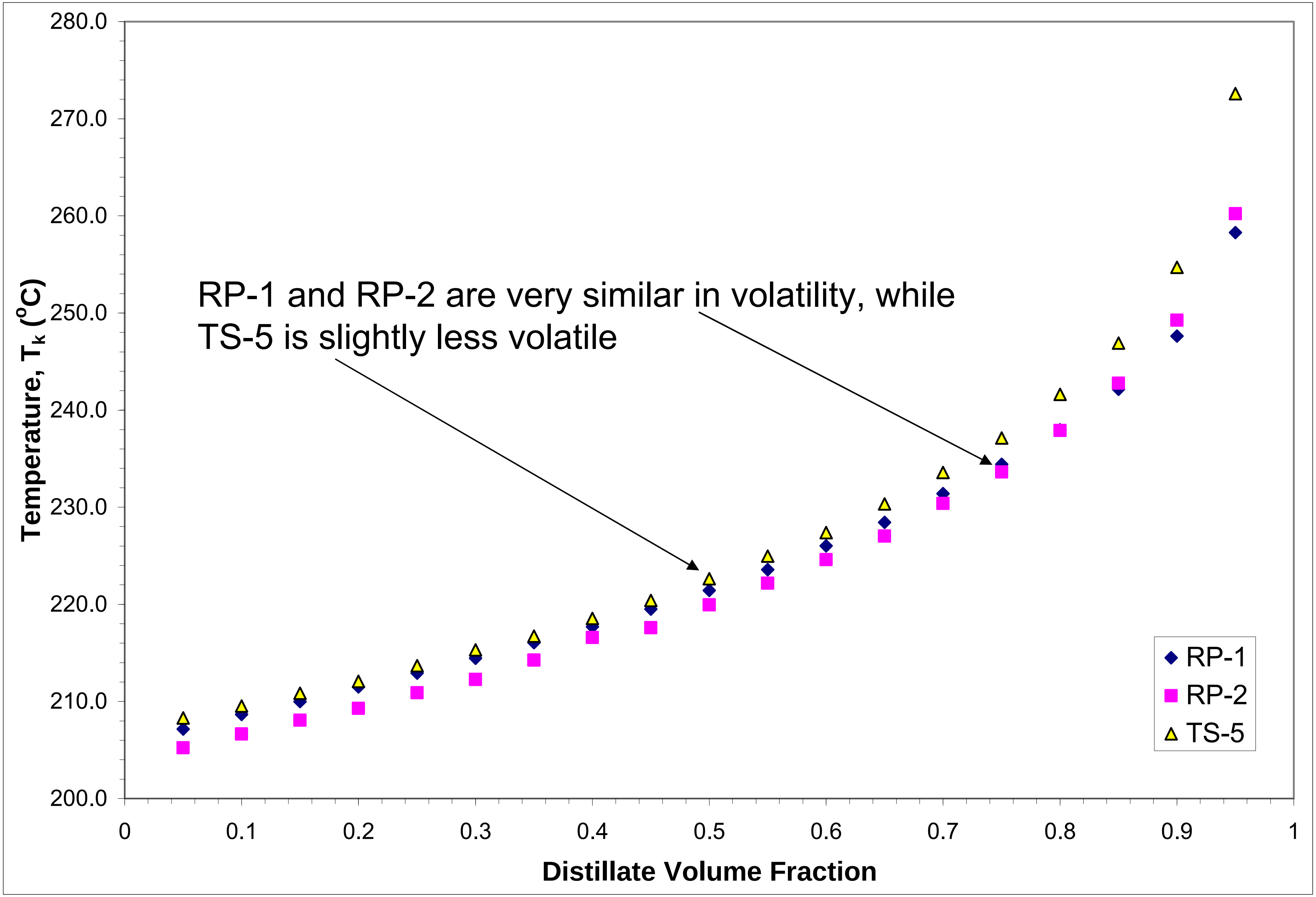
Our results were summarized in NISTIR 6646, and the preliminary RP-1 fluid file was developed

We start with:

- Comprehensive chemical analysis
- Distillation curves (of the advanced variety)

RP-1 Distillation Curves





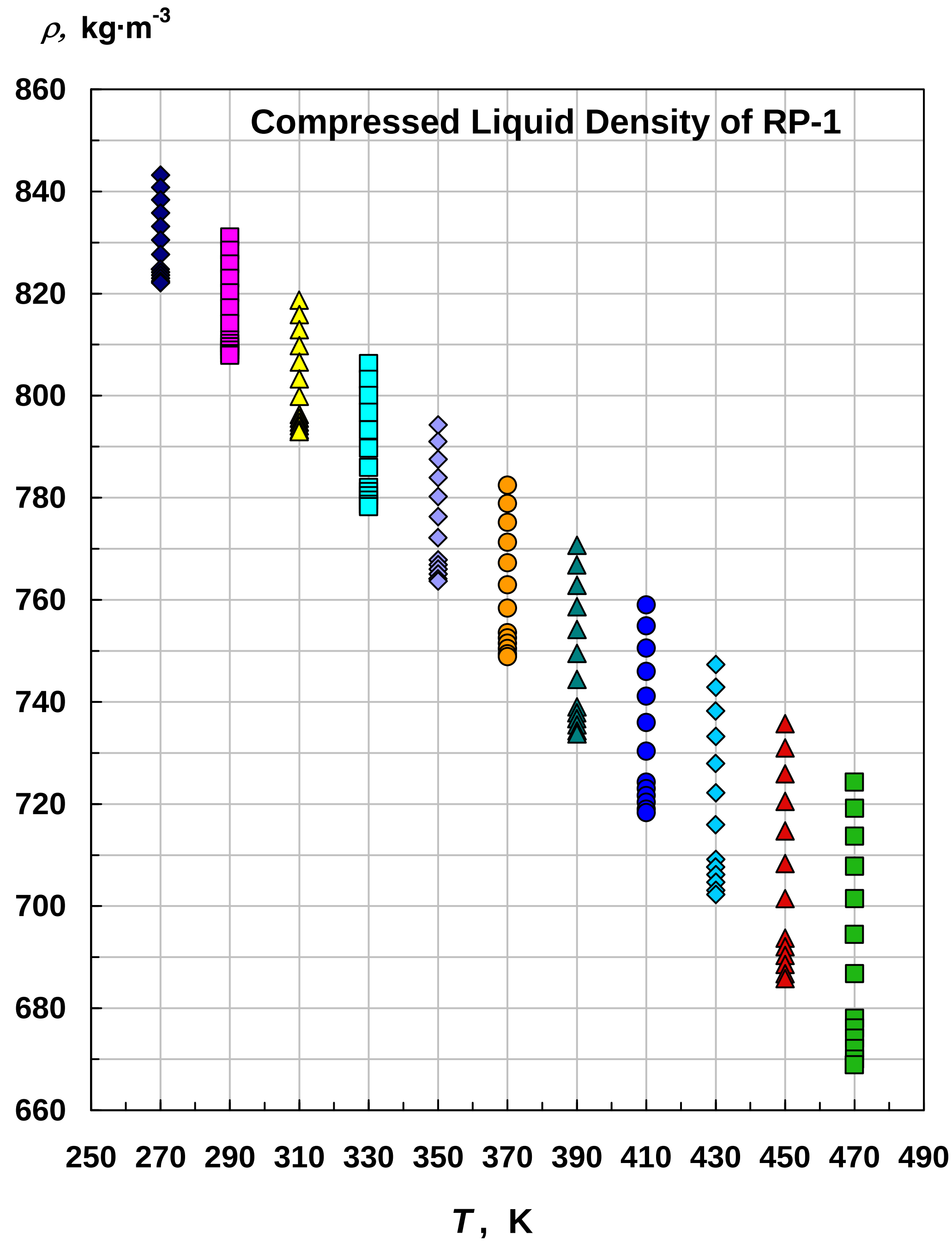
RP-1 and RP-2 are very similar in volatility, while TS-5 is slightly less volatile
Temperature, T_k (°C)
280.0
270.0
260.0
250.0
240.0
230.0
220.0
210.0
200.0
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
Distillate Volume Fraction
RP-1
RP-2
TS-5

Now, complete the property suite:

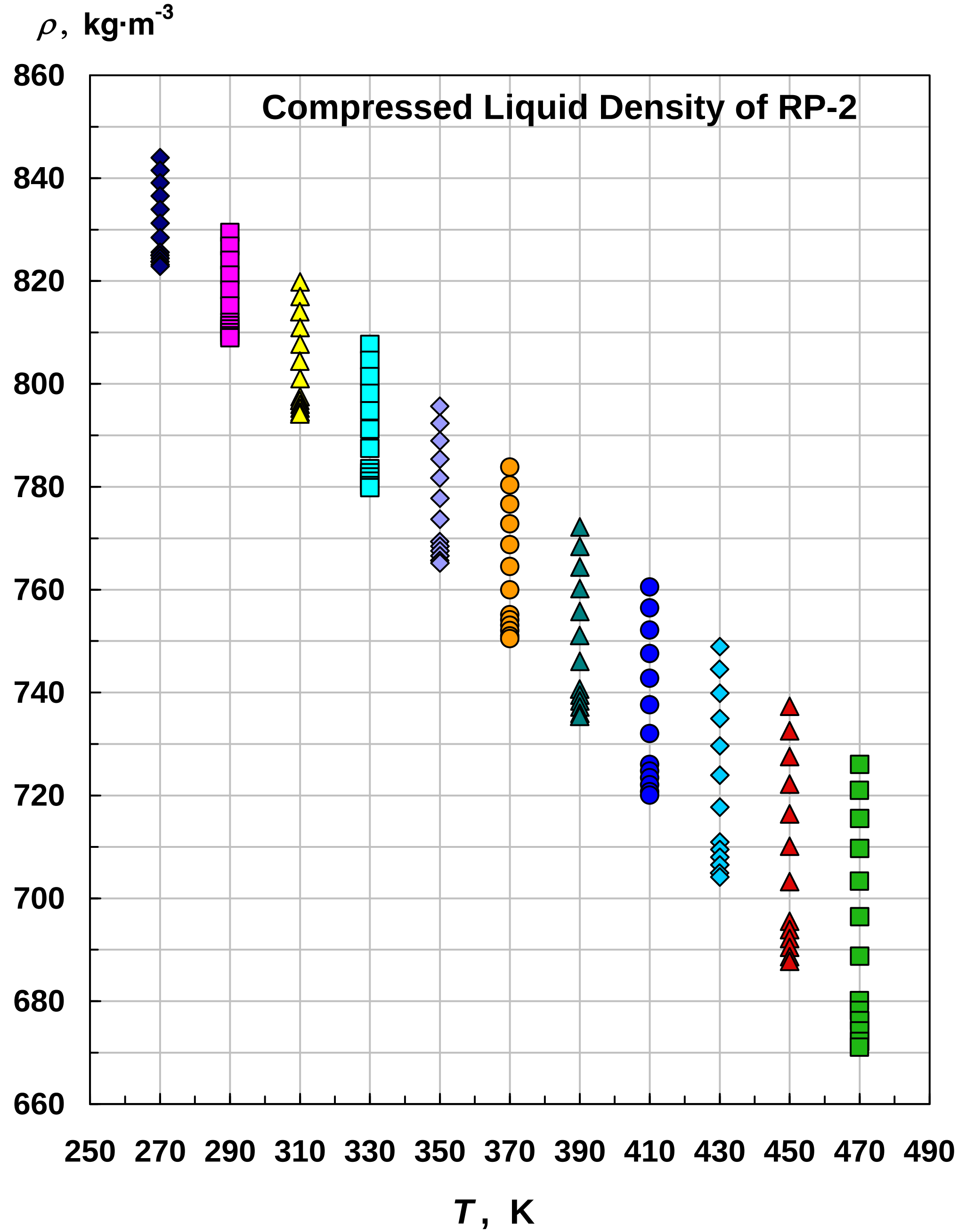
ρ, υ, λ, C_v, etc.

Density:

Experimental details were discussed earlier

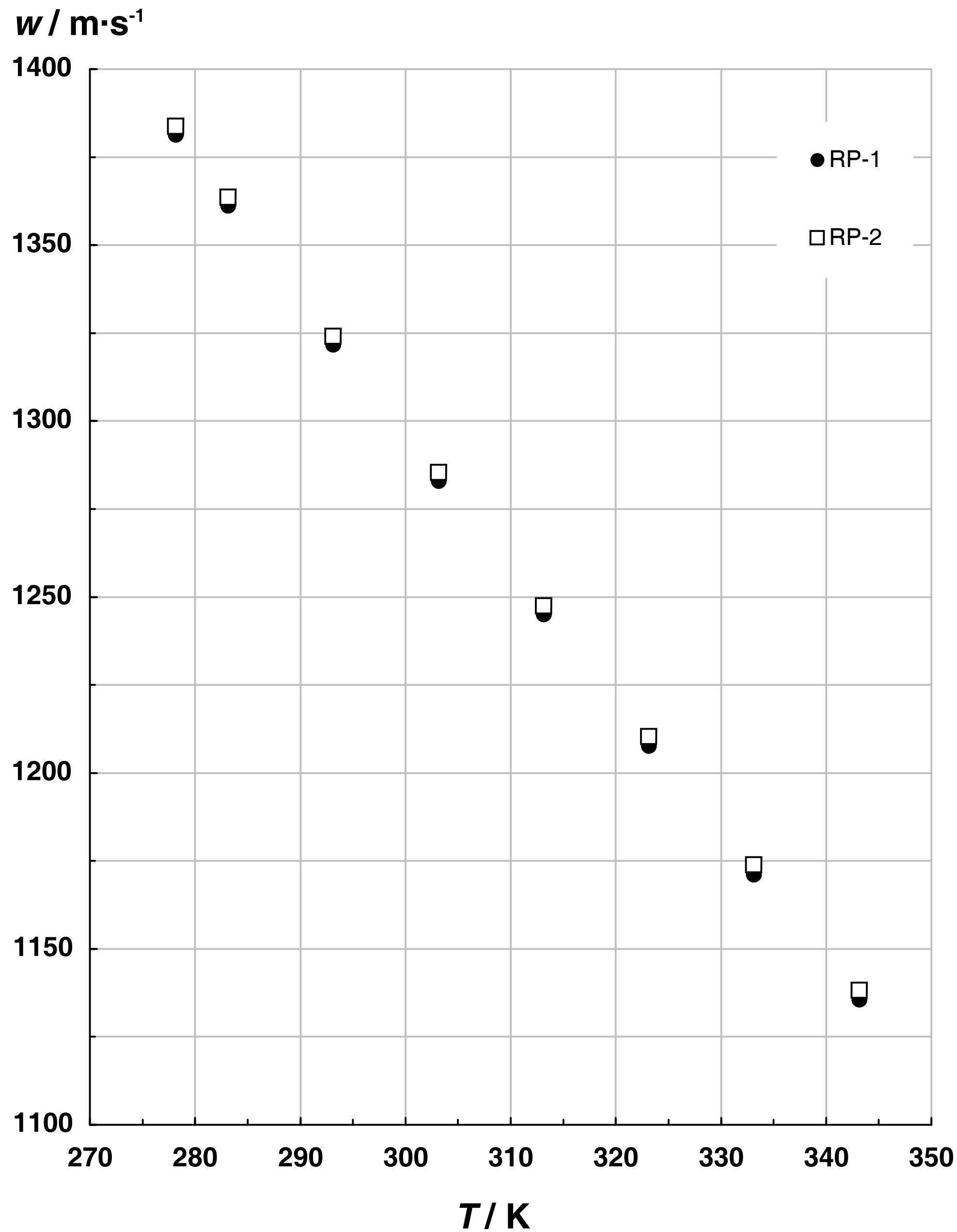


And for RP-2:

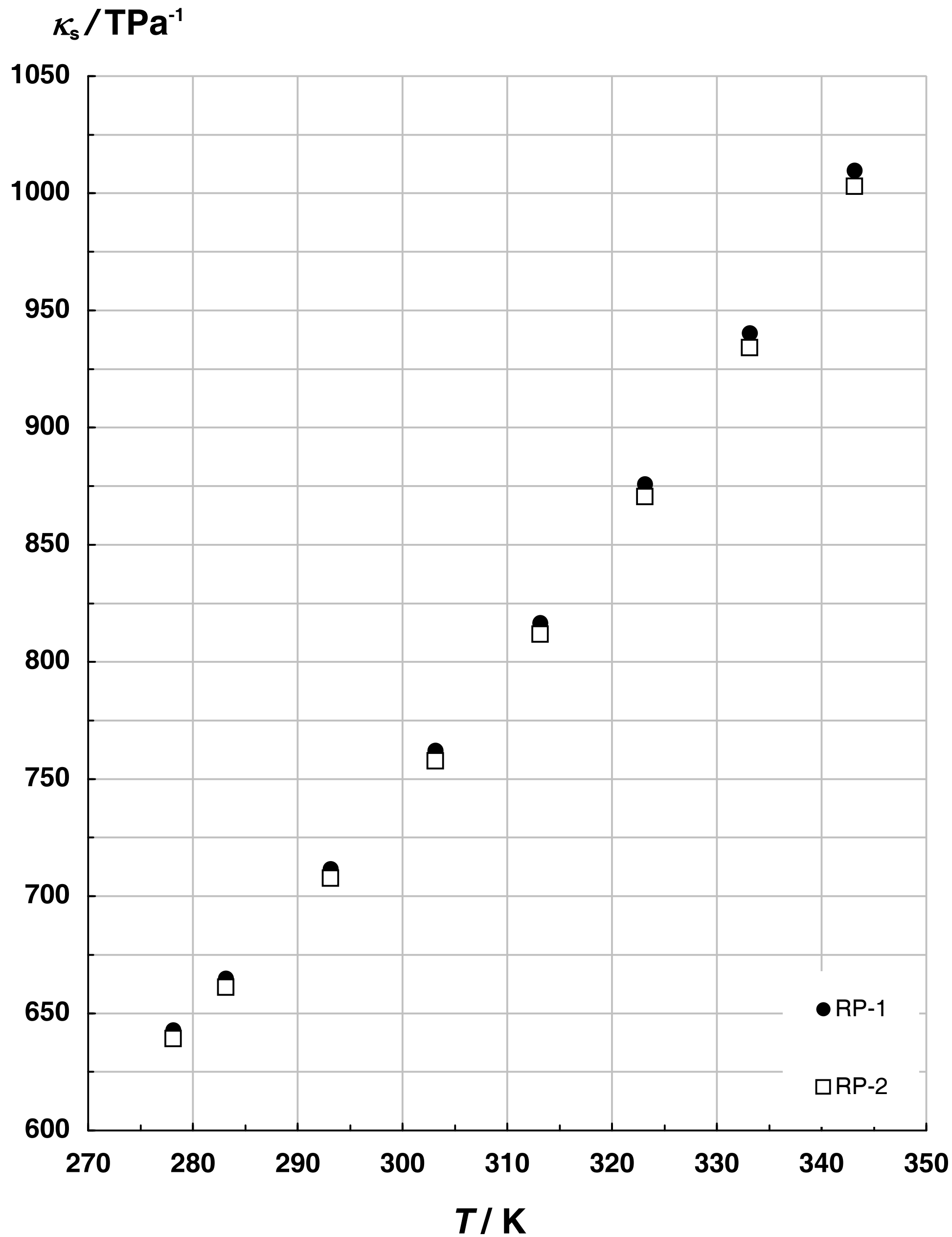


ρ, kg·m-3
Compressed Liquid Density of RP-2
860
840
820
800
780
760
740
720
700
680
660
250 270 290 310 330 350 370 390 410 430 450 470 490
T, K

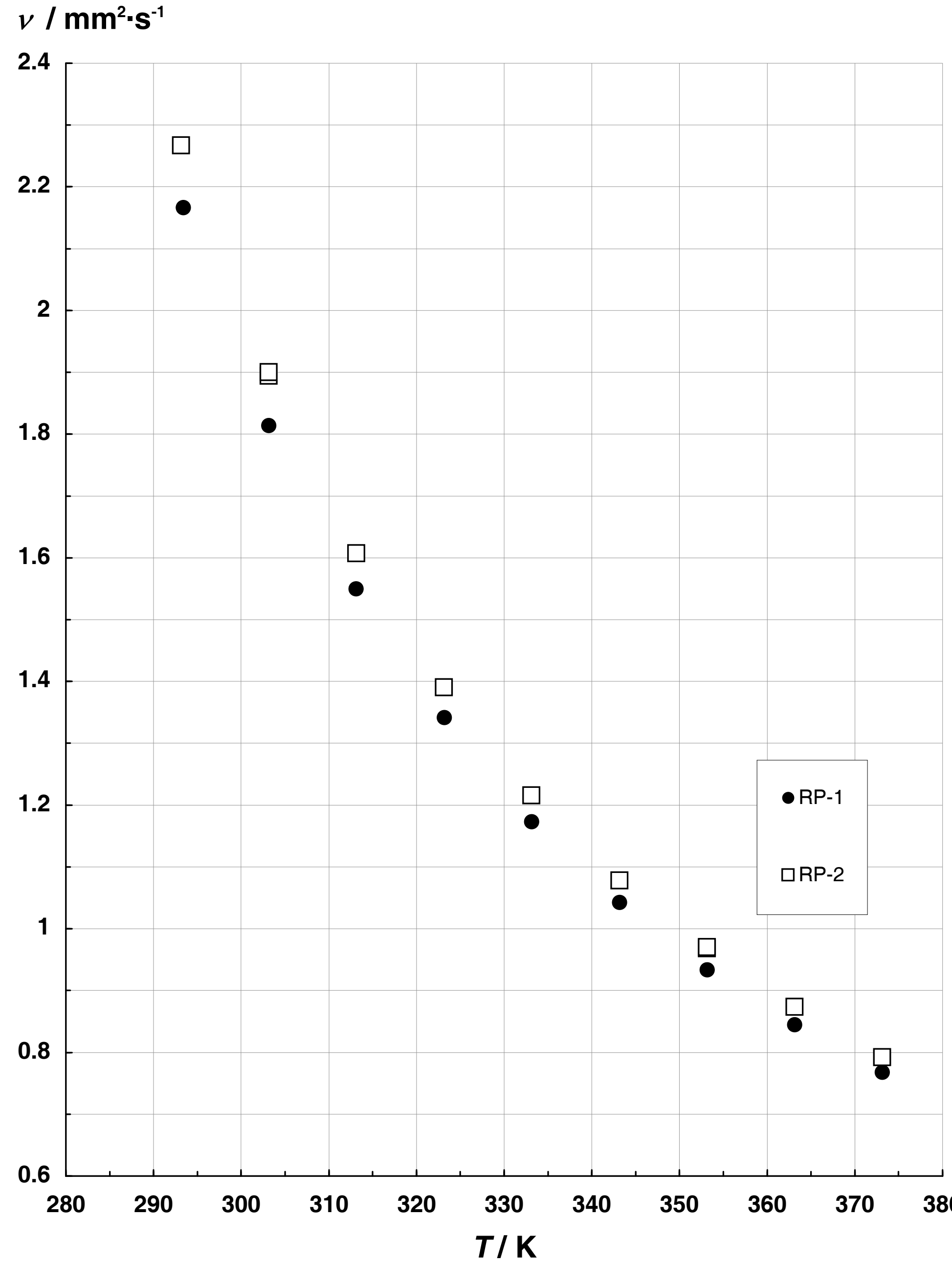
Speed of sound of RP-1 and RP-2 as a function of temperature at ambient pressure.



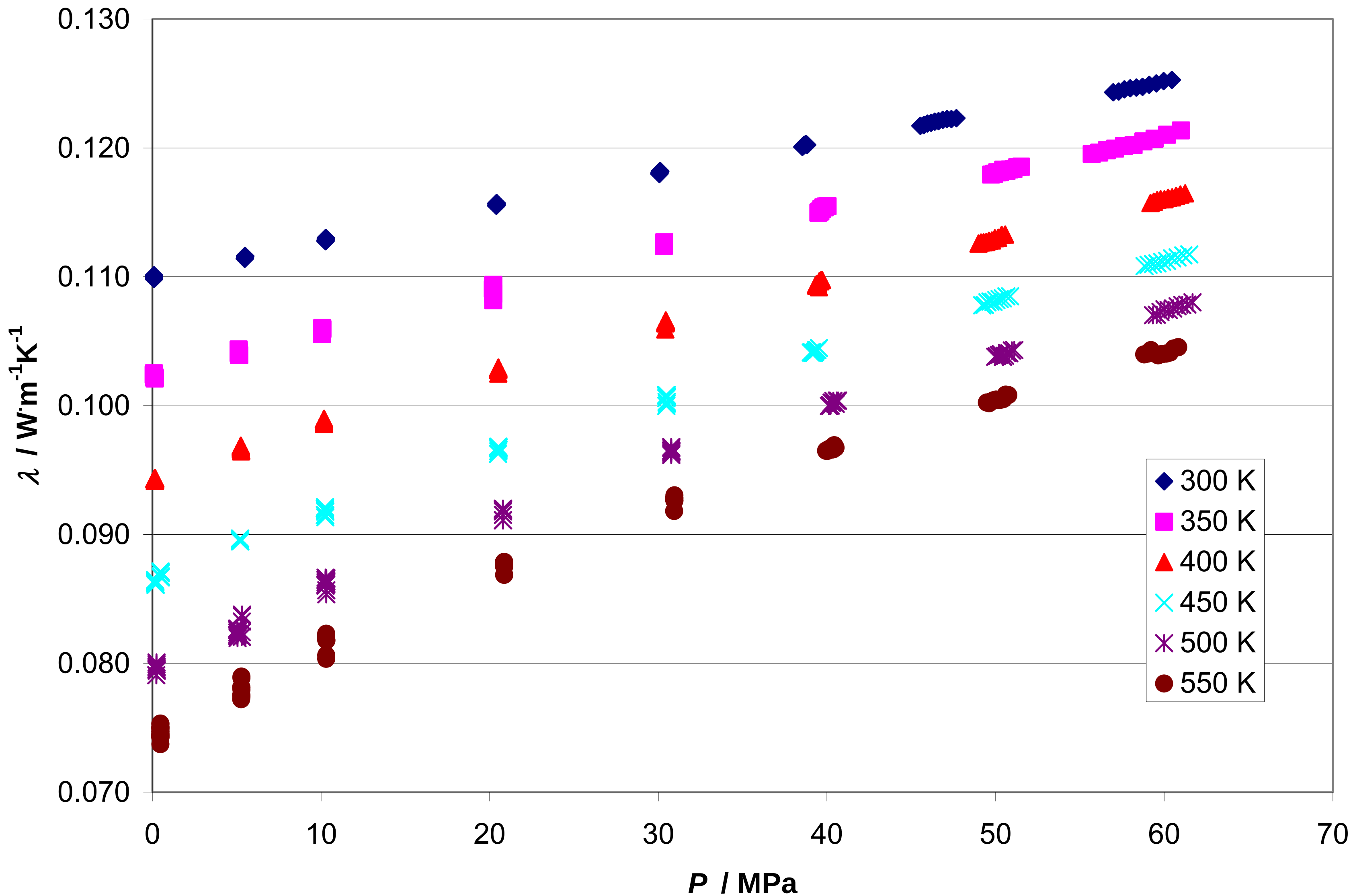
Adiabatic compressibility data of RP-1 and RP-2 as a function of temperature at ambient pressure.



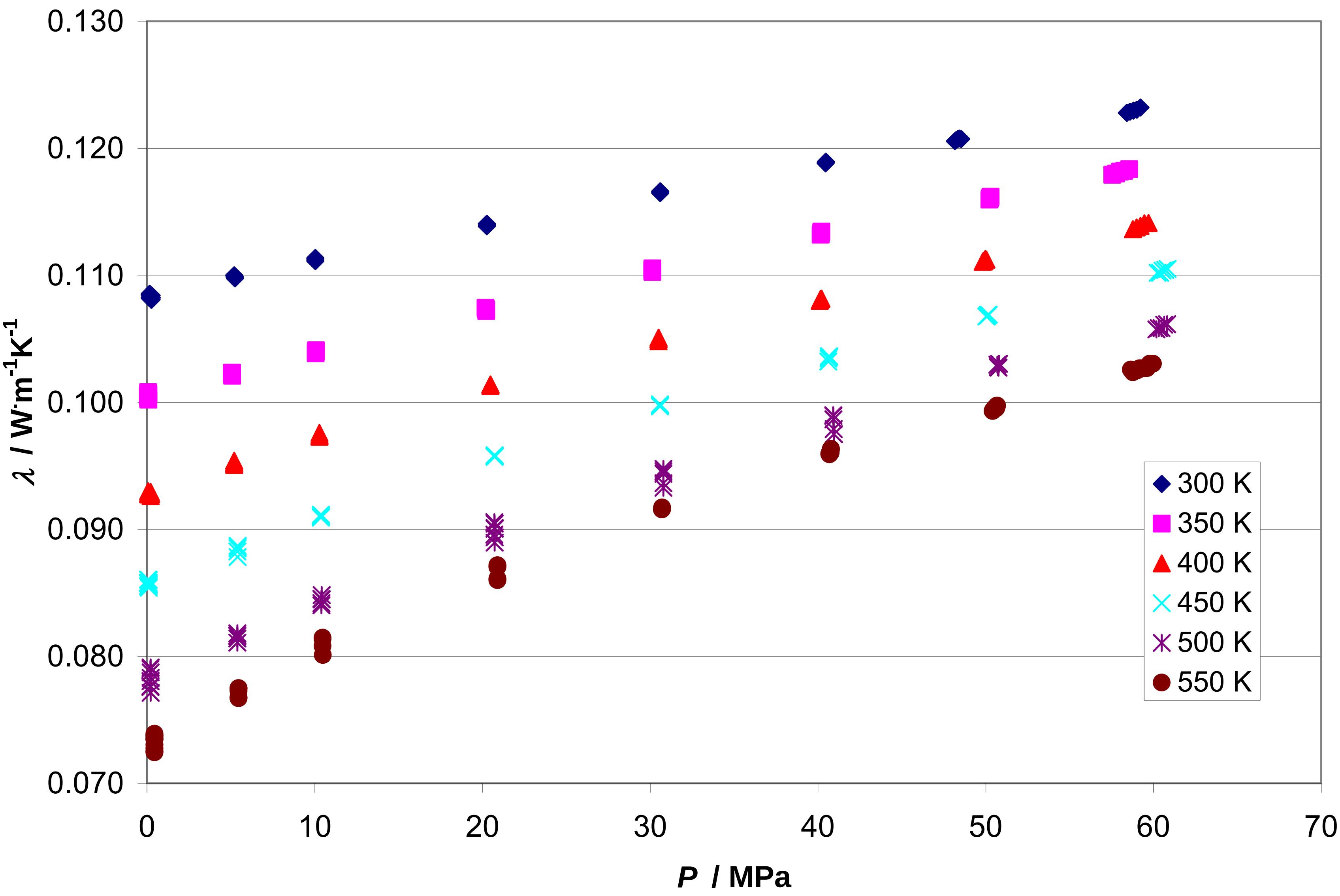
Kinematic viscosity of RP-1 and RP-2 as a function of temperature at ambient pressure.



Thermal Conductivity of RP-1 (New Sample)



Thermal Conductivity of RP-2



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In parallel, a study of decomposition was done:

- Decomposition studies have been part of the NIST protocol since we left cryogenics
- With RP-2, the decomposition is important as a measurement.
  - straight RP-2, RP-2 with additives, corrosivity studies

Explicit consideration of sample decomposition was begun of necessity:

- Straty, G.C., Palavra, A.M.F., Bruno, T.J., PVT Properties of Methanol at Temperatures to 300 ^{o}C, *Int. J. Thermophys,* 7(5), 1077, 1986.

- Straty, G.C., Ball, M.J., Bruno, T.J., PVT of toluene at temperatures to 673 K, *J. Chem. Eng. Data*, 33,115,1988.

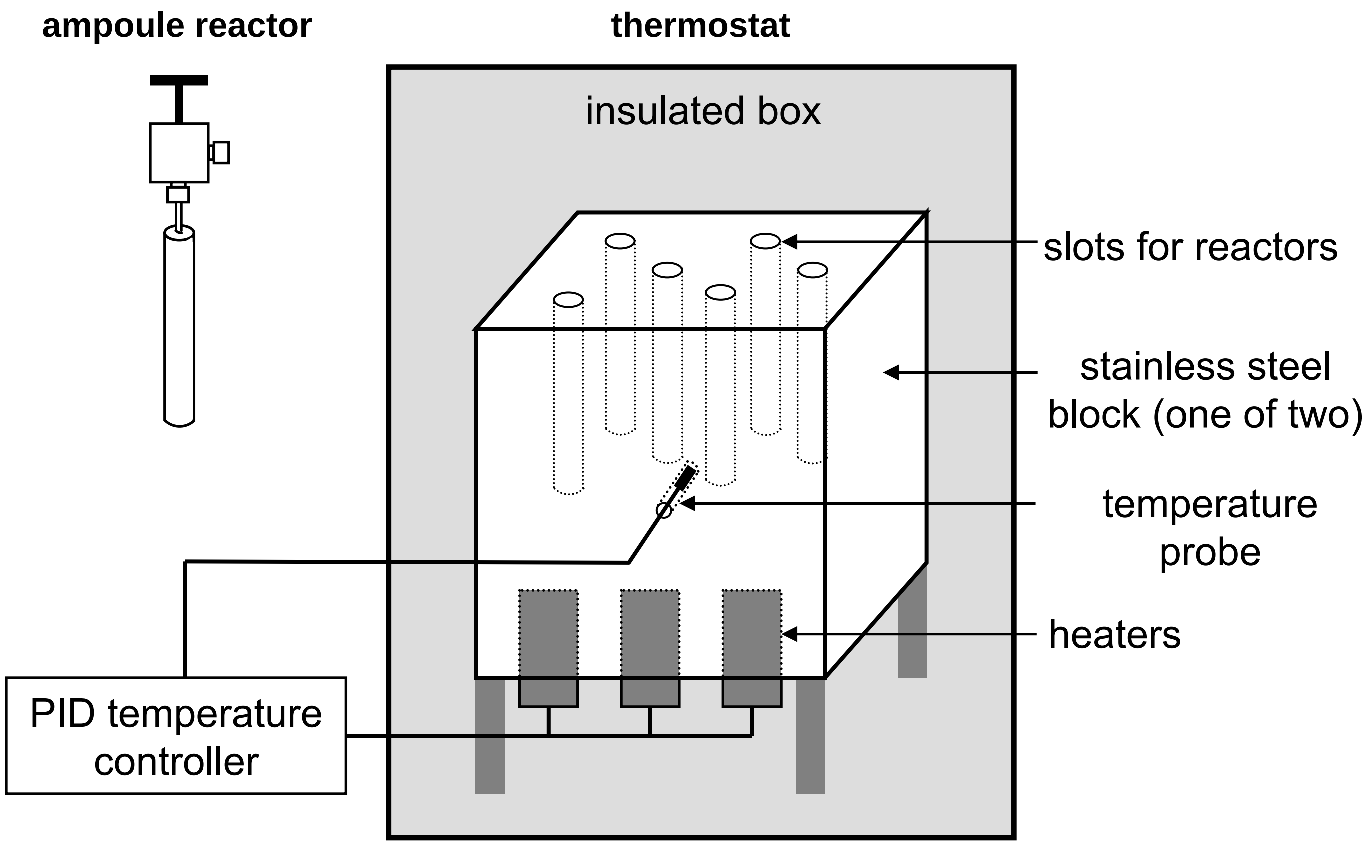
Experimental effort involves numerous high value, one-of-a kind apparatus:

- VLE Instruments
- Viscometers
  - torsional crystal
  - Stabinger
  - gravitational
- Densimeters
  - dual sinker
  - rapid screening
- Thermal Conductivity
  - low and high temperature hot wire
- Speed of Sound
- Etc.

PVT and VLE of methanol

At only 100 ^{o}C, the sample decomposed into CO, H_2, and synthetic products

Samples are thermally stressed in stainless steel ampoule reactors



Ampoule reactors:

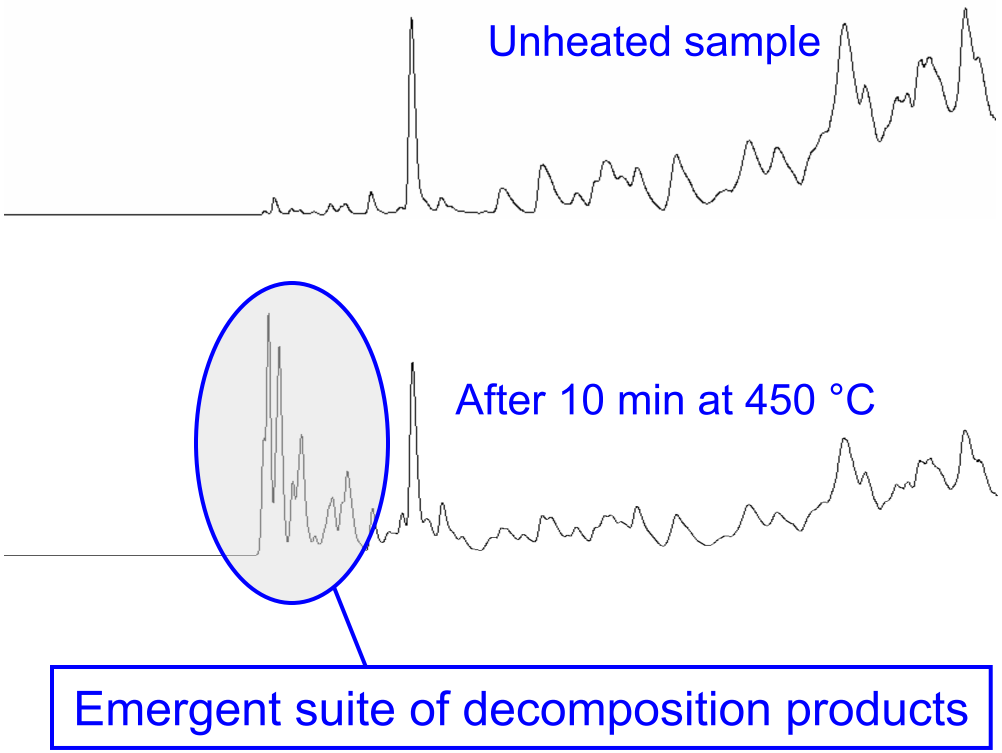
Temperatures to 450 ^{o}C

Pressures to 10,000 psi

(once, by accident, to 36,000 psi)

Extent of decomposition determined by analysis

GC-FID of RP-2



The light decomposition products are used for the kinetic analysis

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

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

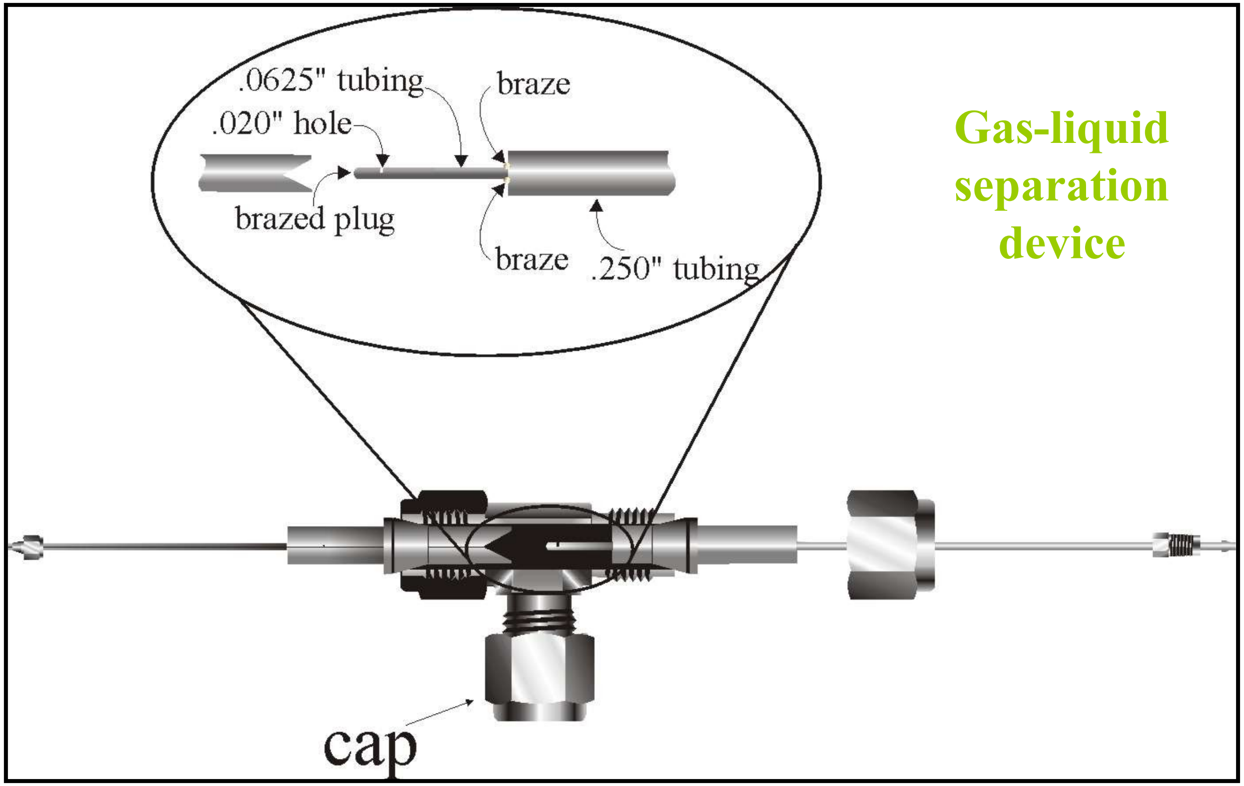
$$-\frac{d[A]}{dt} = \frac{d[B]}{dt} = k'[A]$$

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

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

Separate phase analysis is performed

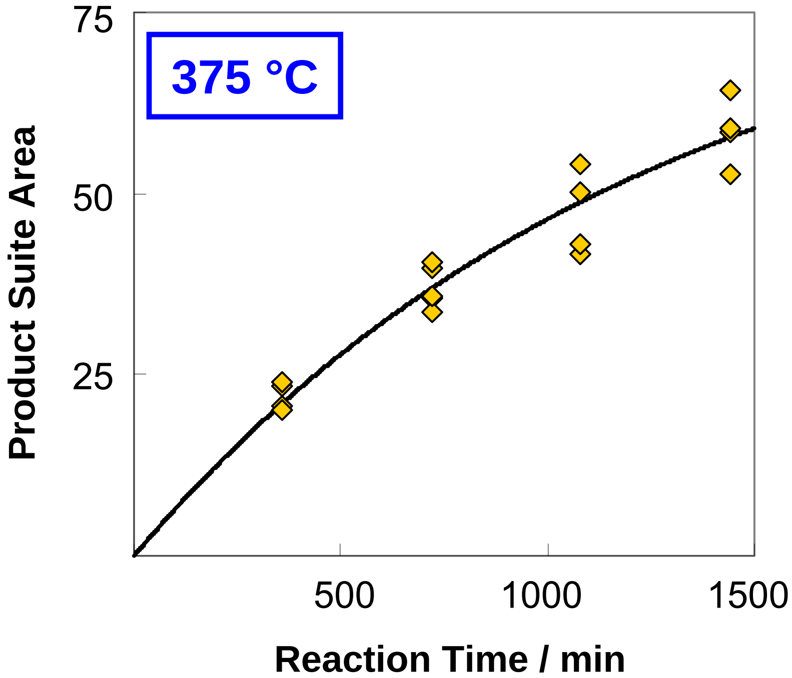
determine thermal or catalytic mechanisms

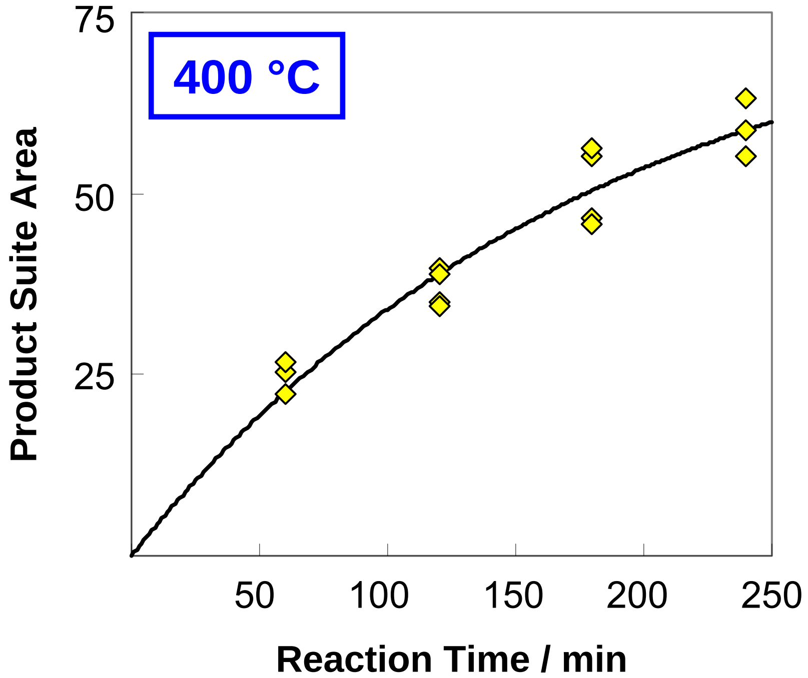


Liquid and gas phases analyzed by FTIR, GC-FID and GC-MS

Bruno, T.J., Conditioning of multiphase flowing samples for chemical analysis, *Sep. Sci. Tech.*, 40, 1721-1732, 2005.

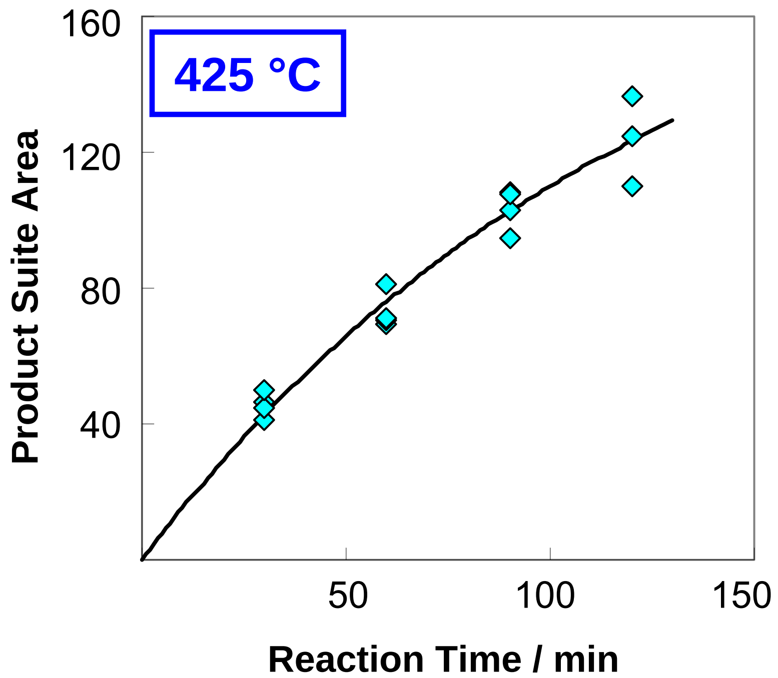
Decomposition kinetics of RP-2

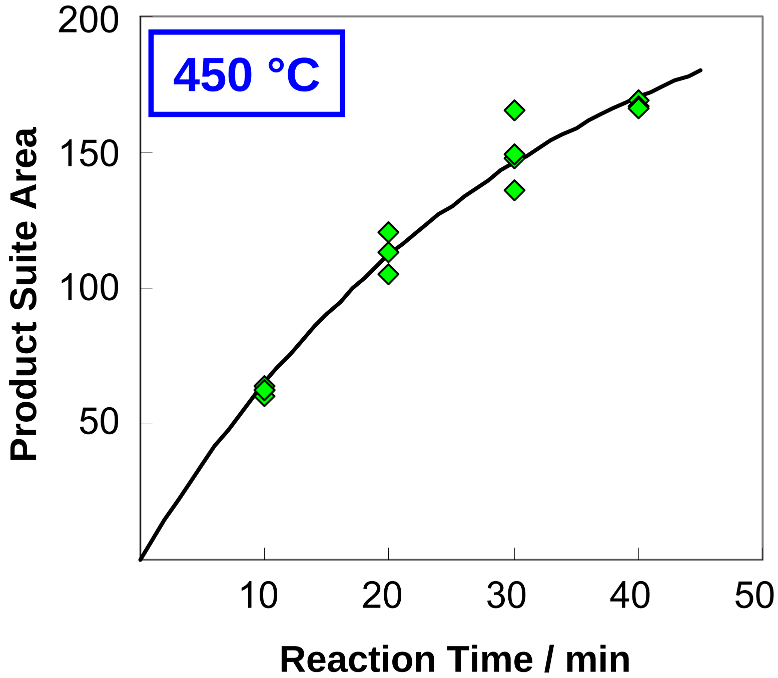




The rate constant for decomposition, *k′*, is obtained from the fit.

Decomposition kinetics of RP-2





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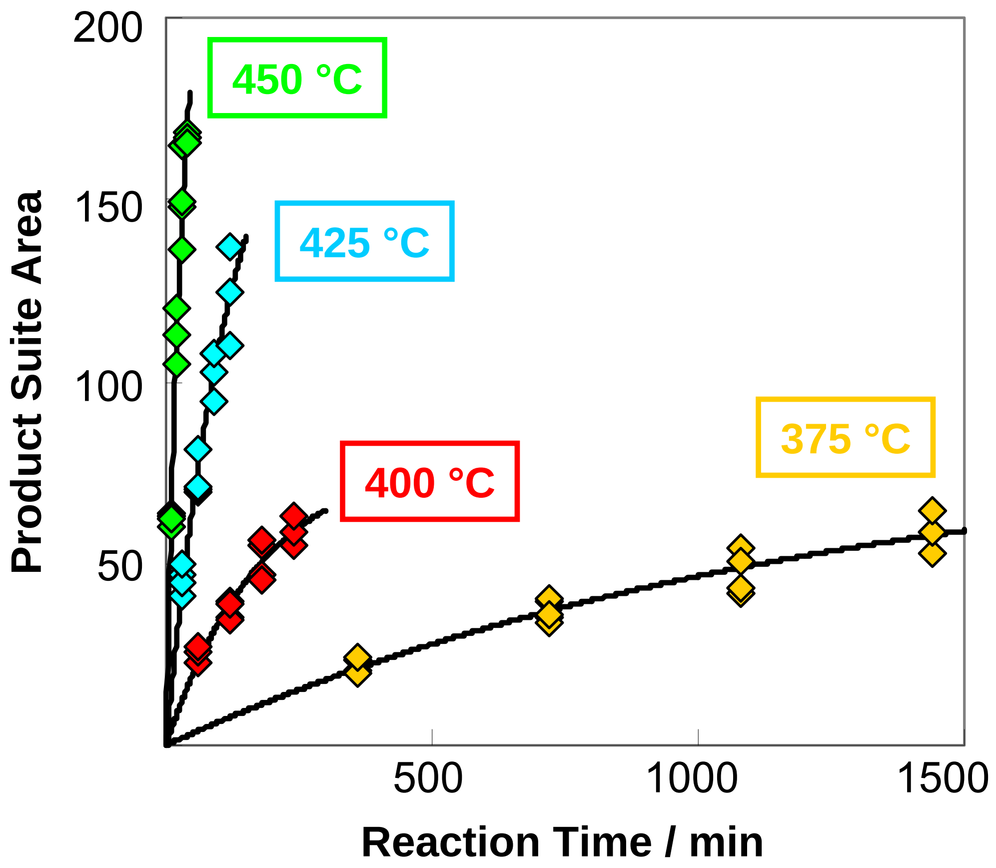
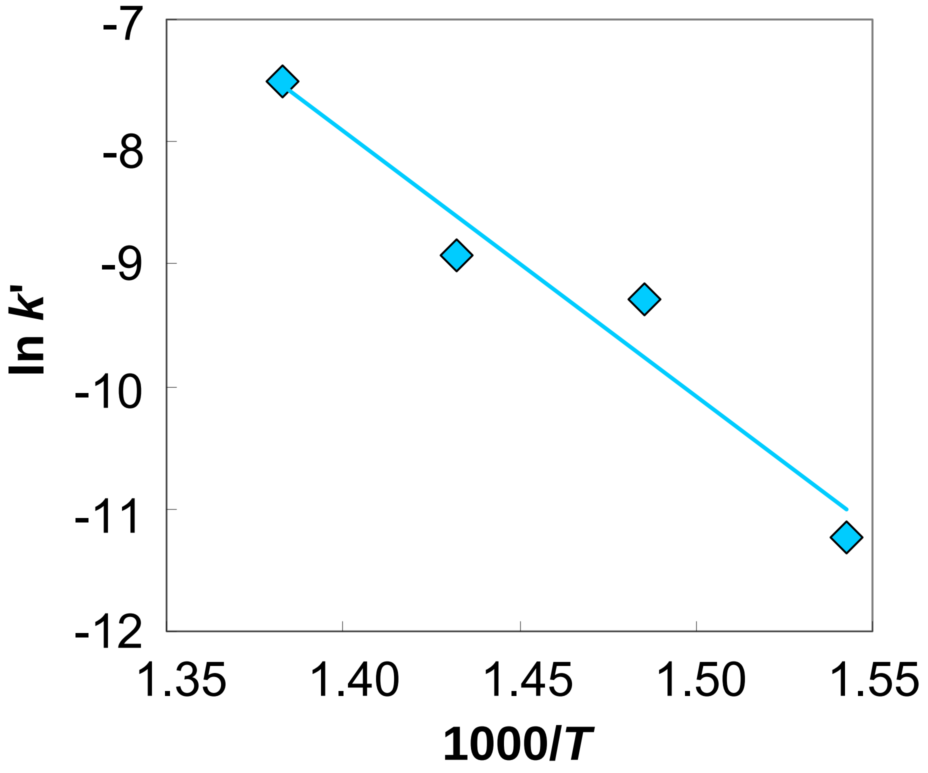
Decomposition kinetics of RP-2

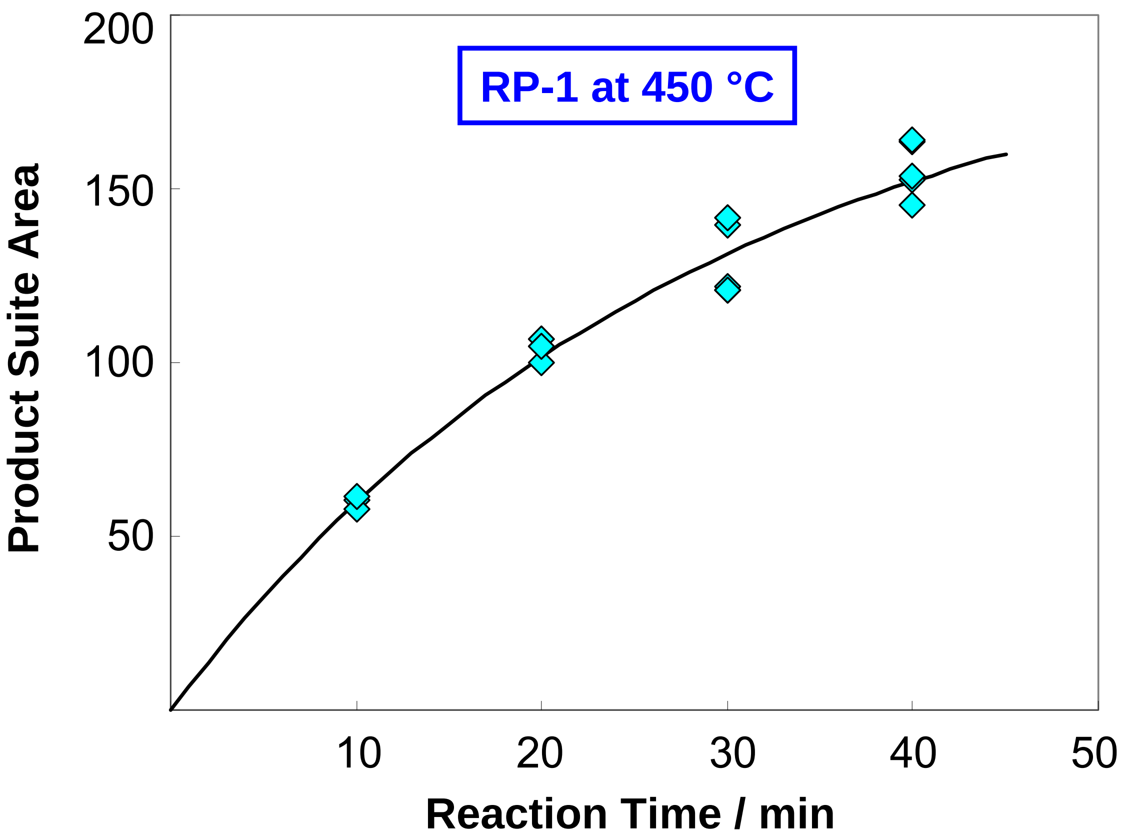


Rate constants for RP-2 decomposition

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	$(5.47 \pm 0.80)\times10^{-4}$



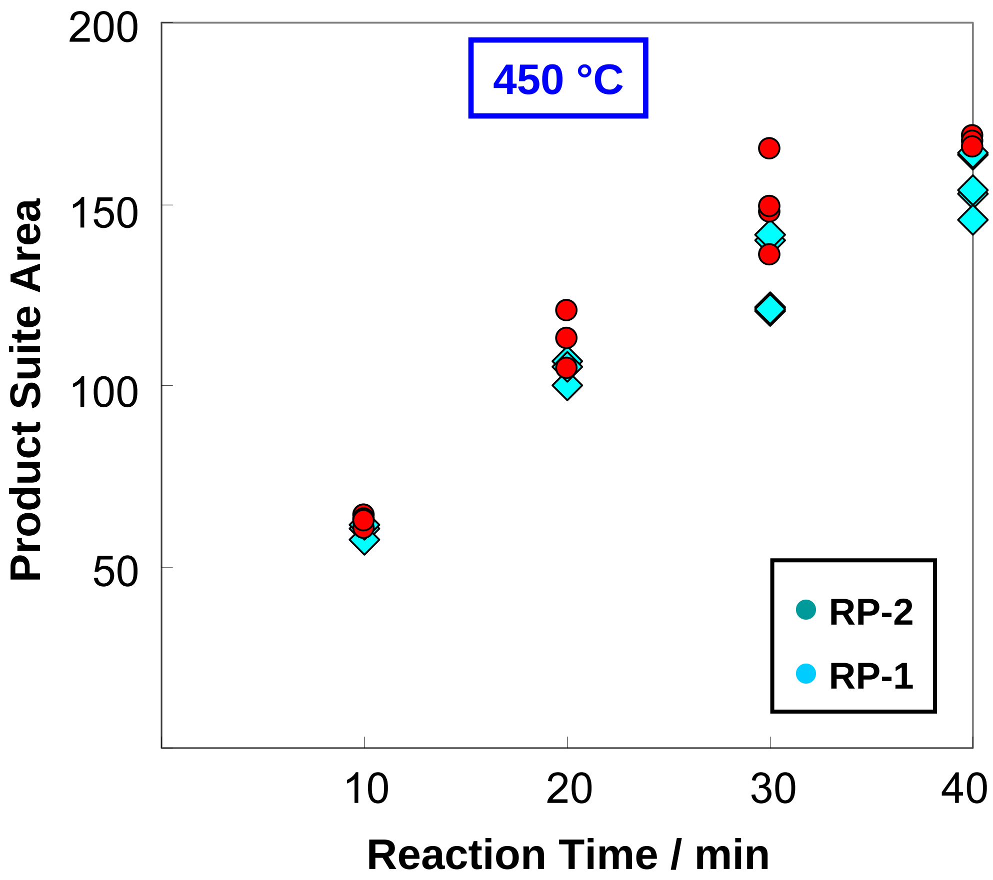
Decomposition kinetics of RP-1



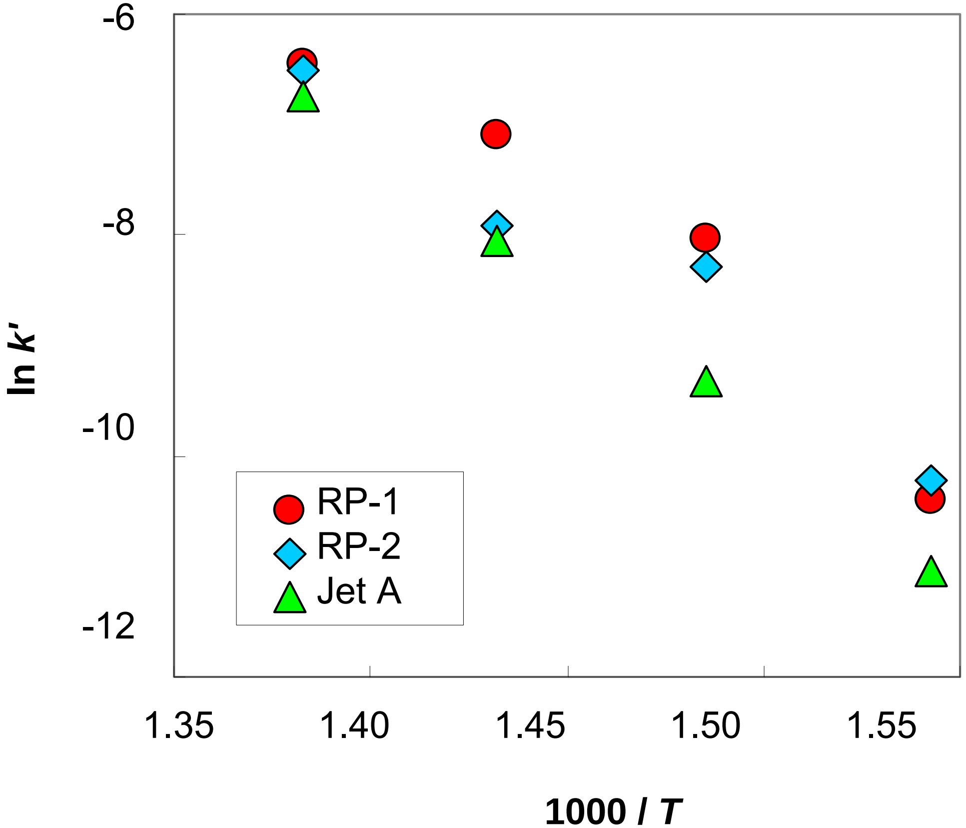
The decomposition of RP-1 and RP-2 is very similar.

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

Comparison of RP-1 and RP-2 decomposition



Comparison of Jet A with RP-1 and RP-2

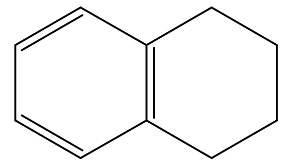


Comparison of RP-1 and RP-2 decomposition

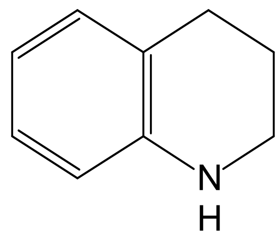
	RP-1	**RP-2**
T / °C	$(k' \pm 1\sigma)$ / s^{-1}	$(k' \pm 1\sigma)$ / s^{-1}
375	$(1.13 \pm 0.04)\times10^{-5}$	$(1.33 \pm 0.30)\times10^{-5}$
400	$(1.19 \pm 0.33)\times10^{-4}$	$(9.28 \pm 2.01)\times10^{-5}$
425	$(3.08 \pm 0.77)\times10^{-4}$	$(1.33 \pm 0.33)\times10^{-4}$
450	$(5.84 \pm 1.33)\times10^{-4}$	$(5.47 \pm 0.80)\times10^{-4}$

Decomposition of RP-2 with additives

- RP-2 with 5% tetralin



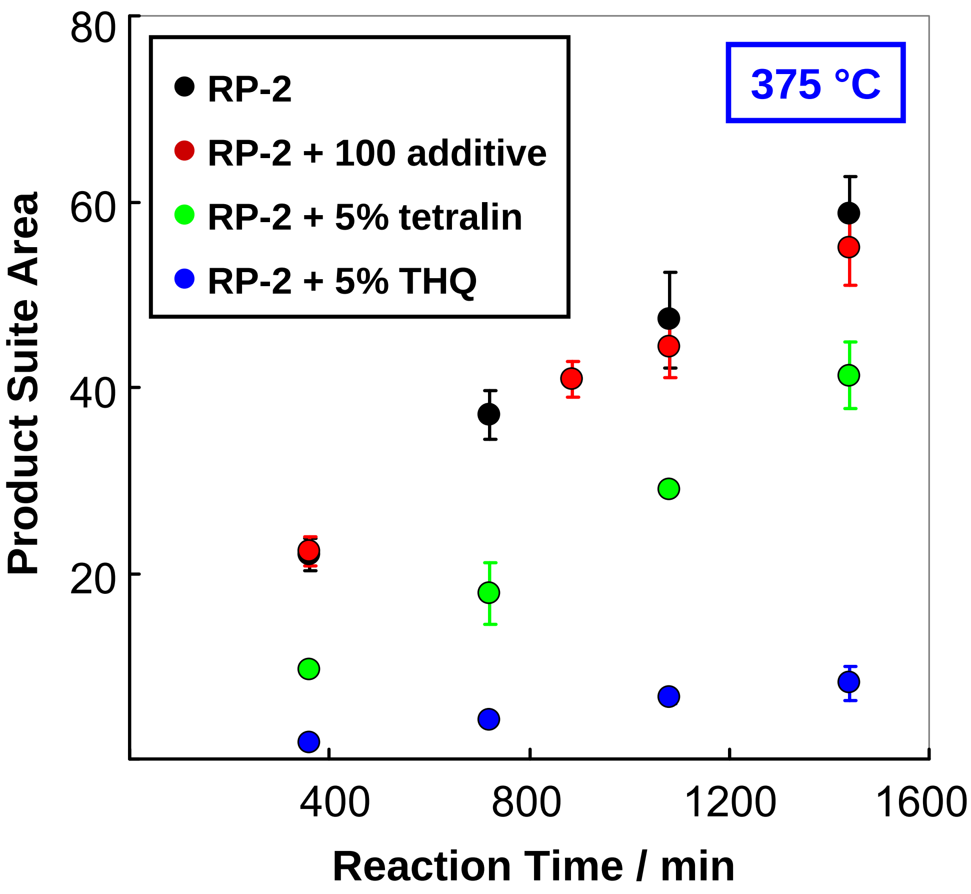
- RP-2 with 5% THQ



- RP-2 with 256 ppm of the additive mixture in JP-8 +100
  - contains a chelator, antioxidant, and surfactant

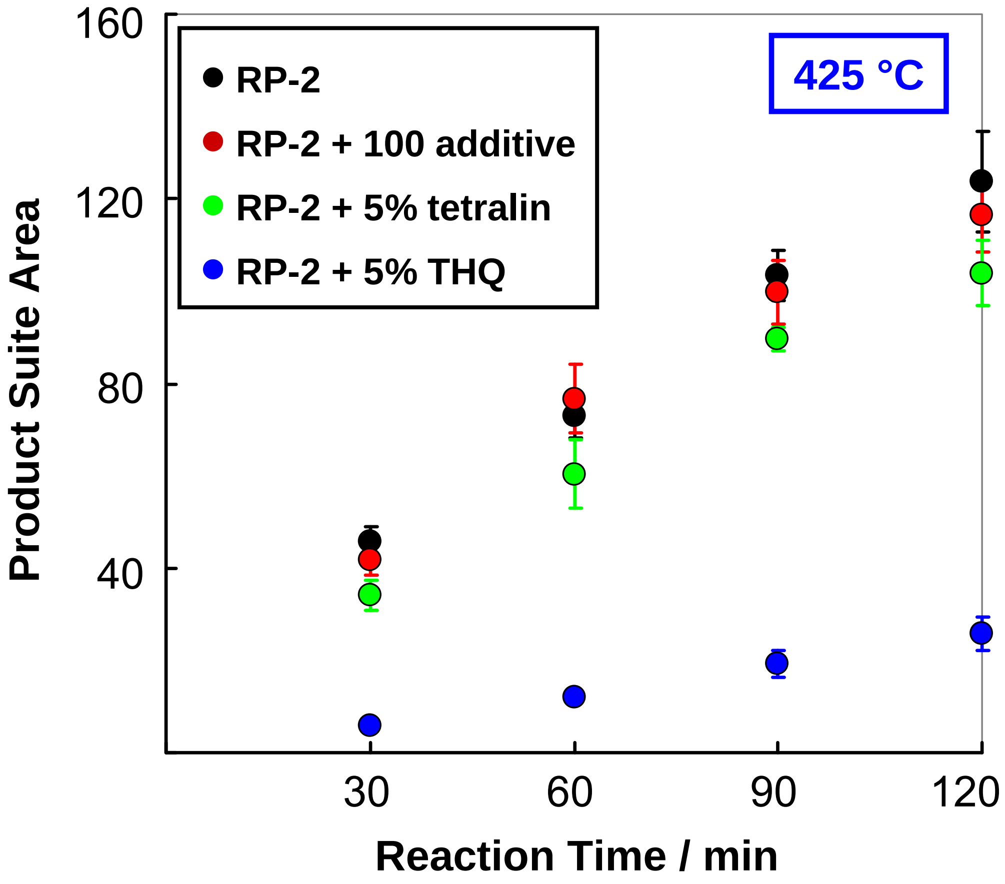
Hydrogen donors increase thermal stability by interrupting radical decomposition pathways.

Decomposition of RP-2 with additives



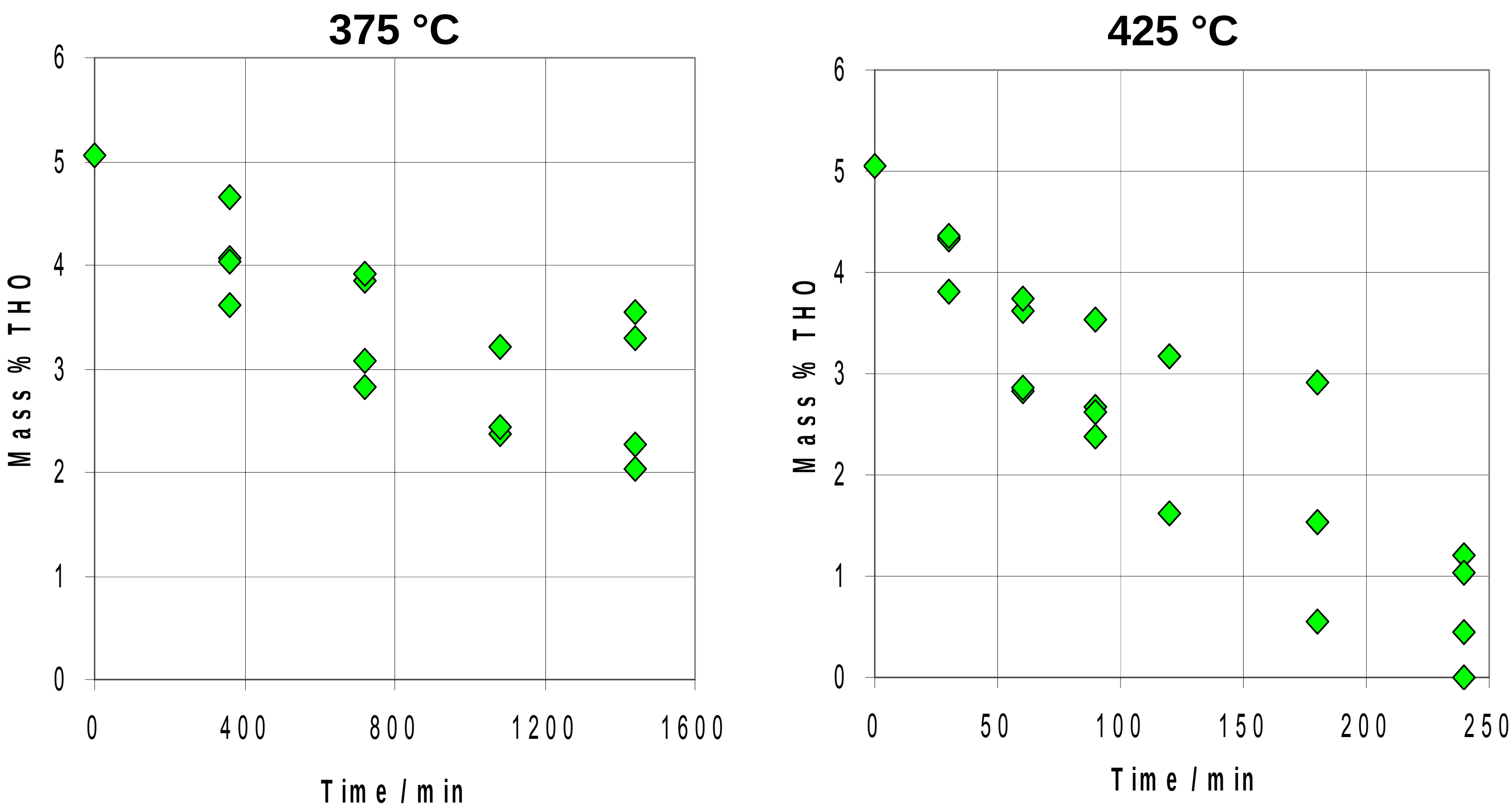
5% THQ lowers the rate of decomposition by about an order of magnitude.

Decomposition of RP-2 with additives



The stabilizing effect is smaller at higher temperature.

Concentration of THQ during decomposition



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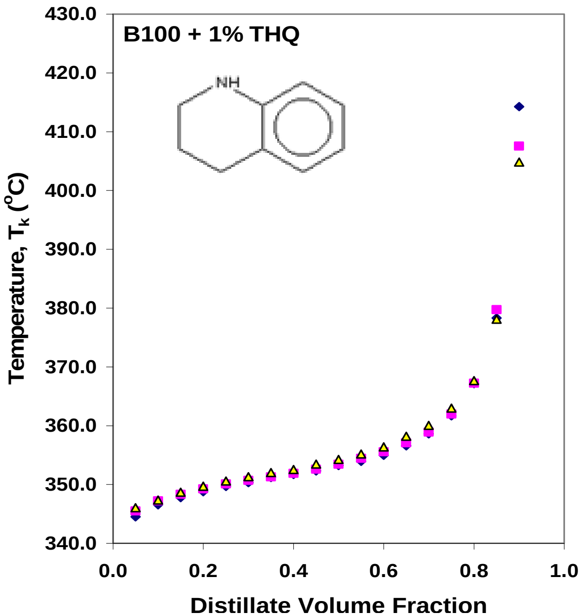
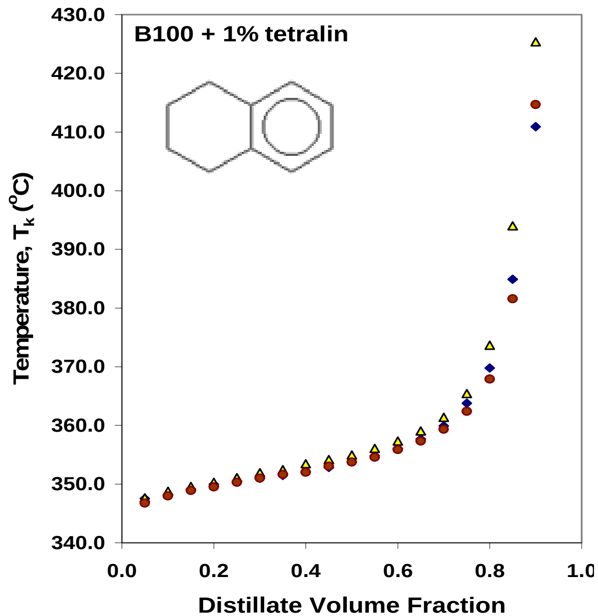
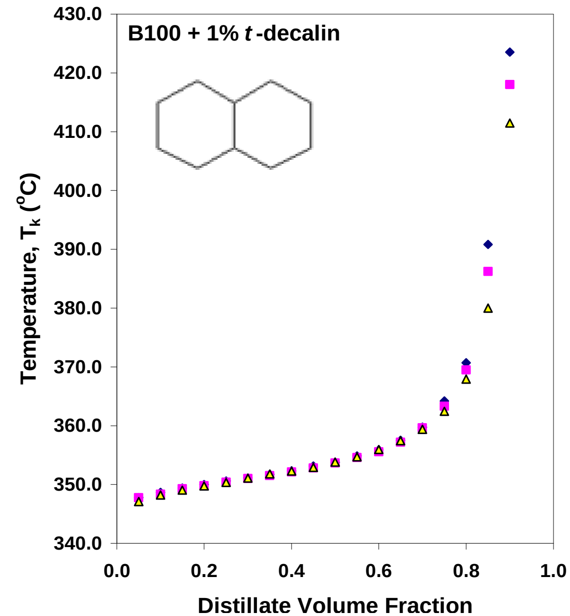
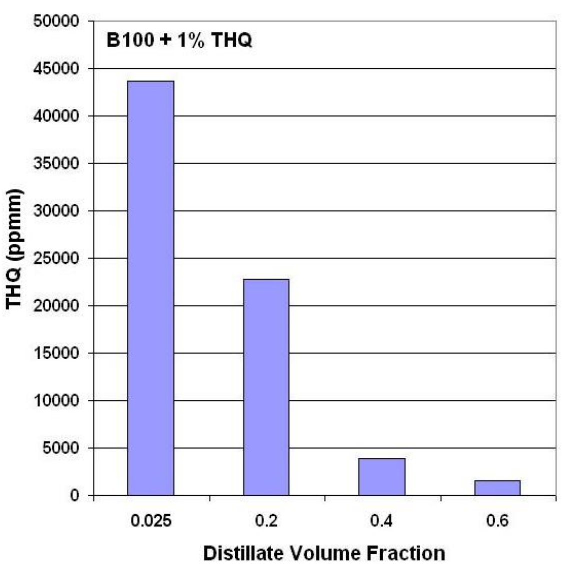
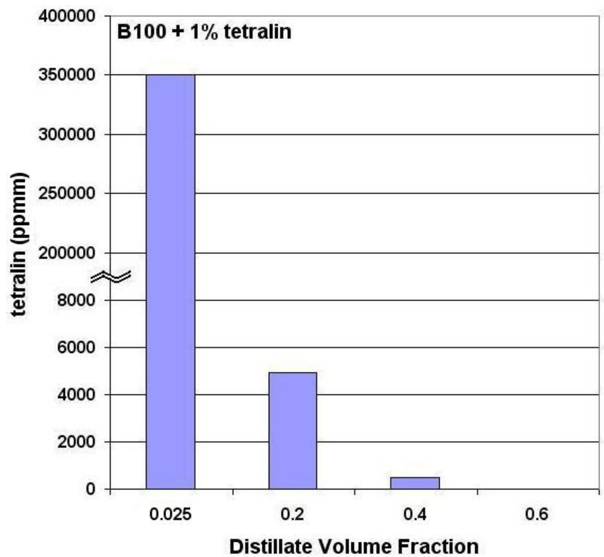
Parallels results with B100 (biodiesel):

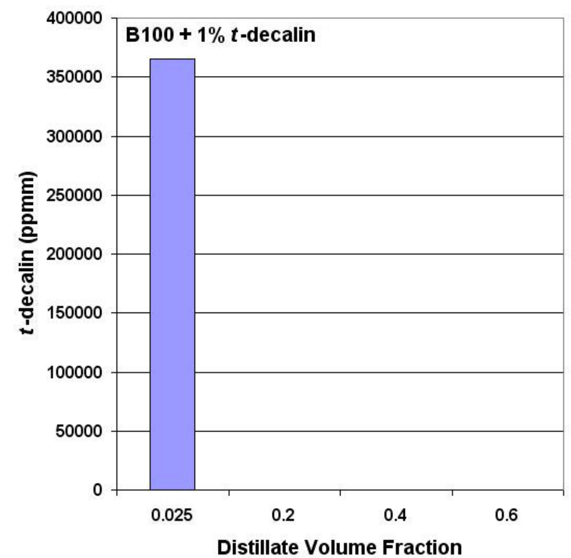


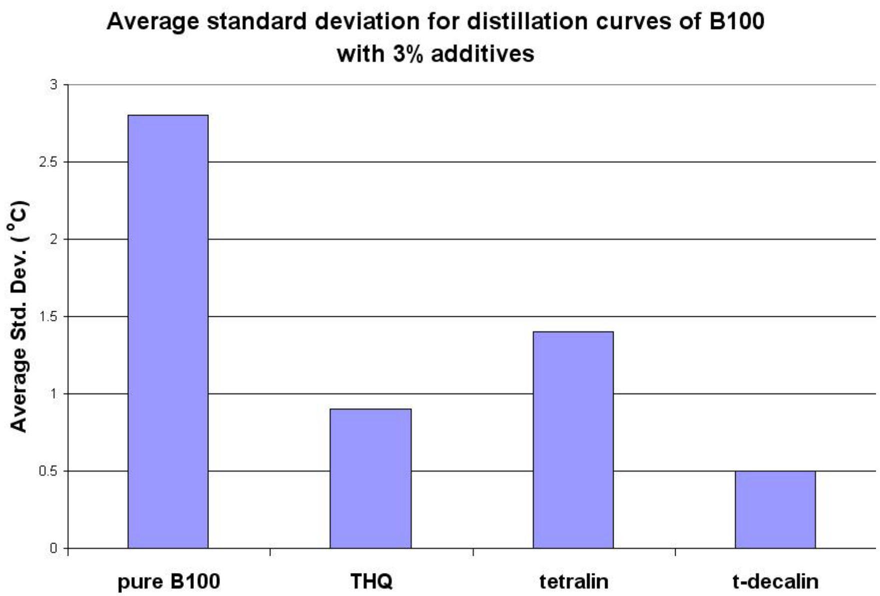


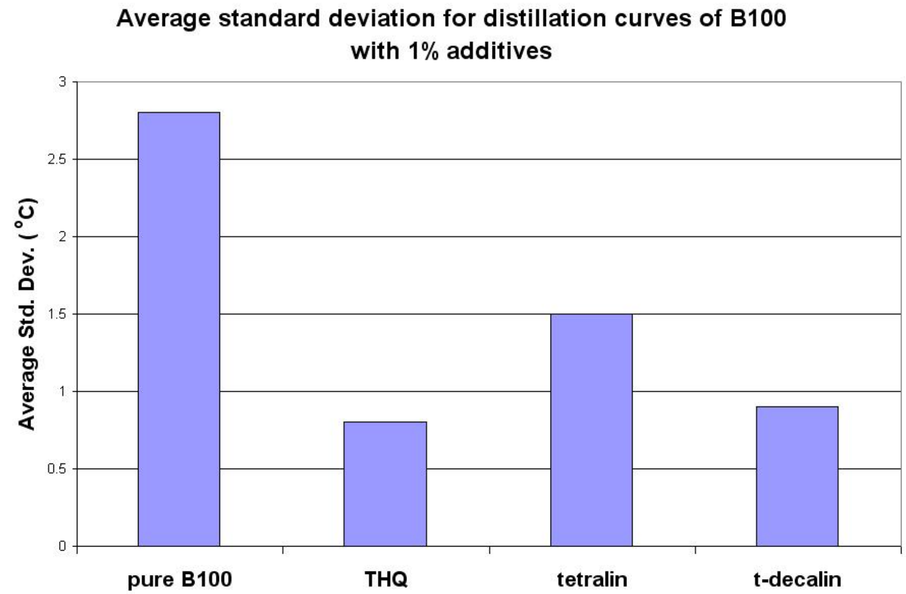








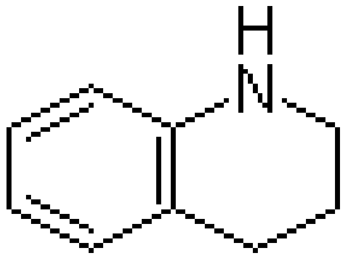




Lower is better!

A clear high-temperature stabilization effect occurs.

Stabilization of RP-2:



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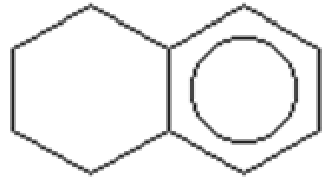

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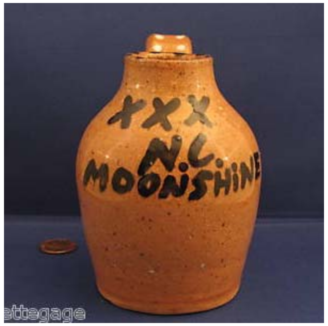
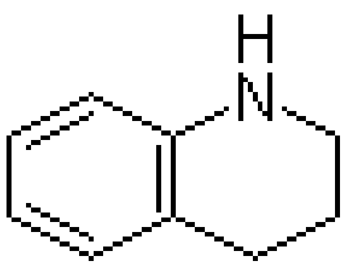


tetrahydroquinoline   tetralin   +100

Stabilization of B100:



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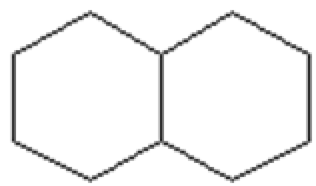

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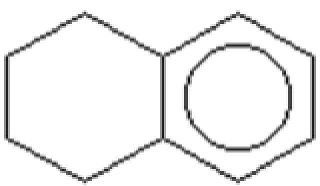
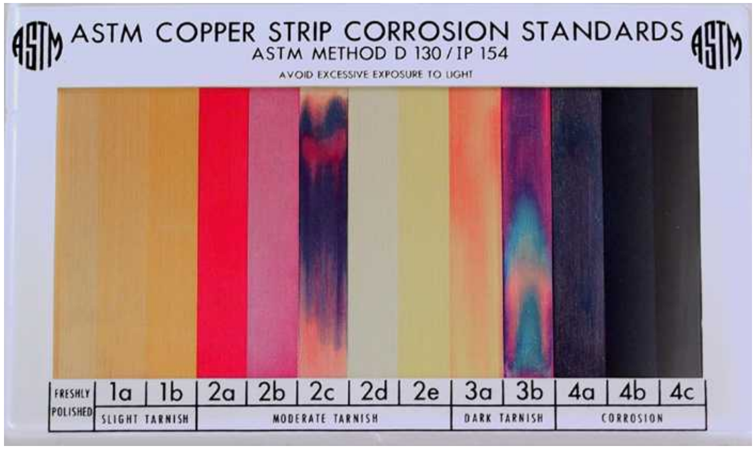


tetrahydroquinoline   *t*-decalin   tetralin

Corrosivity of decomposed RP-1



An improved copper strip corrosion test, developed at NIST, was used to determine the corrosivity of four liquids based on RP-1:

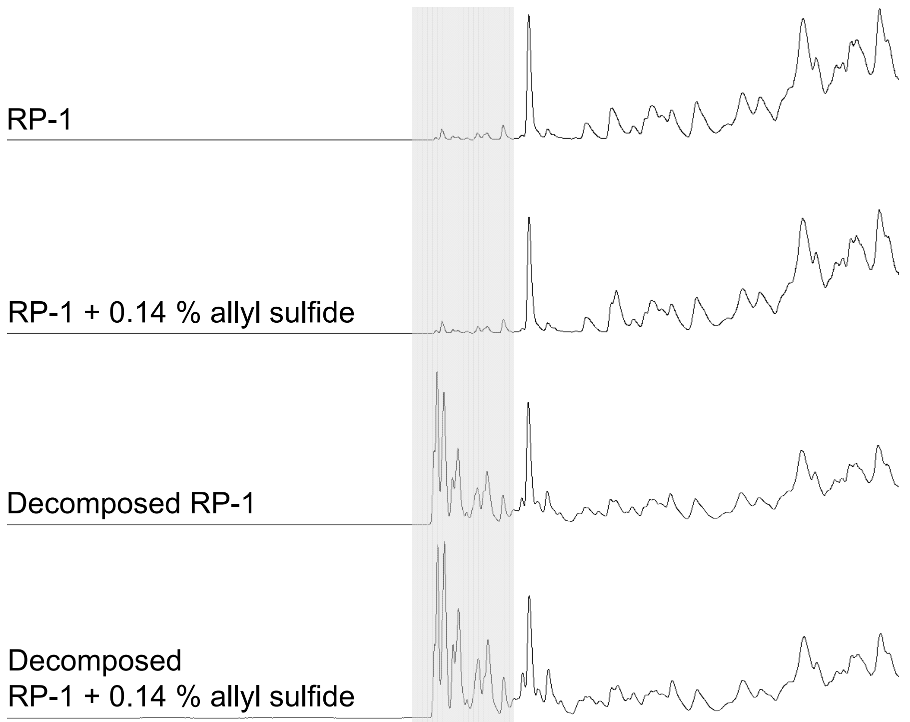
(1) RP-1
(2) RP-1 + 0.14 % allyl sulfide
(3) RP-1 after 2 h at 400 °C
(4) RP-1 + 0.14 % allyl sulfide after 2 h at 400 °C

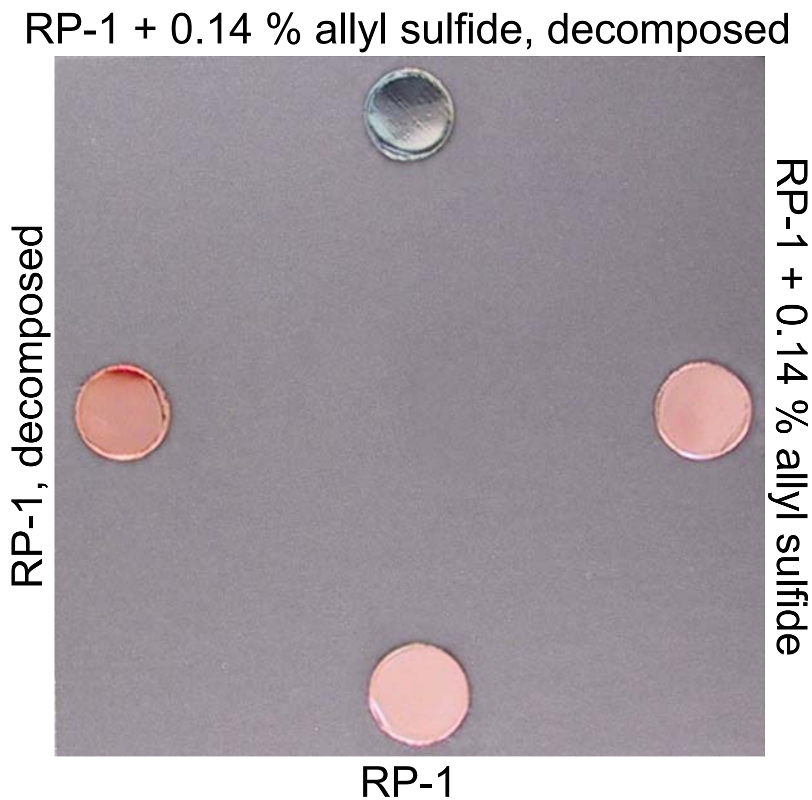
ETP copper coupons

1018 steel coupons

Corrosivity of decomposed RP-1

GC analysis with a flame ionization detector



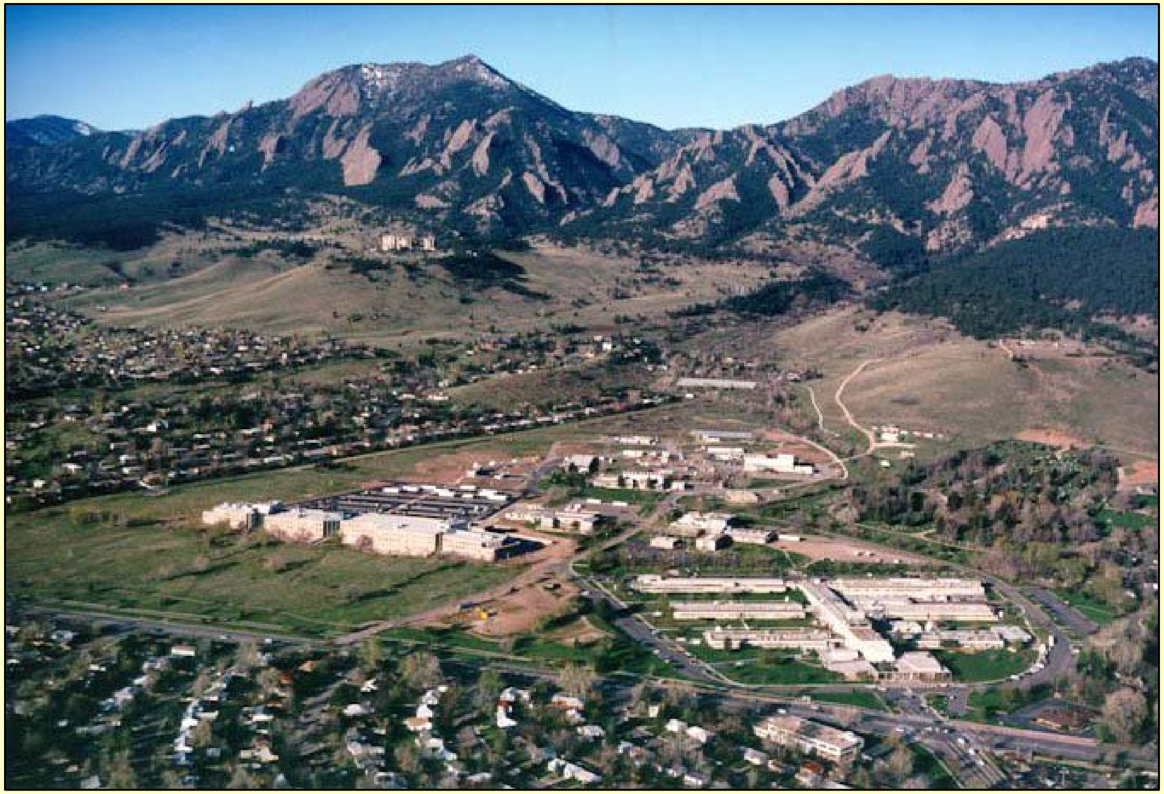


Decomposition greatly increased the corrosivity of the mixture, and slightly increased the corrosivity of RP-1.

Corrosivity of decomposed RP-1

Sample	CSCT	L*	[sulfur] / ppm
RP-1 + 0.14 % allyl sulfide, decomposed	4a	160	3.1
RP-1 + 0.14 % allyl sulfide	1a	199	28.8
RP-1, decomposed	1b	189	not detected
RP-1	untarnished	197	not detected

Rocket and Hypersonic Vehicle Propellant Workshop:



Place:
NIST Boulder Laboratories

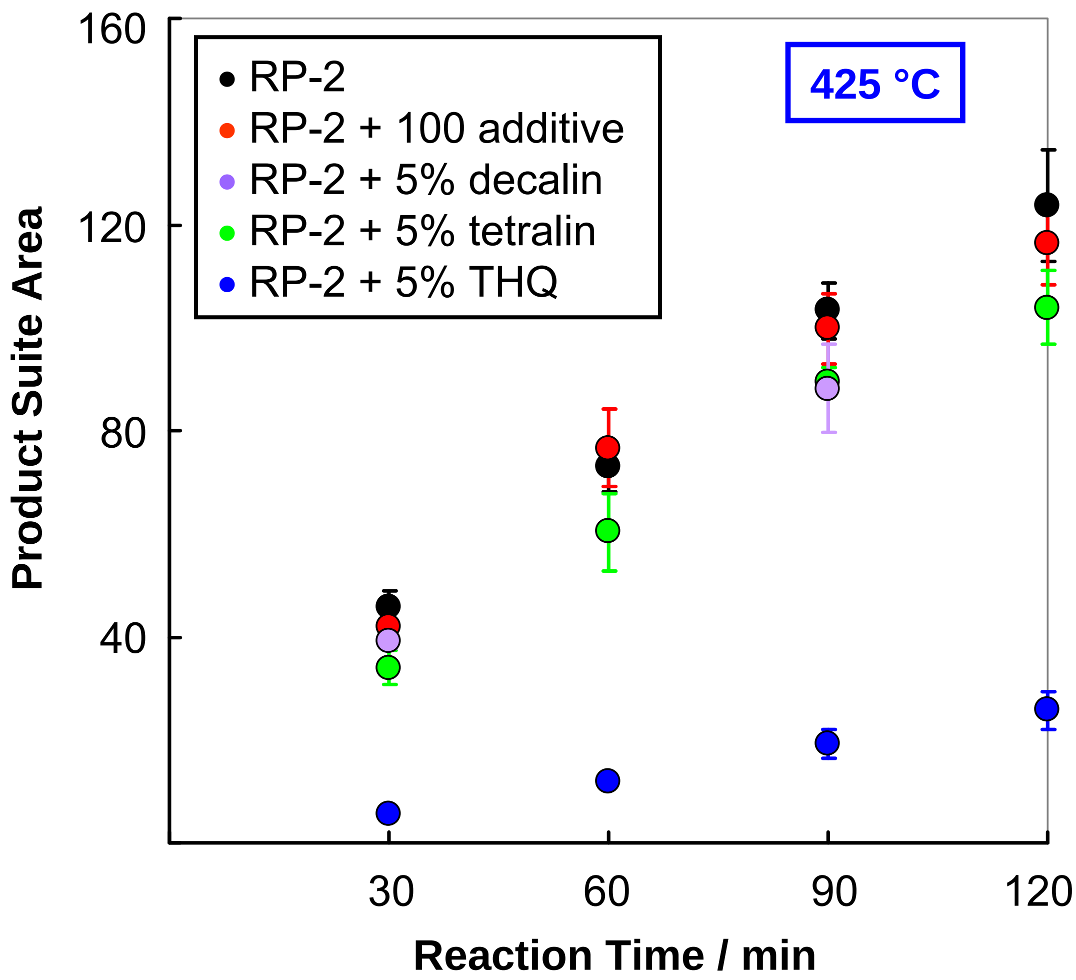
Time:
Sept. 25 - 26, 2008

" Rollout of RP fluid files"

Acknowledgements:

- AFRL-EAFB
- Matt Billingsley, Ron Bates and Steve Hanna
- Tim Edwards, AFRL-WPAFB

Decomposition of RP-2 with additives



Thermal Conductivity of RP-1 (2003)