Measurement and Modeling of Alternative and Renewable Turbine Fuels:

-Application of the ADC Method-

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Boulder, CO

Continuing on my theme from yesterday,

- Fundamental properties offer important advantages over fit-for-purpose or empirical properties
  - Fundamental properties are linked to fundamental theory
    - Math ⟷ Measurement
    - Partner for innovation

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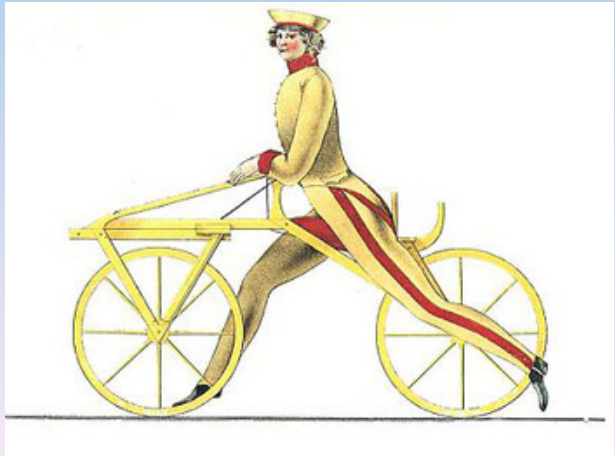
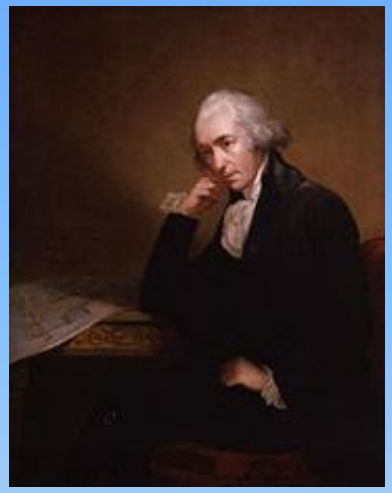


Look familiar?

“Techies” have been filling in the blanks since:



Industrial Revolution?

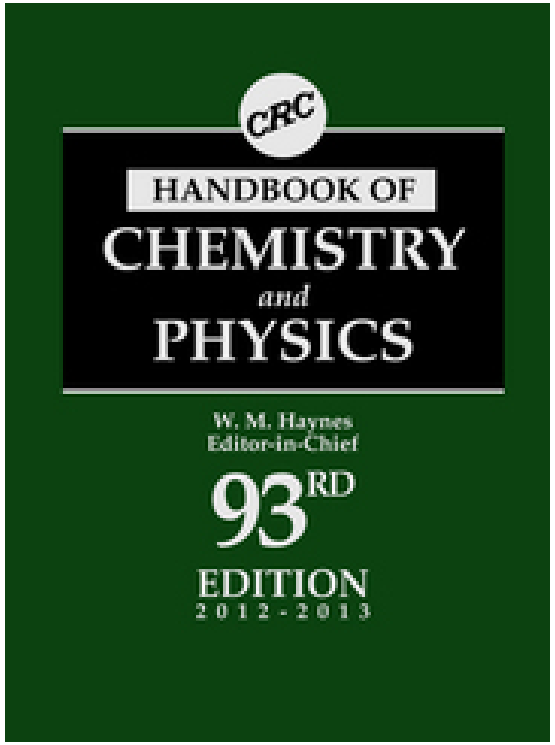
Watt ponders the steam engine

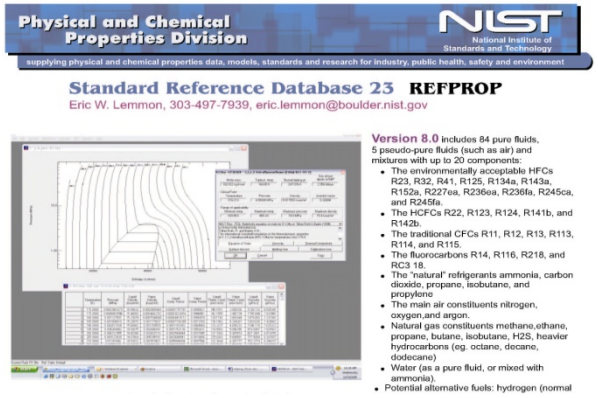
Ancient Rome?

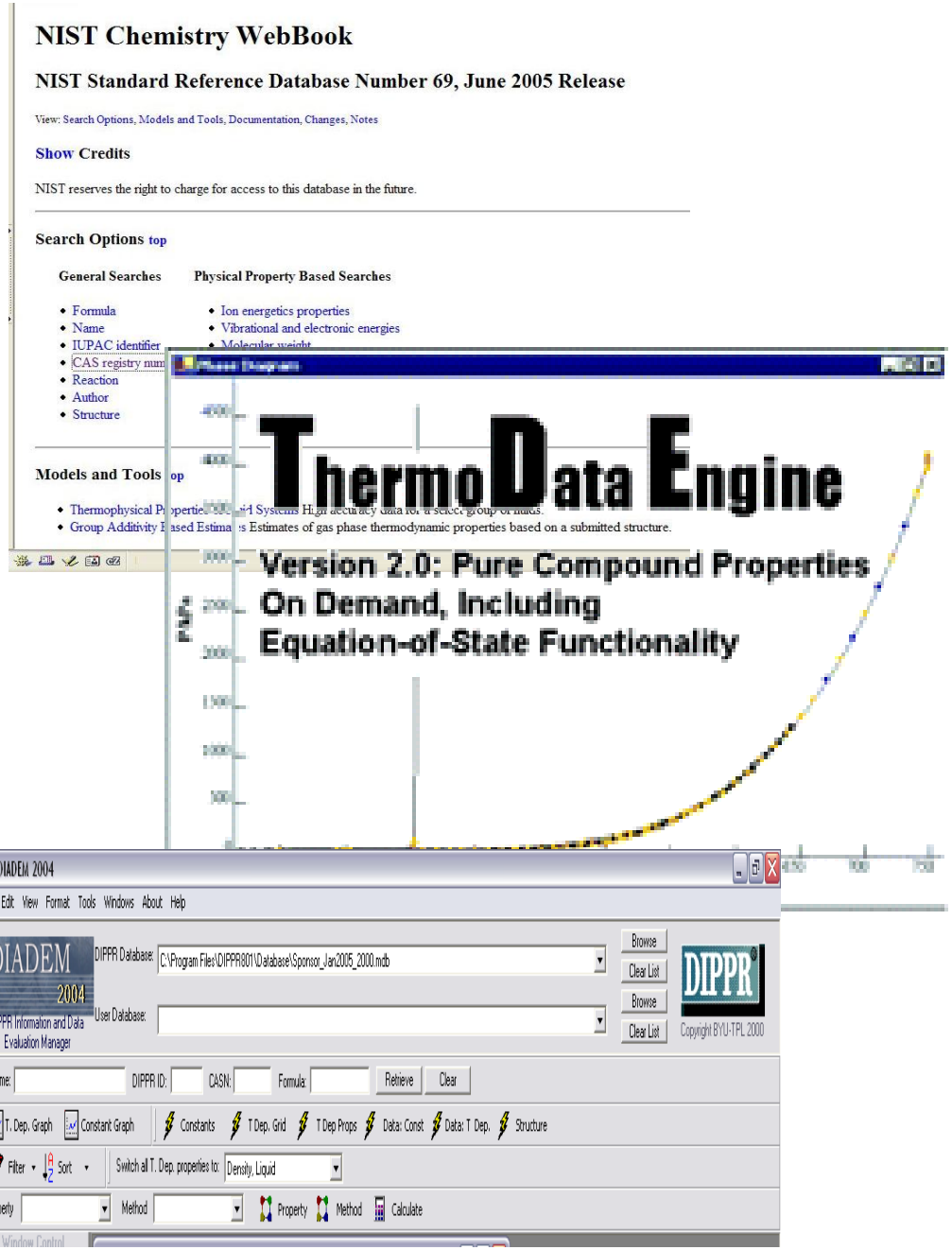
Cave Dwellers?

The need for reliable information has been a constant throughout human progress.

For simple cases,







Most fluids that are useful to us are a bit more complex

Complex Means:

- Many components
  - thousands, and that's just the start
- Heterogeneous
  - polar, nonpolar, dipolar aprotic,…
  - water, solids,…

Analysis Means:

1. What's in the stuff,
2. What are the properties of the stuff

3. How do 1 and 2, above, relate to each other.

<u>Petroleomics:</u> relationship between the chemical composition of a fossil fuel and its properties and reactivity.

A.G. Marshall and R.P. Rogers, *Acc. Chem. Res.* 2004, *37*, 53-59.

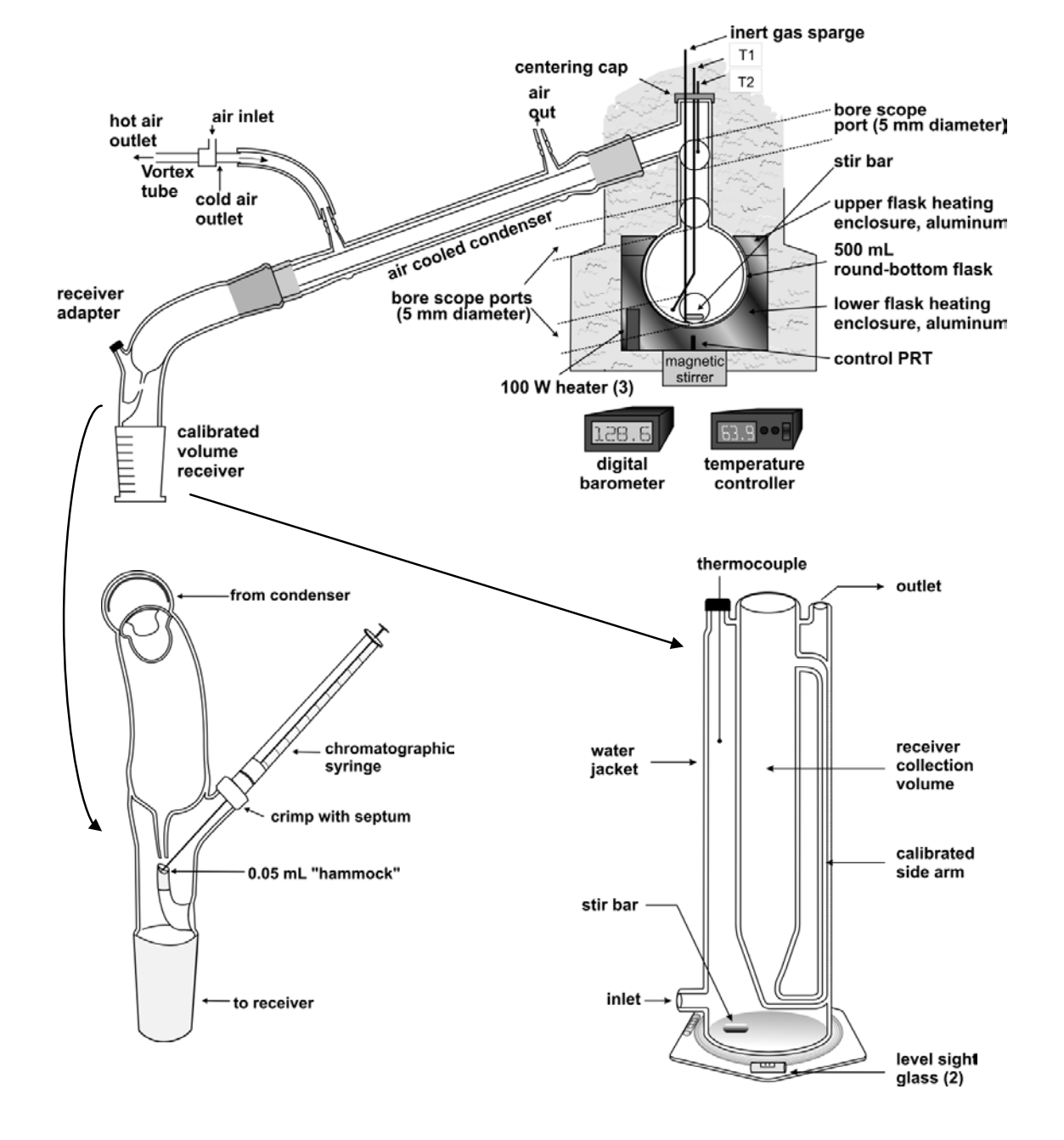
Fuel Test Methods:

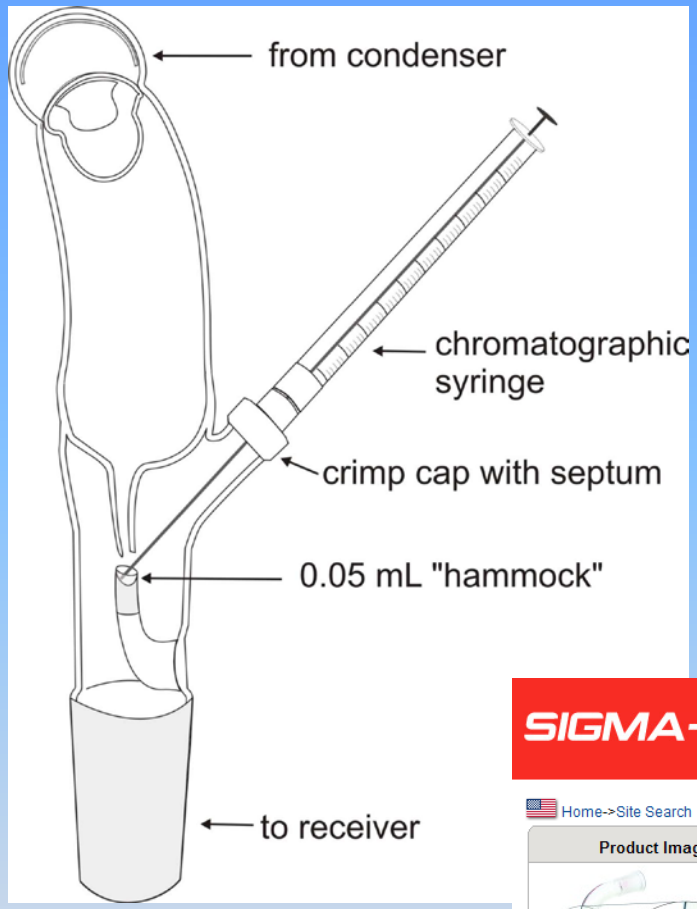
- Volatility
- Vapor Pressure
- Cetane index
- Antiknock index
- Gravity
- Acidity
- Color
- etc., etc….

At the top of the list for good reasons!

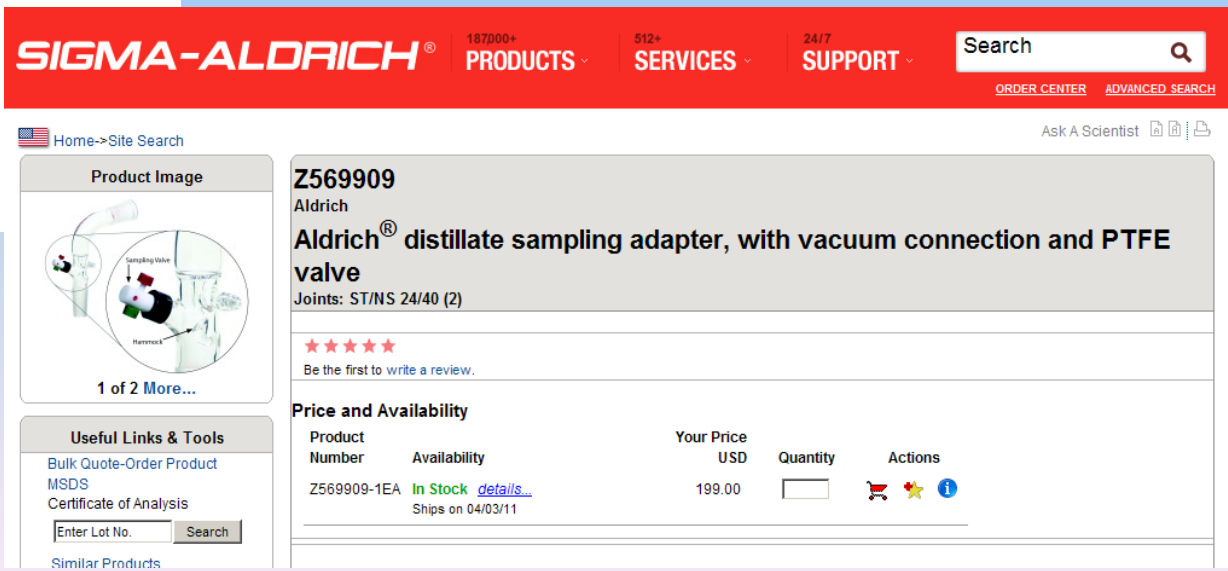
ADC Apparatus,

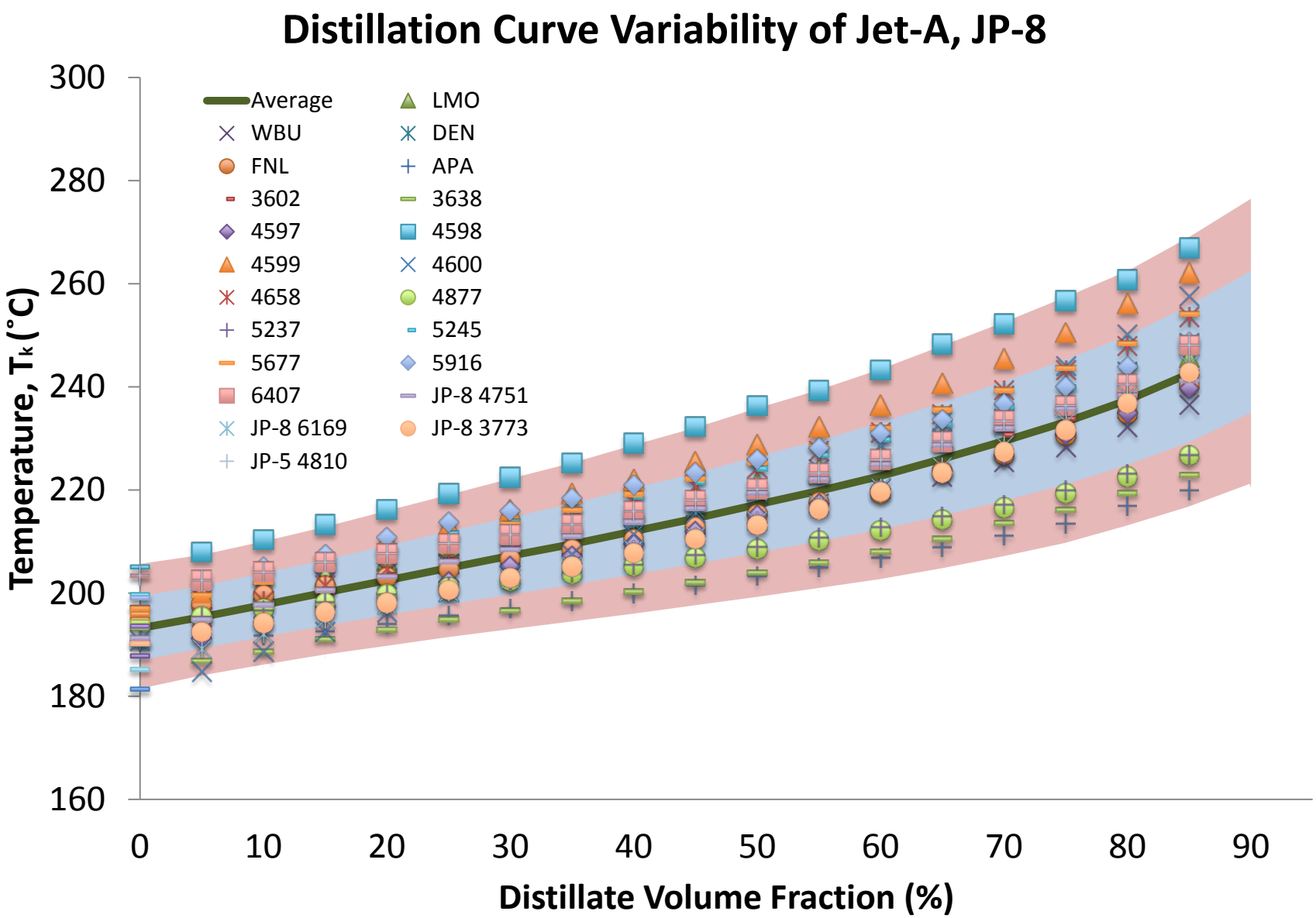
plus, what ever analytical instrument we can apply to a given problem.



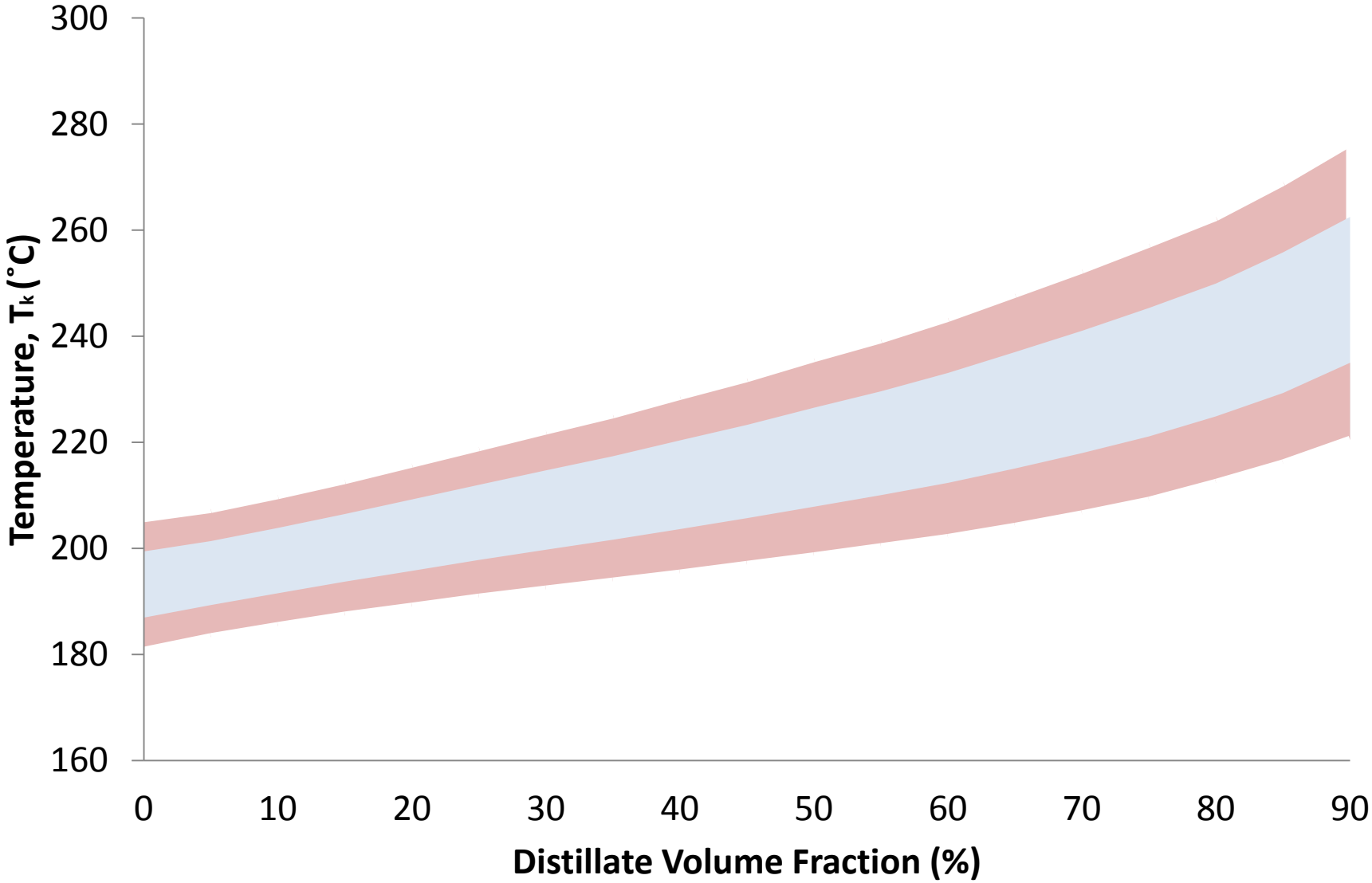


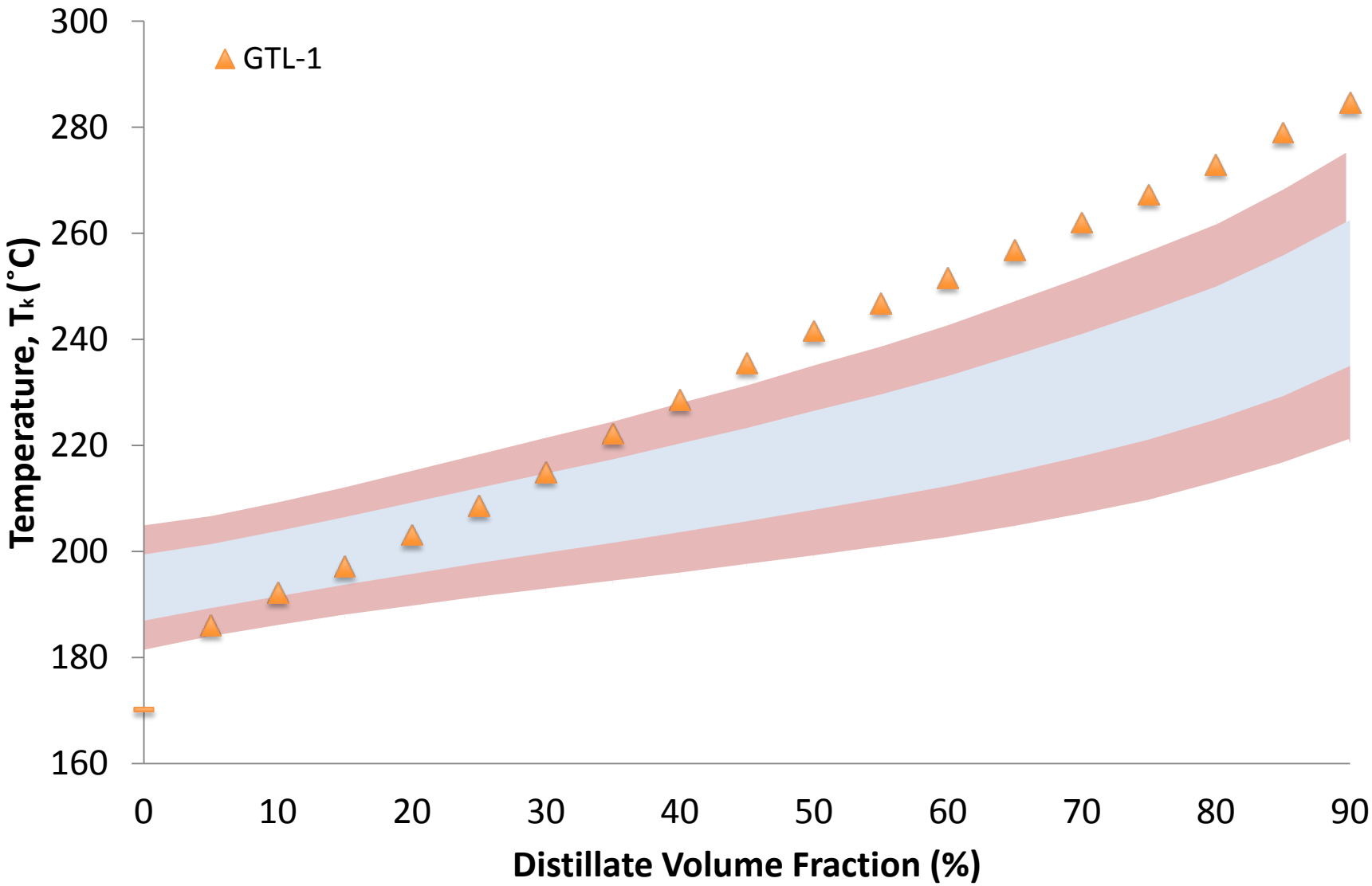
The new sampling adapter has been adopted as a product by **Sigma-Aldrich**, and is in the catalog.

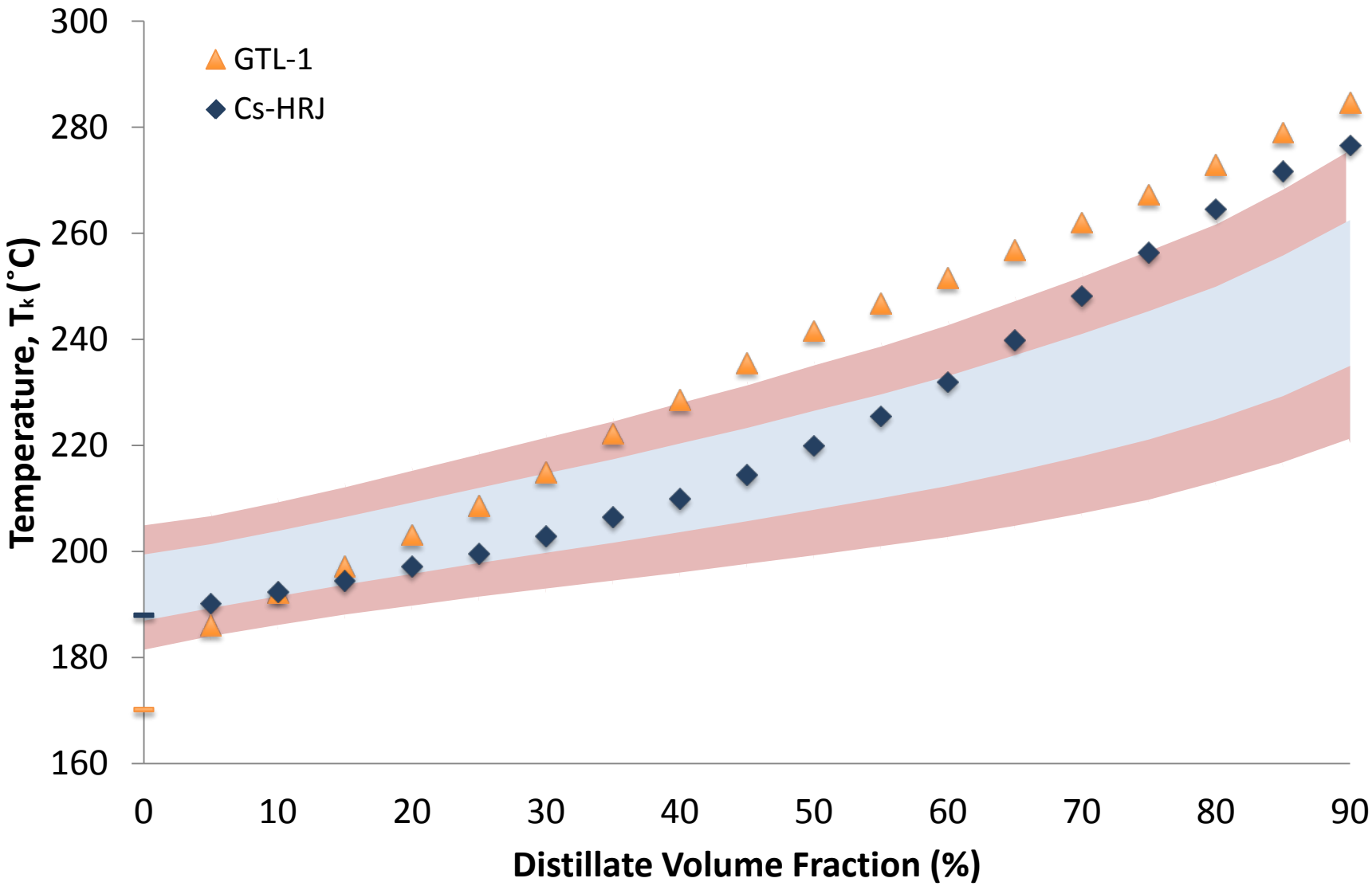


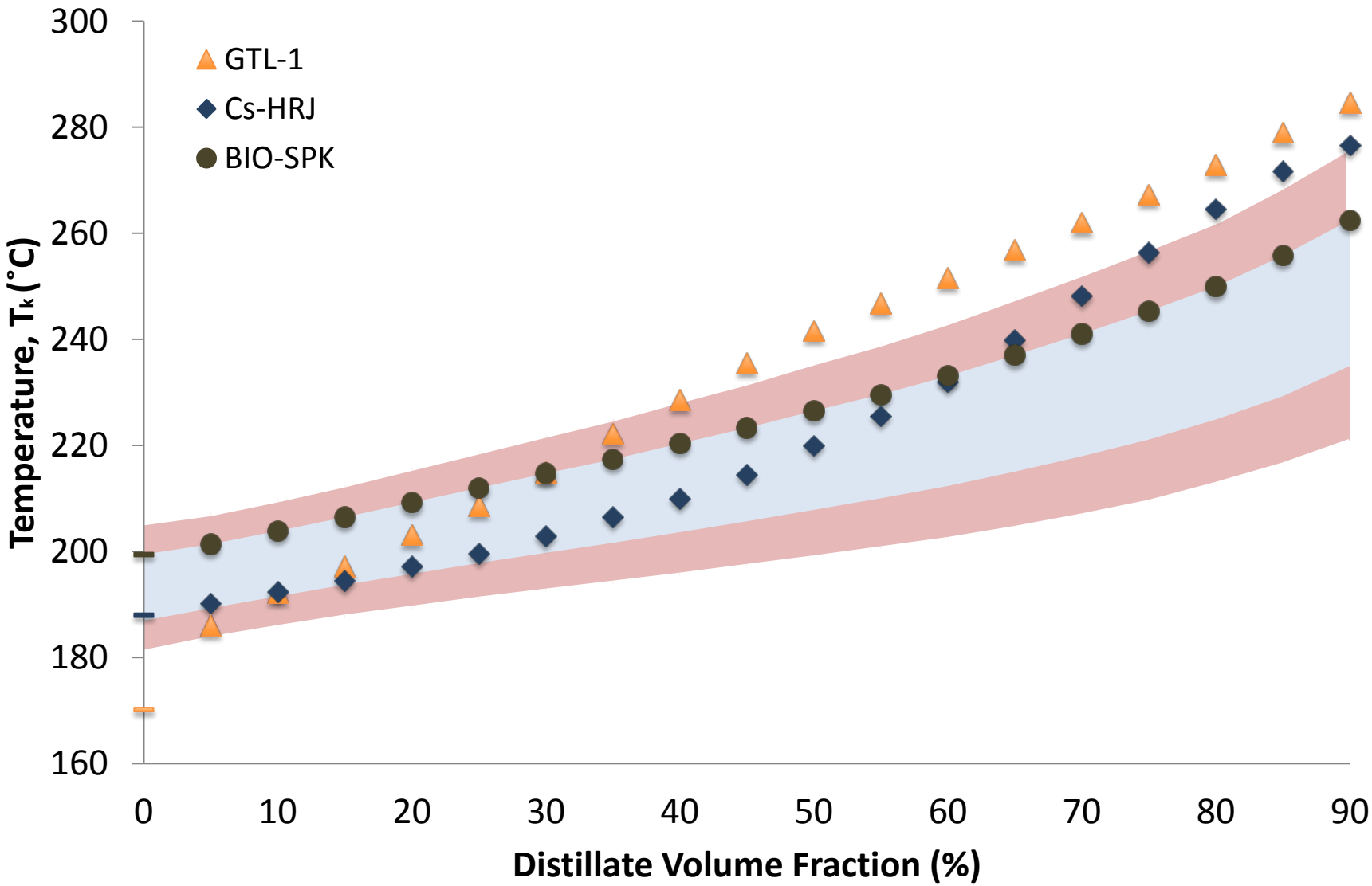


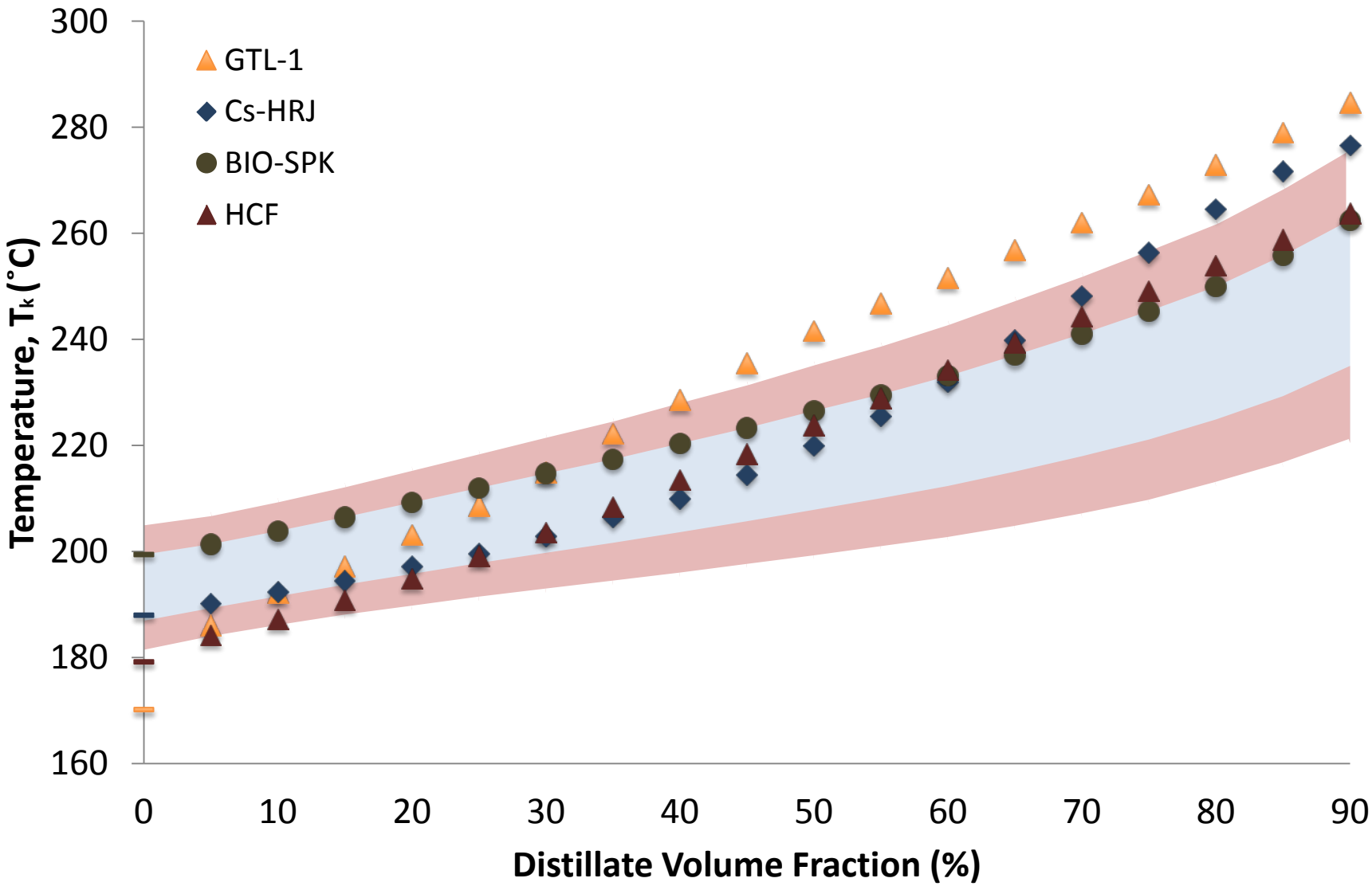
Burger, J. L., **Bruno, T.J.,** Application of the advanced distillation curve method to the variability of jet fuels, *Energy & Fuels*, 26, 3661 – 3671, 2012.

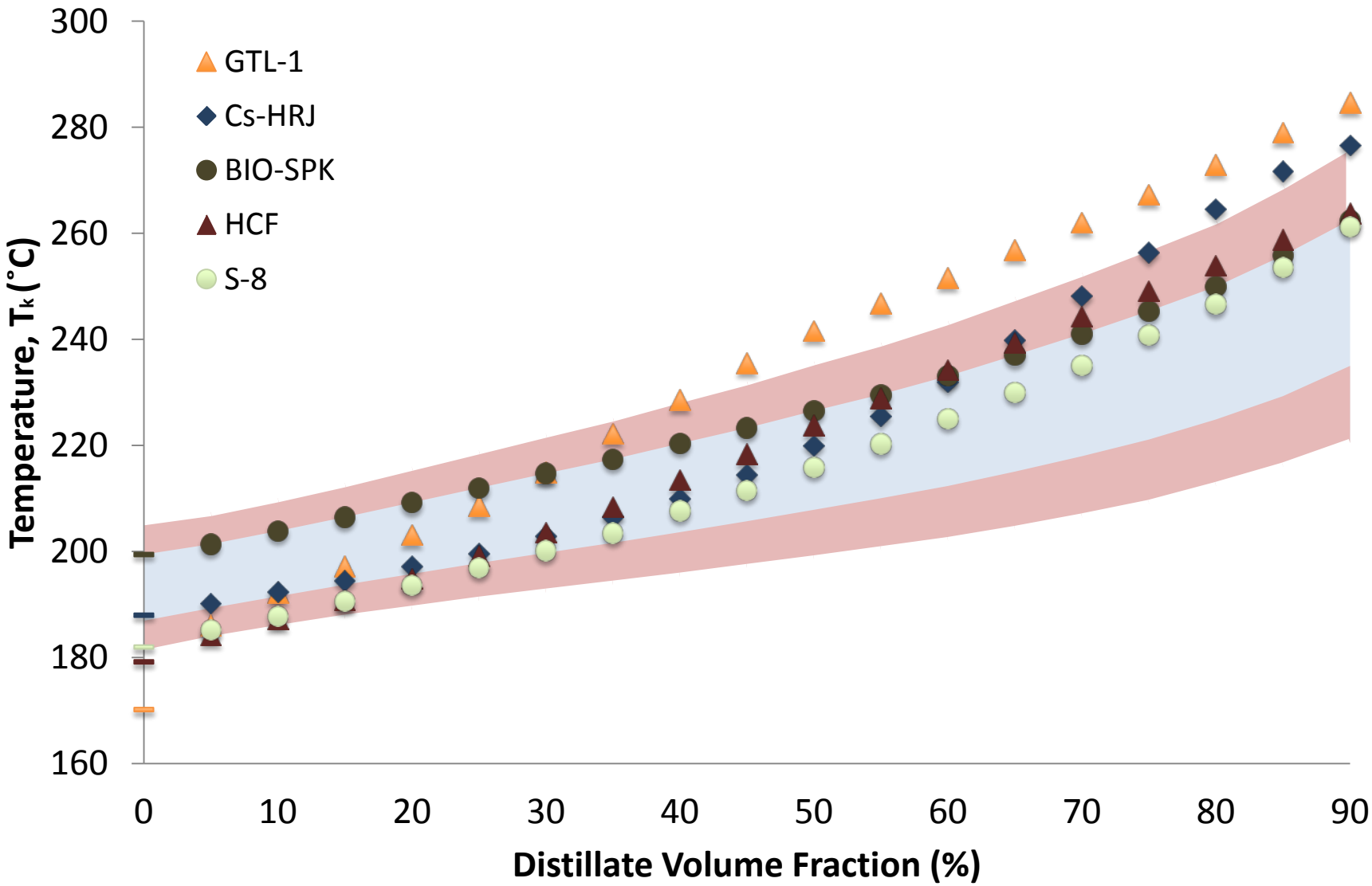

300
280
260
240
220
200
180
160
Temperature, Tk (˚C)
0
10
20
30
40
50
60
70
80
90
Distillate Volume Fraction (%)

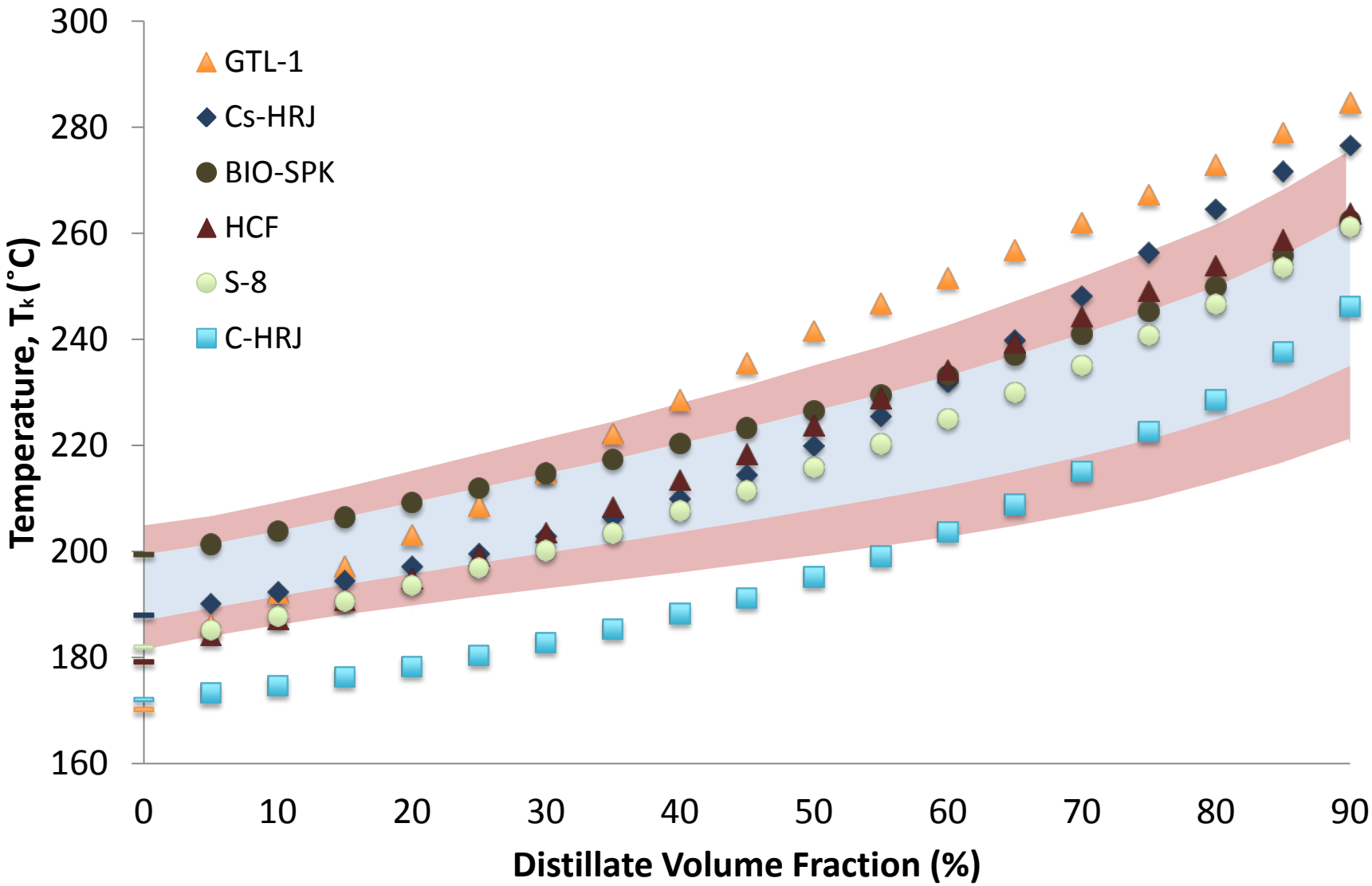

GTL-1
300
280
260
240
220
200
180
160
Temperature, Tk (°C)
0
10
20
30
40
50
60
70
80
90
Distillate Volume Fraction (%)

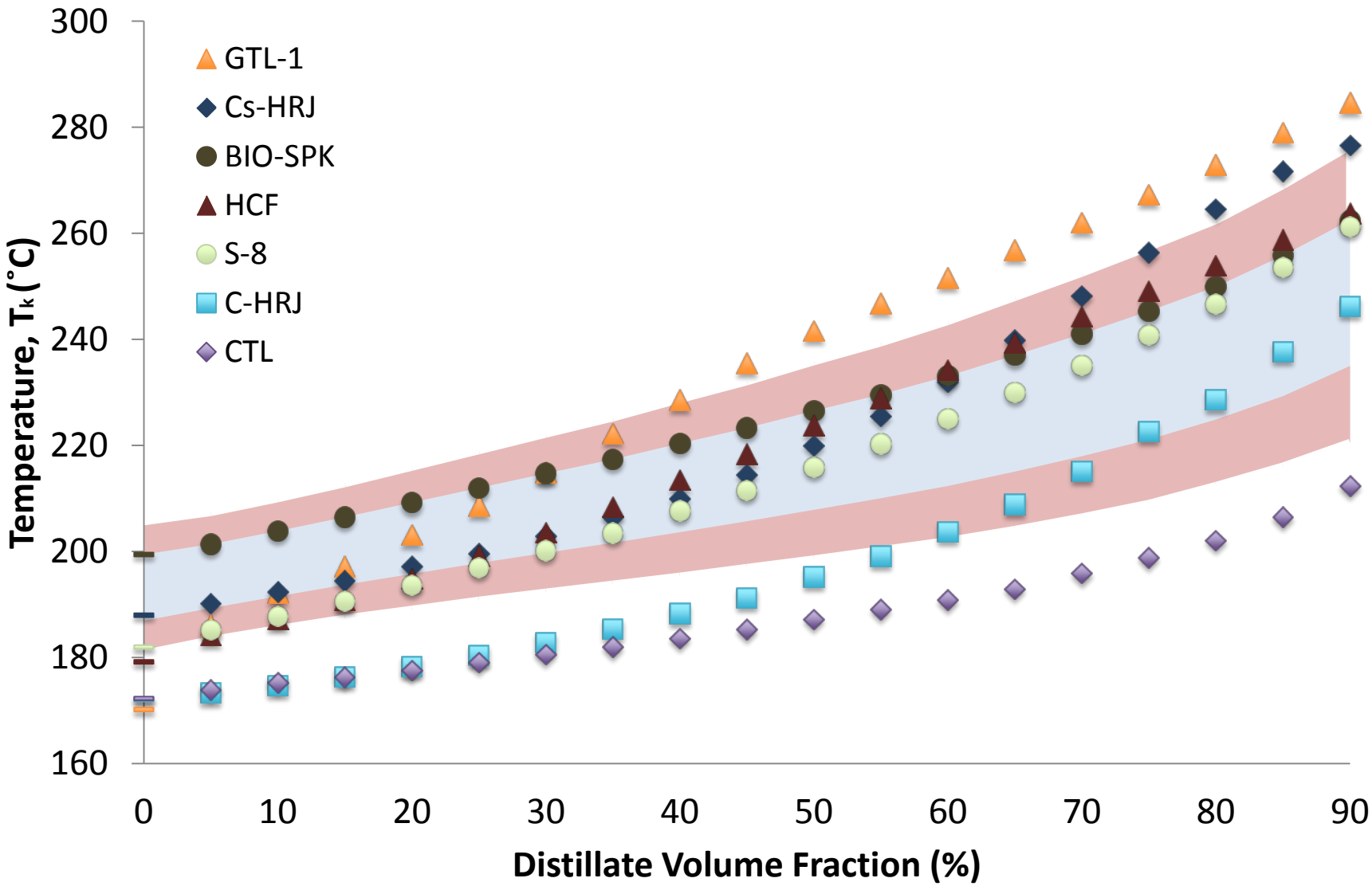

GTL-1
Cs-HRJ
Temperature, Tk (°C)
300
280
260
240
220
200
180
160
0
10
20
30
40
50
60
70
80
90
Distillate Volume Fraction (%)

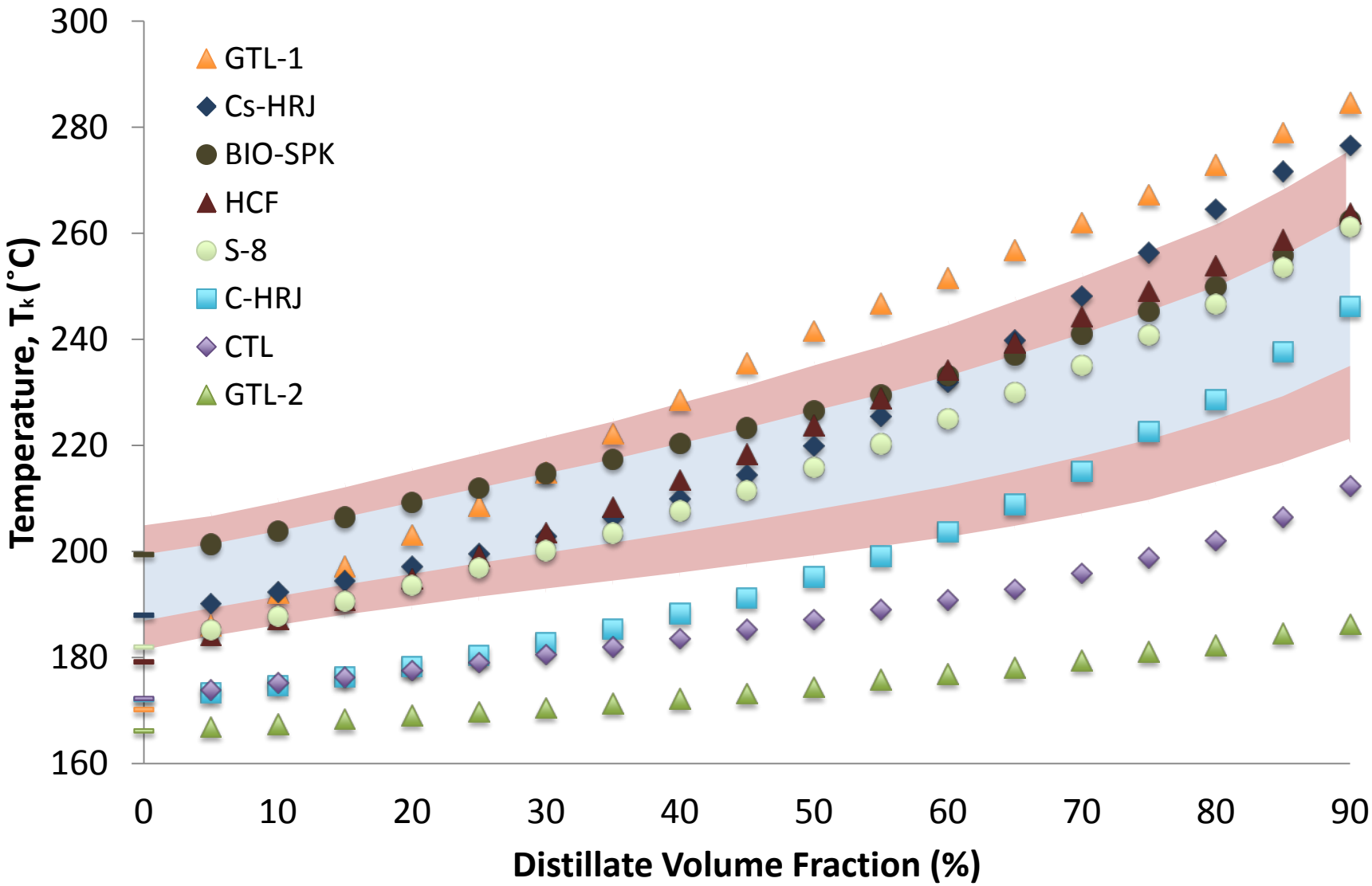

GTL-1
Cs-HRJ
BIO-SPK
Temperature, Tk (°C)
300
280
260
240
220
200
180
160
0
10
20
30
40
50
60
70
80
90
Distillate Volume Fraction (%)

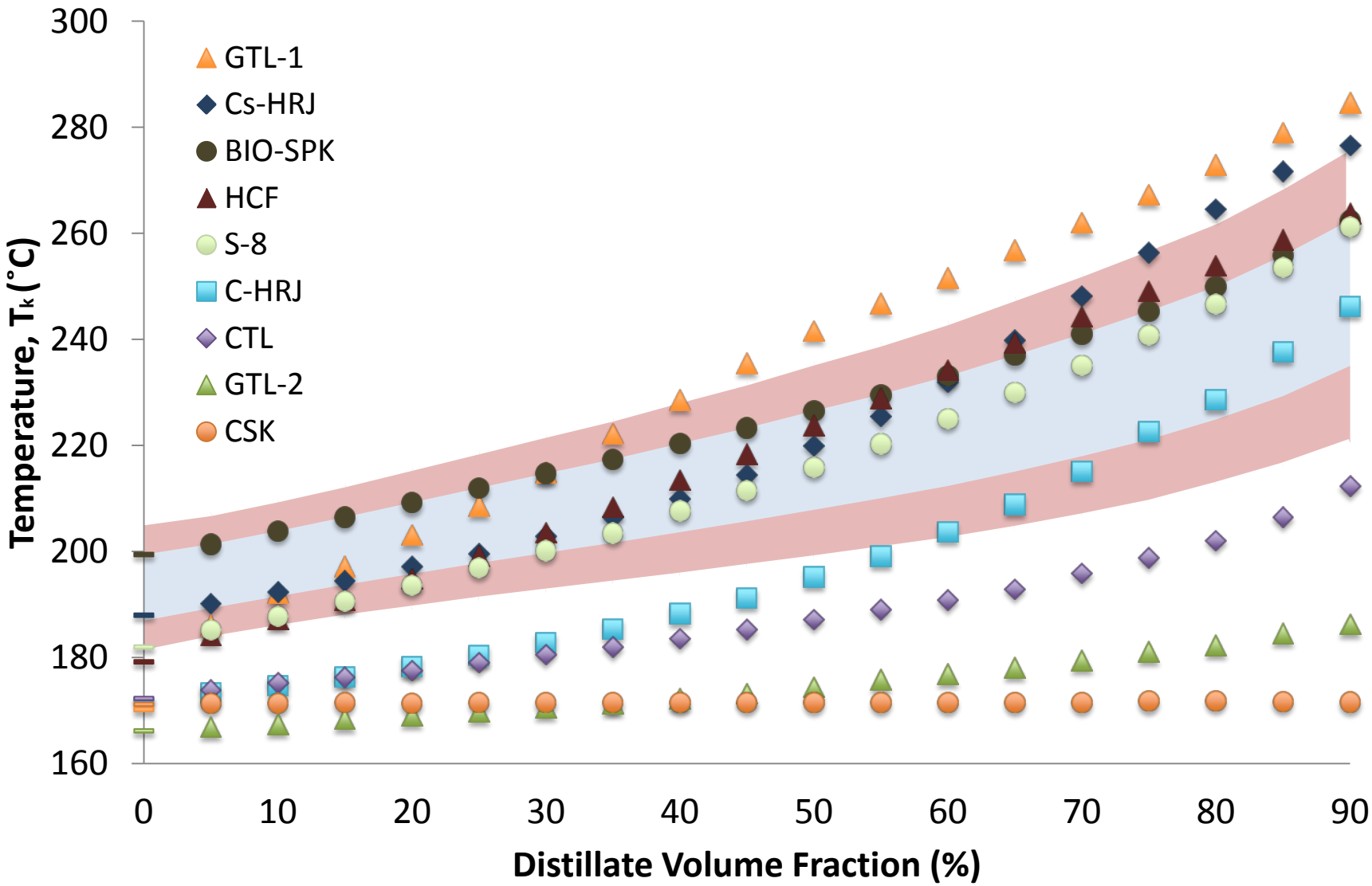

GTL-1
Cs-HRJ
BIO-SPK
HCF
Temperature, Tk (°C)
300
280
260
240
220
200
180
160
0
10
20
30
40
50
60
70
80
90
Distillate Volume Fraction (%)


GTL-1
Cs-HRJ
BIO-SPK
HCF
S-8
Temperature, Tk (°C)
300
280
260
240
220
200
180
160
0
10
20
30
40
50
60
70
80
90
Distillate Volume Fraction (%)

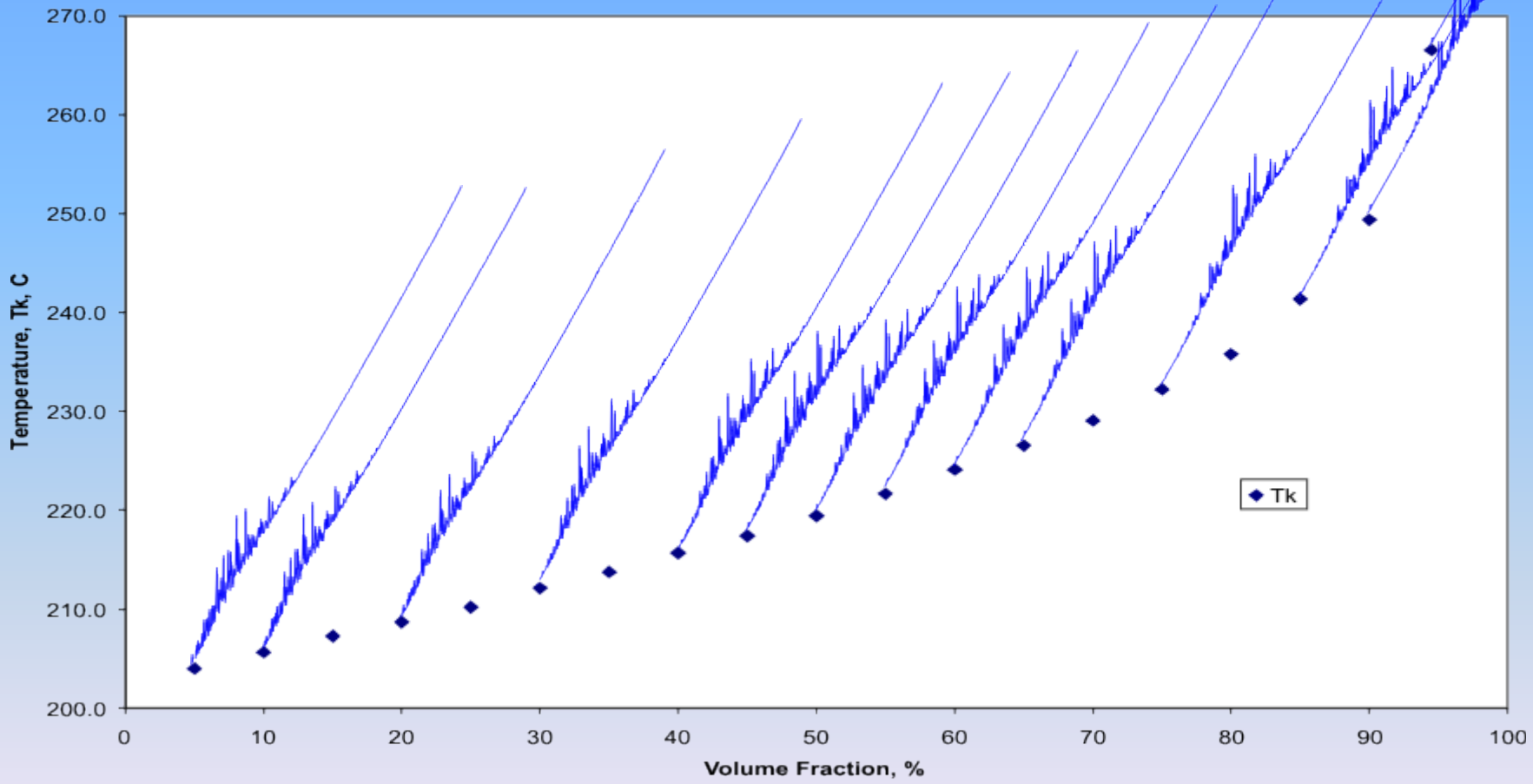

GTL-1
Cs-HRJ
BIO-SPK
HCF
S-8
C-HRJ
Temperature, Tk (°C)
300
280
260
240
220
200
180
160
0
10
20
30
40
50
60
70
80
90
Distillate Volume Fraction (%)


GTL-1
Cs-HRJ
BIO-SPK
HCF
S-8
C-HRJ
CTL
Temperature, Tk (°C)
300
280
260
240
220
200
180
160
0
10
20
30
40
50
60
70
80
90
Distillate Volume Fraction (%)


GTL-1
Cs-HRJ
BIO-SPK
HCF
S-8
C-HRJ
CTL
GTL-2
Temperature, Tk (°C)
300
280
260
240
220
200
180
160
0
10
20
30
40
50
60
70
80
90
Distillate Volume Fraction (%)


GTL-1
Cs-HRJ
BIO-SPK
HCF
S-8
C-HRJ
CTL
GTL-2
CSK
Temperature, Tk (°C)
300
280
260
240
220
200
180
160
0
10
20
30
40
50
60
70
80
90
Distillate Volume Fraction (%)

ADC of a Typical Kerosene



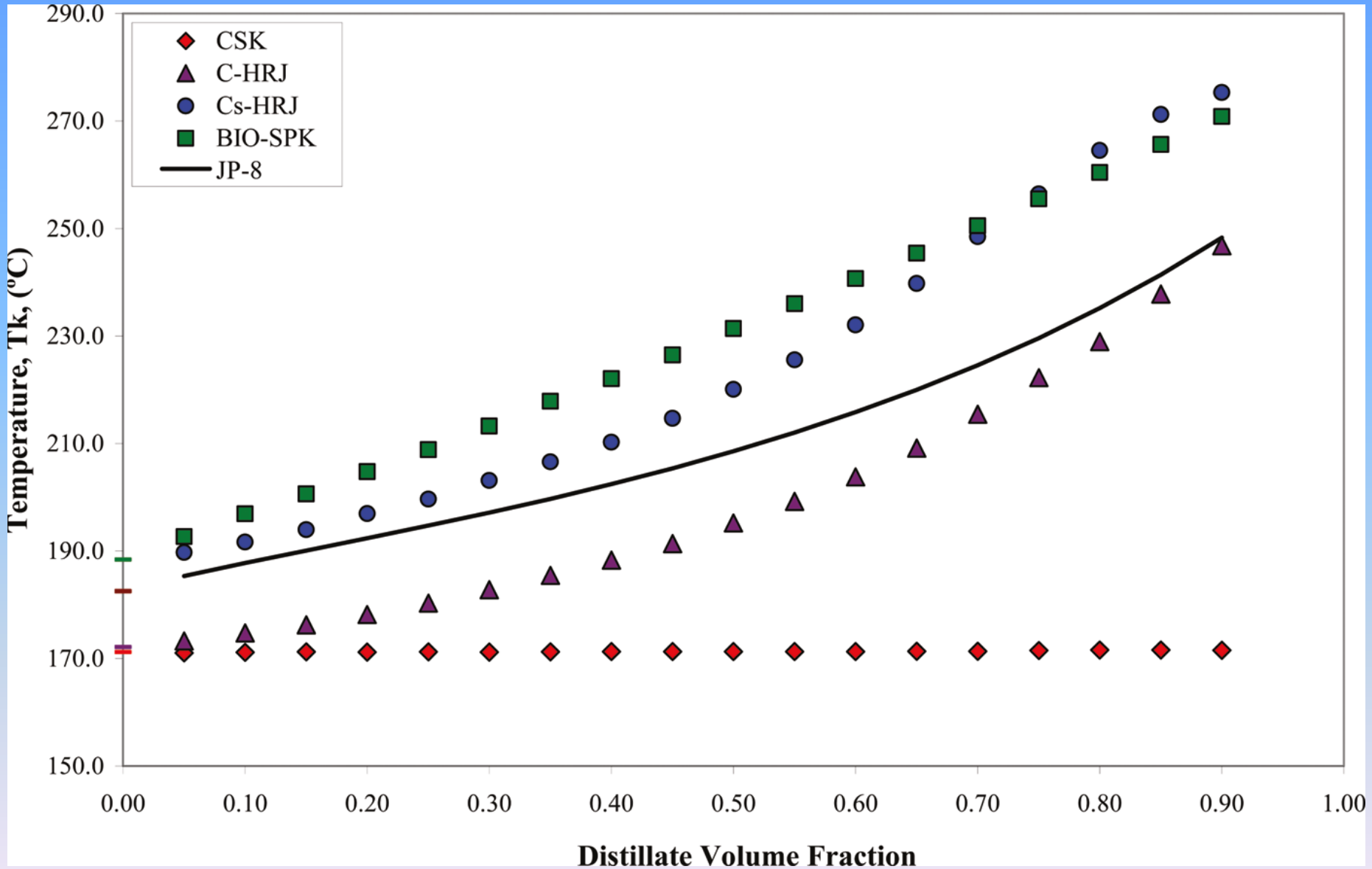
This opens the door to add <u>thermochemistry:</u>

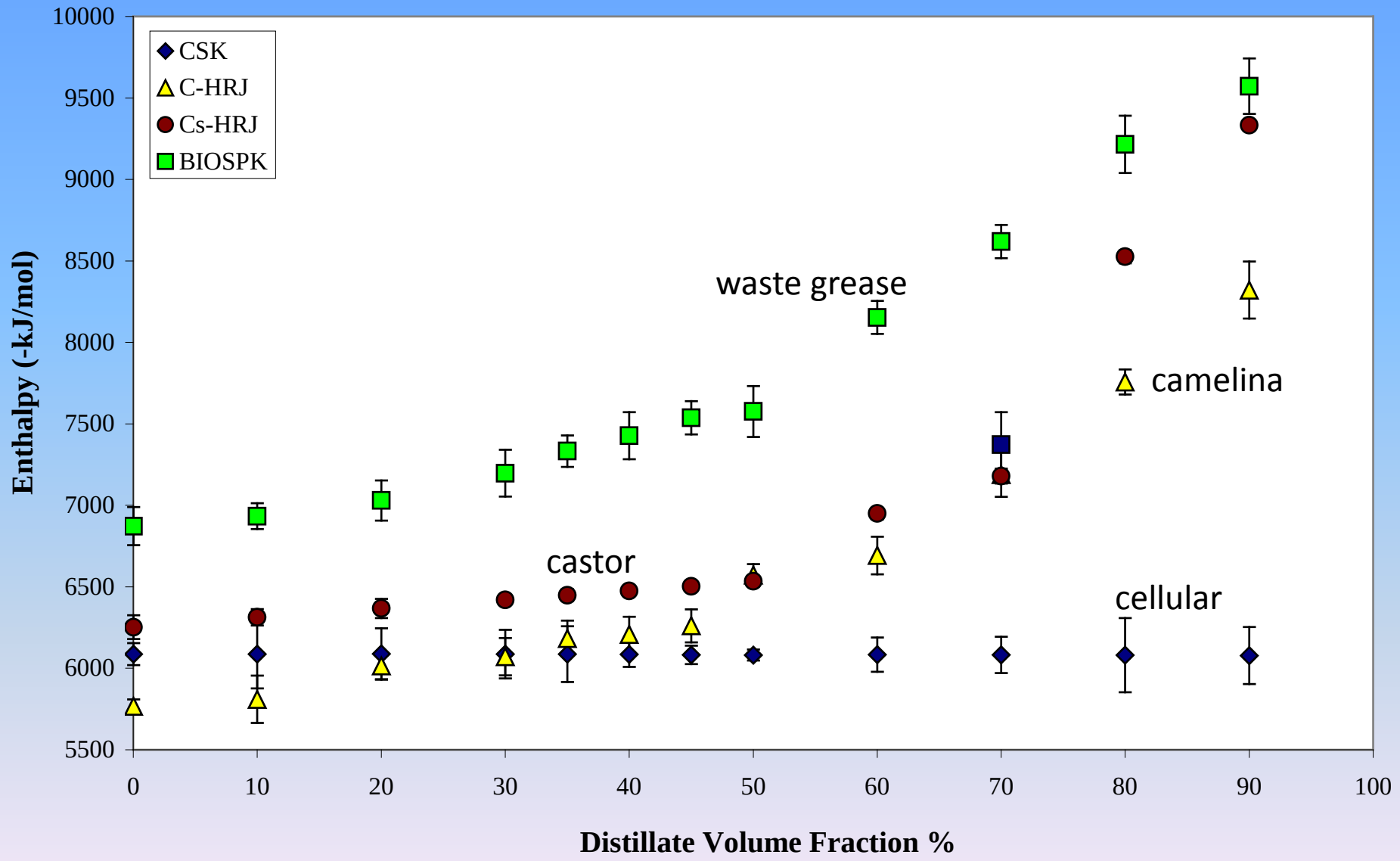
- Since we have the composition of each fraction, estimate mole fractions of each component.

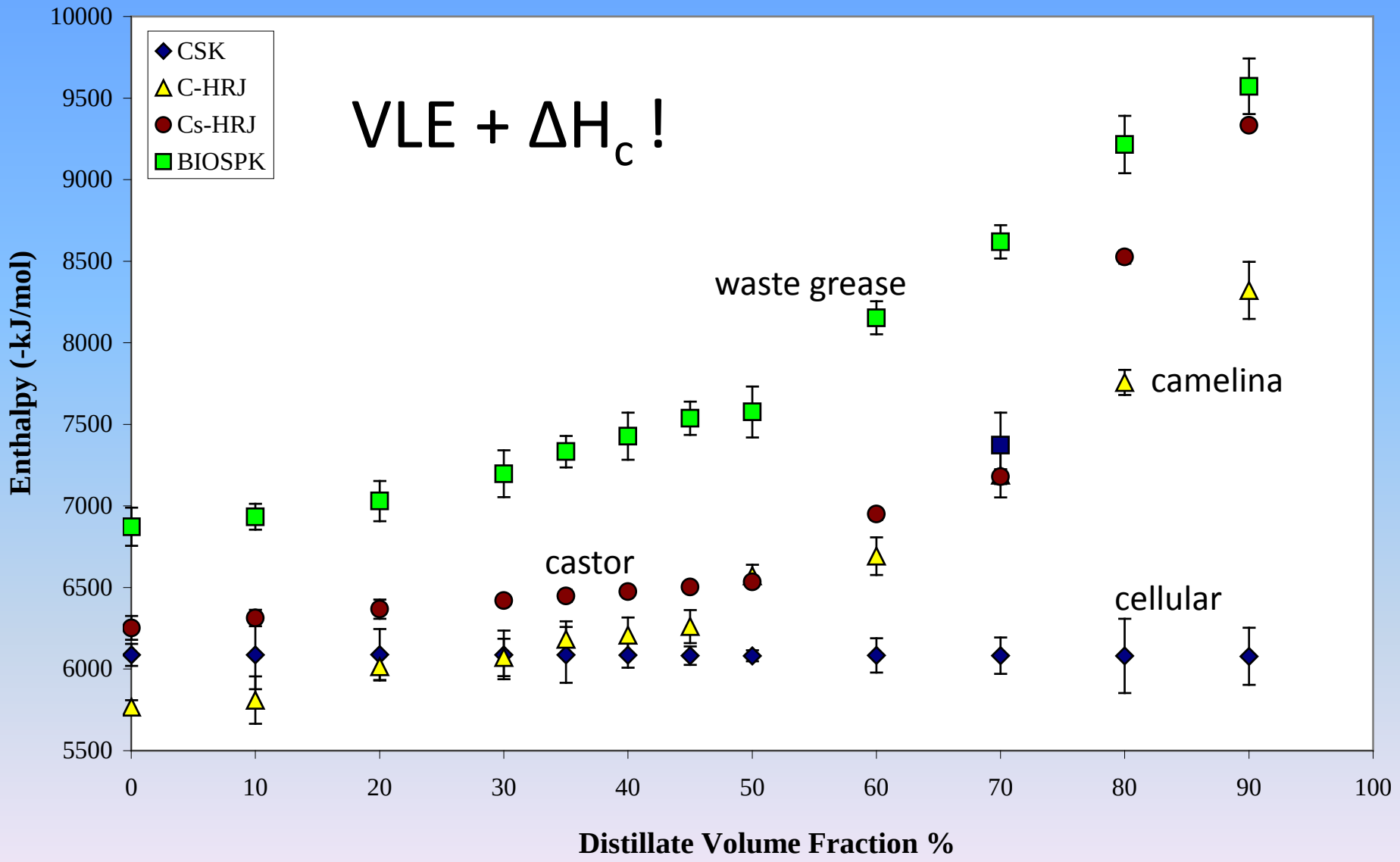
- Calculate the fractional ΔH_{com} for each:

$$-\Delta H_c = \sum x_i(-\Delta H_i)$$

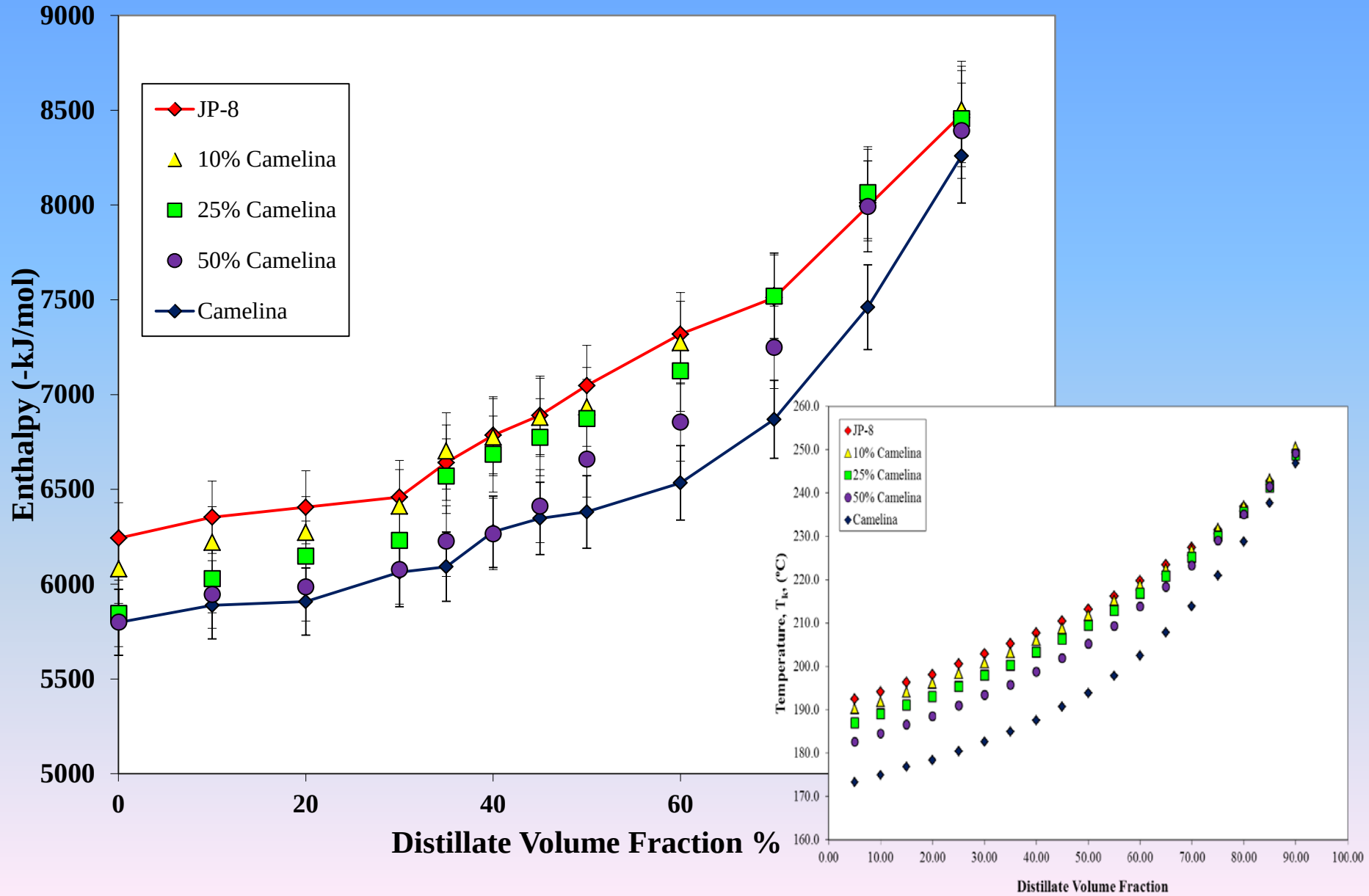
- Calculate the ΔH_c for the fraction


CSK
C-HRJ
Cs-HRJ
BIO-SPK
JP-8
290.0
270.0
250.0
230.0
210.0
190.0
170.0
150.0
Temperature, Tk, (°C)
0.00
0.10
0.20
0.30
0.40
0.50
0.60
0.70
0.80
0.90
1.00
Distillate Volume Fraction


CSK
C-HRJ
Cs-HRJ
BIOSPK
waste grease
camelina
castor
cellular
Enthalpy (-kJ/mol)
Distillate Volume Fraction %
10000
9500
9000
8500
8000
7500
7000
6500
6000
5500
0
10
20
30
40
50
60
70
80
90
100


VLE + ΔHc !
CSK
C-HRJ
Cs-HRJ
BIOSPK
waste grease
camelina
castor
cellular
Enthalpy (-kJ/mol)
Distillate Volume Fraction %
10000
9500
9000
8500
8000
7500
7000
6500
6000
5500
0
10
20
30
40
50
60
70
80
90
100

JP-8 + Camelina:



Helmholtz Equation of State

- Formulated in terms of $a(T, \rho)$ instead of $p(T, \rho)$

$$a(\rho,T) = a^0(\rho,T) + a^r(\rho,T)$$

ideal gas contribution

residual contribution

- All single phase properties can be calculated as derivatives of the Helmholtz energy

$$p = \rho^2 \left(\frac{\partial a}{\partial \rho} \right)_T$$

Old Man Helmholtz

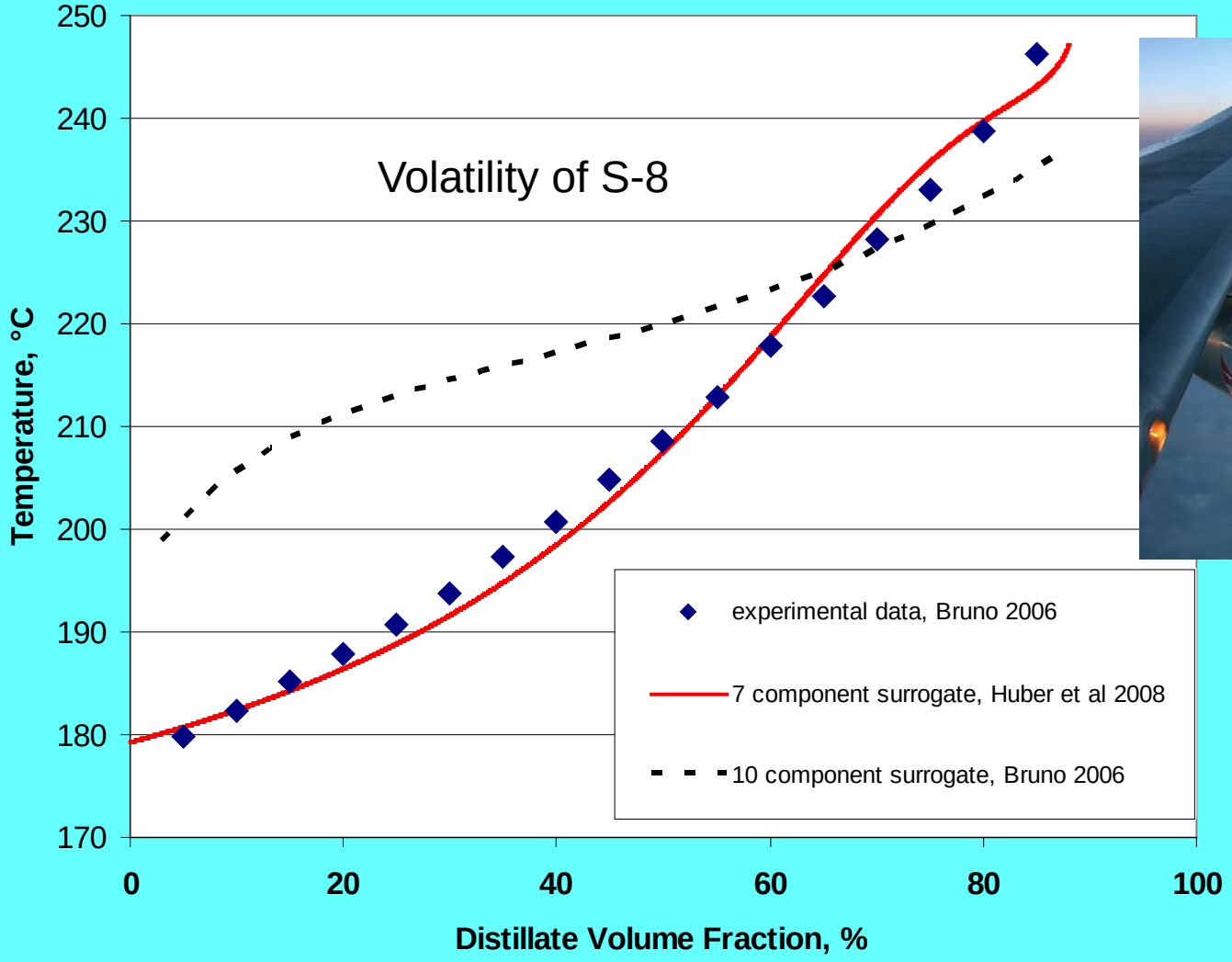
- Typical form of residual contribution

$$\alpha^r(\delta,\tau) = \frac{a^r}{RT} = \sum N_k \delta^{d_k} \tau^{t_k} + \sum N_k \delta^{d_k} \tau^{t_k} e^{-\delta^{l_k}}$$

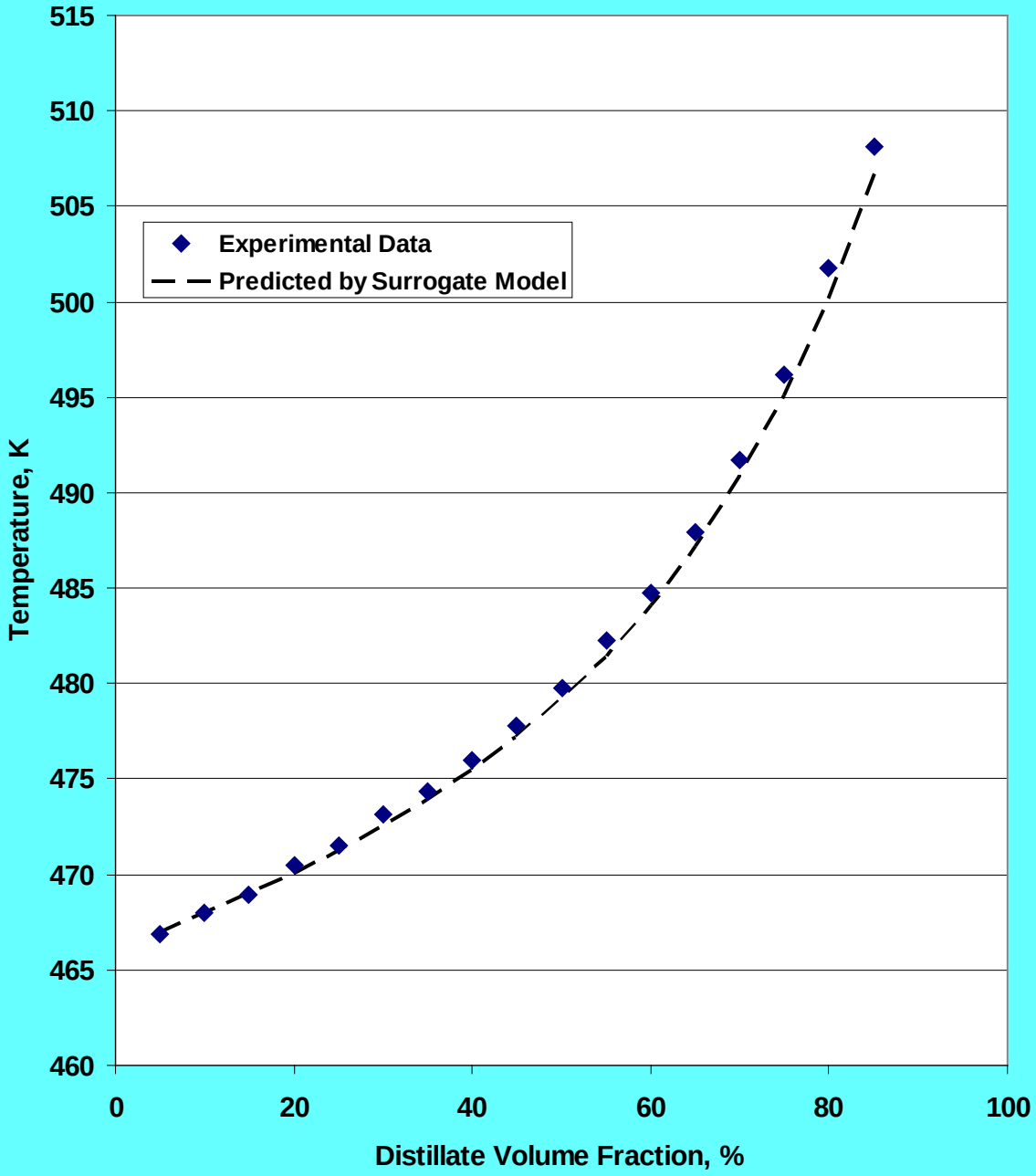
summations typically have 4-20 terms

$$\delta = \frac{\rho}{\rho_c} \qquad \tau = \frac{T_c}{T}$$

So, what if I ignore the volatility (i.e., the distillation curve)?



Approved for public release; distribution unlimited.



And predictively, for JP-900

Approved for public release; distribution unlimited.

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

- [x] Temperature
- [x] Pressure
- [x] Density
- [ ] Volume
- [ ] Int. Energy
- [x] Enthalpy
- [x] 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

Select Units

Dimension	Units
Temperature	K
Pressure	MPa
Volume	dm³
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

Documentation

- Bruno, T.J., Improvements in the measurement of distillation curves. 1. a composition explicit approach, Ind. Eng. Chem. Res., 45, 4371-4380, 2006. (4th most cited paper in Ind. Eng. Chem. Res, for 2006)
- Bruno, T.J., Smith, B.L., Improvements in the measurement of distillation curves. 2. application to aerospace/aviation fuels RP-1 and S-8, Ind. Eng. Chem. Res., 45, 4381-4388, 2006. (5th most cited paper in Ind. Eng. Chem. Res, for 2006)
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- Ott, L. S.; Bruno, T. J. Corrosivity of fluids as a function of distillate cut: application of an advanced distillation curve method. Energy & Fuels; 21, 2778-2784, 2007.
- Smith, B.L., Bruno, T.J., Application of an advanced distillation curve measurement to mixtures of jet-A + synthetic Fischer-Tropsch S-8, J. Propulsion and Power, 24(3), 618-624, 2008.

More documentation

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- Huber, M.L.,Smith, B.L., Ott, L.S., Surrogate mixture model for the thermophysical properties of a coal derived fluid, , Energy & Fuels, 22, 3249-3257, 2008.
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- Ott, L. S.; Smith, B. L.; Bruno, T. J. Advanced distillation curve measurement of a bio-derived pig manure crude oil, including corrosivity and composition assessment. Fuel, 87, 3374-3387, 2008.
- Smith, B.L., Ott, L.S., Bruno, T.J., Composition-explicit distillation curves of diesel fuel with glycol ether oxygenates, Env. Sci. Tech., 40(20), 7682-7689, 2008..
- Ott, L.S., Smith, B.L., Bruno, T.J., Composition explicit distillation curves of mixtures of diesel fuel with biomass derived oxygenates, Energy & Fuels, 22, 2518-2526, 2008.
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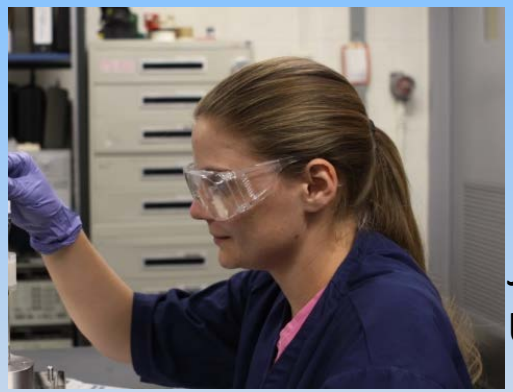

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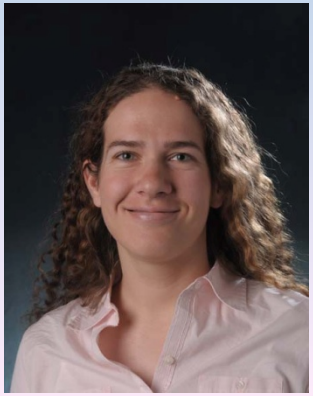

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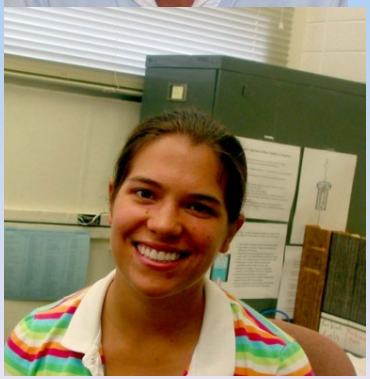

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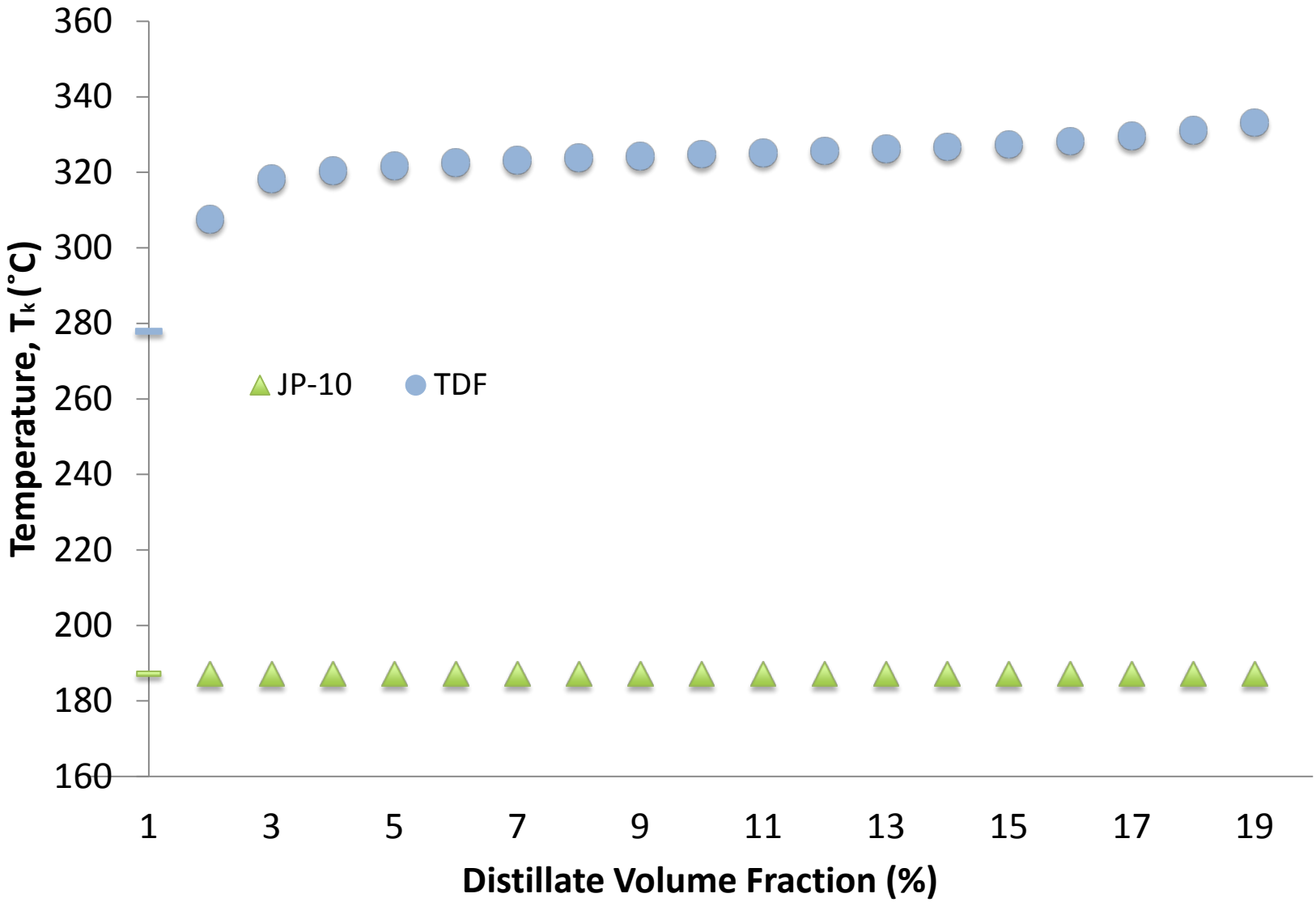

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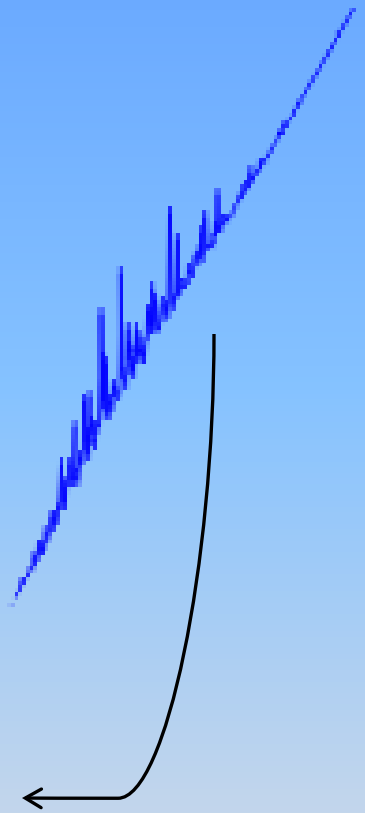
Compound Name	Enthalpy of Combustion, -ΔH, kJ/mol	% Molar Composition	Fractional Enthalpy of Combustion, kJ/mol
n-decane	6294.2	6.02	379.0
2,3,6-trimethyloctane	6940.4	1.59	110.4
(4-methylpentyl) cyclohexane	7376.5	1.34	99.1
5-methyldecane	6952.7	1.43	99.5
x-methyldecane	6952.7	2.74	190.2
2-methyldecane	6952.7	2.20	152.8
x-methyldecane	6952.7	2.69	187.0
1-methyl-4-(1-methylethyl)benzene	5549.8	1.43	79.5
n-undecane	6903.6	15.77	1089.0
5-methyl undecane	7567.8	1.82	137.7
t-butyl benzene	5557.1	1.53	85.2
3,7-dimethyl decane	5549.8	1.40	78.0
1-methyl-2-(1-methylethyl)benzene	5554.8	4.50	249.9
n-dodecane	7513.7	18.18	1366.0
2,6-dimethyl undecane	8182.9	3.79	310.3
4-methyldodecane	8182.9	1.38	113.2
2-methyldodecane	8182.9	2.45	200.7



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