Thermophysical Properties DIVISION

Towards Consensus Standards for Reference Data for Biofuels

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International Conference on Biofuels Standards

Standards and Measurement Needs for New Transportation Fuels

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Themes of Discussion

- Who needs property data? Why?
- Historical parallels
- What's being done? Future Plans

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Stakeholders in Properties Issues

Properties for Production, Distribution, and End Use

- **Design/Optimization involving processing, refining, distilling**
- **Innovative design of equipment (e.g. engines, including operating parameters)**
- **Blending Optimization**
- **Policymakers (measures of sustainability)**
- **Legal Metrology**
- **Operations involving processing, refining, distilling**

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Conclusions of Workshop (2008)

"…better knowledge of fuel properties would lead to better designs and shorter development times of everything from production facilities to emissions control systems."

urface

Importance of Properties (Uncertainties)

Plant Operations
Some rough rules of thumb. For a $1M operation:

- 1% uncertainty in density costs $10k
- 1 % uncertainty in phase boundary costs $100k
- 1 % uncertainty in viscosity costs $1k

Source: K.R. Cox, Fluid Phase Equil. 1993
A.H. Larsen, Fluid Phase Equil. 1986

Custody Transfer--gas pipeline system

Vendor 1: sells at p1, T1, {x1}
Vendor 2: sells at p2, T2, {x2}

Buyer purchases resultant mixture at p3, T3, {x3}

Auditor discovers $1M per day discrepancy in transaction.

Lessons Learned from Replacement of the CFC Refrigerants

CFCs phased out by regulation (Montreal Protocol—1987)

Established industries/infrastructures challenged

Potential alternatives proposed/discussed

Problems with direct drop-in replacements
(e.g., R11 replaced by R123 in chillers—15 % efficiency penalty)

Properties studied, consensus data achieved (IEA Working Group), designs reviewed, innovation/optimization succeeded

Result:

For R123 - 20 % improvement in energy efficiency.

For U.S. refrigeration industry (R134a) - 60 % improvement in efficiency and large operating cost savings.
(About $50B/yr or 10 EJ per year for all vapor compression equipment in US)

Historical Antecedent: Petrofuels

Petroleum property data efforts: circa 1916 (NBS, Bearce & Peffer)

Coordination of data needs: 1942, API Project 44

Data inadequacies noted 1972, new API data effort

Petroleum measurement tables: 1980

International consensus: ASTM D 1250; API 2540, IP 200 (ADJD 1250CD)
(Adjunct to D1250-04 Temperature and Pressure Volume Correction Factors for Generalized Crude Oils, Refined Products, and Lubricating Oils)

Refinery data needs: 1980's, 1990's

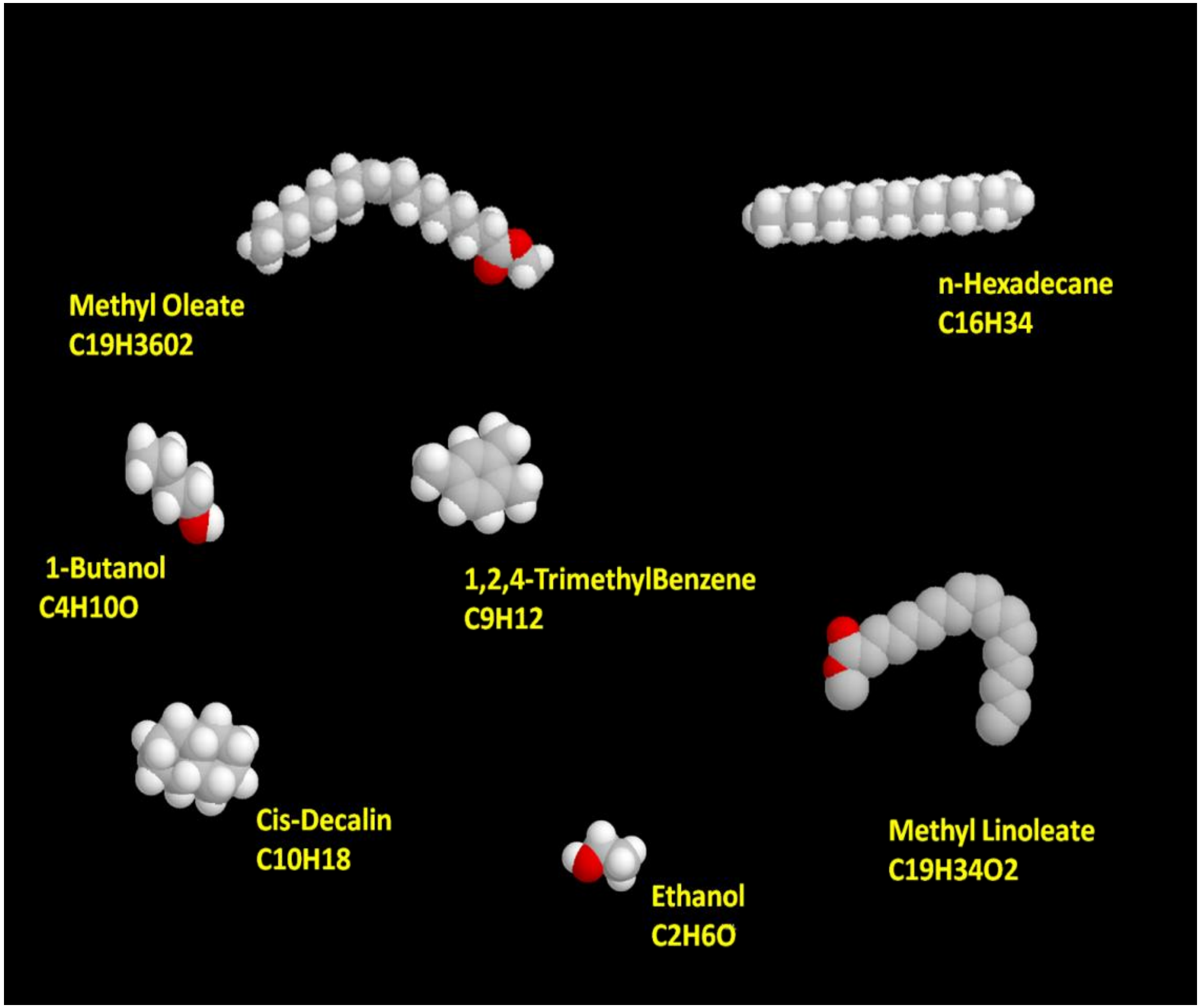
Petrofuel & petrochemical plants: designed & operated under plant simulation software—based on one century of thermophysical properties data.

Biofuels: So What's Different?

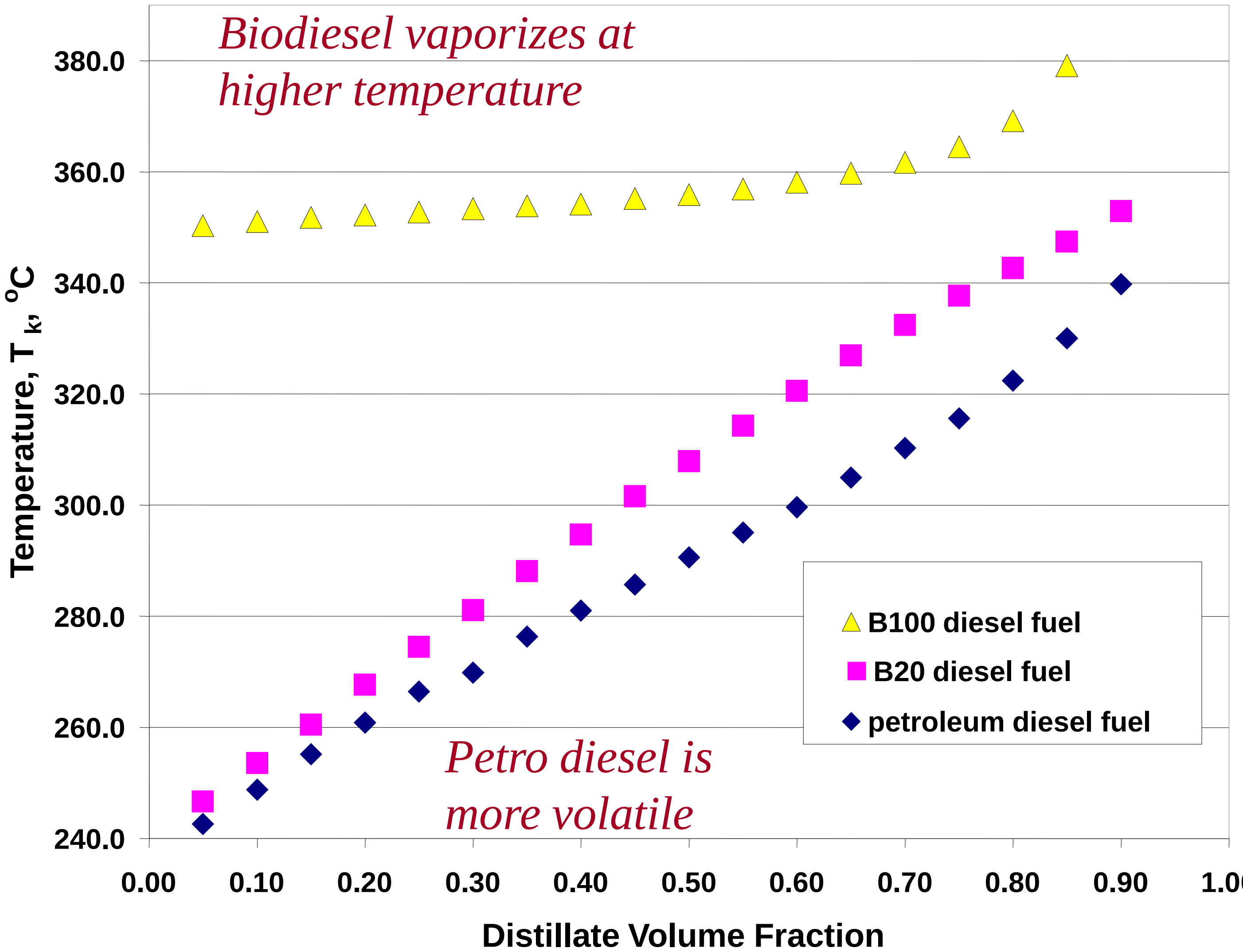
These have different molecules, with differing polarity, reactivity, oxygen content, associative and hydroscopic "parameters," … .

What we're told:

- Old "rules of thumb" do not apply
- Data situation is not adequate
- Models are inconsistent

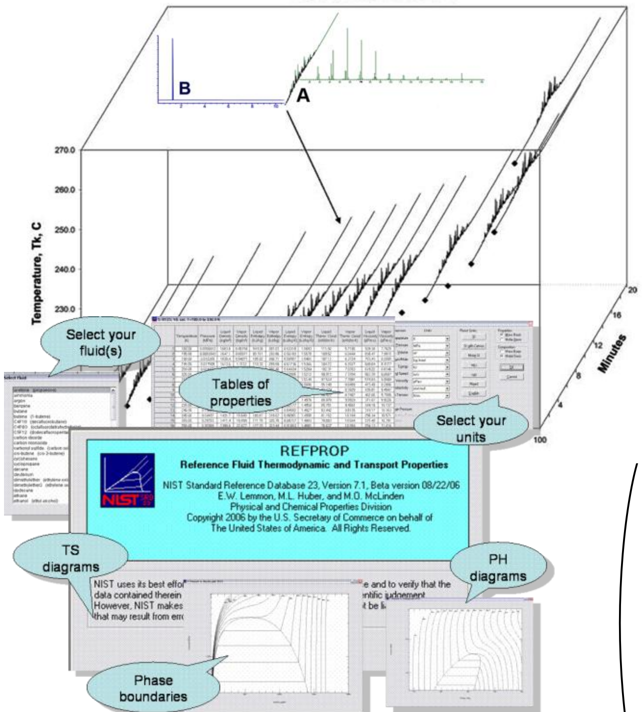


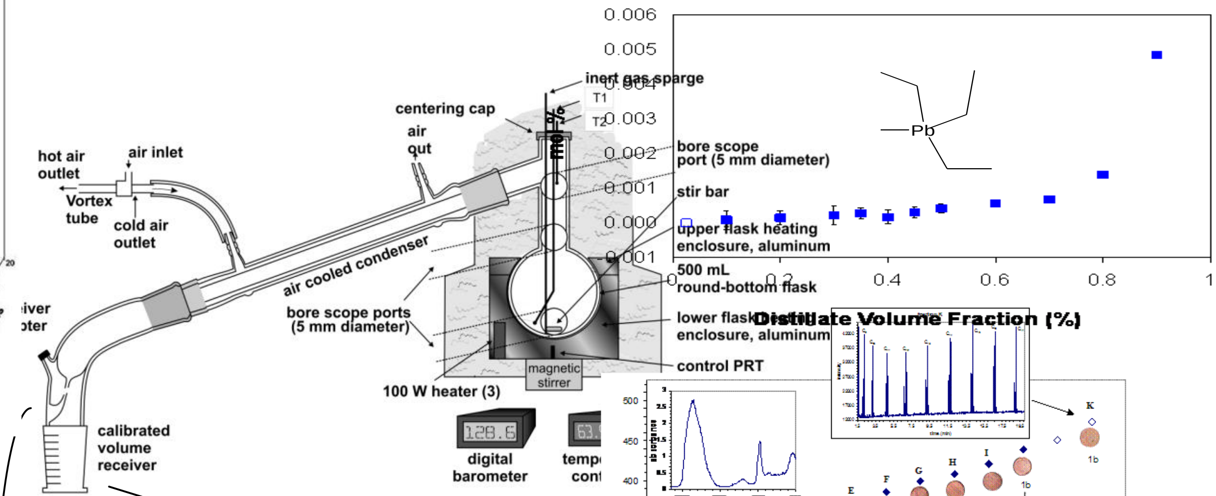
Distillation Curves

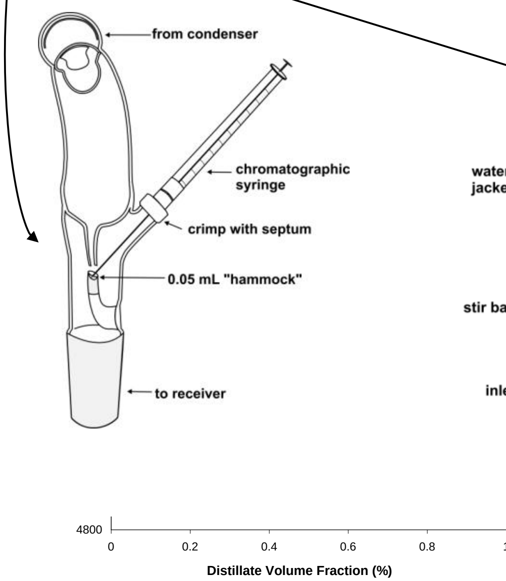


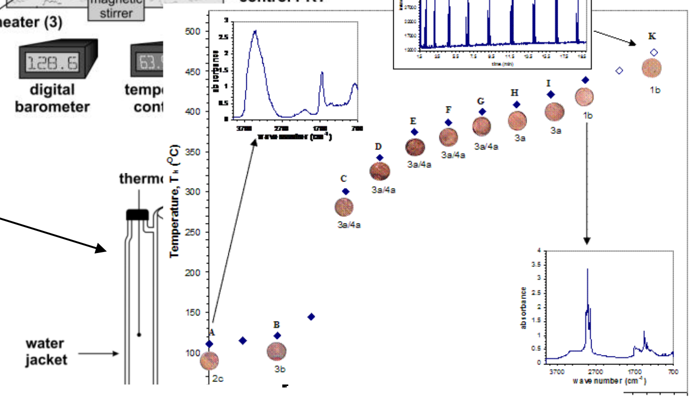
Advanced Distillation Curve

Analytical Protocol for Complex Fluids



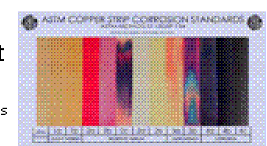


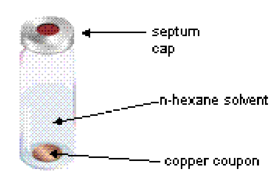


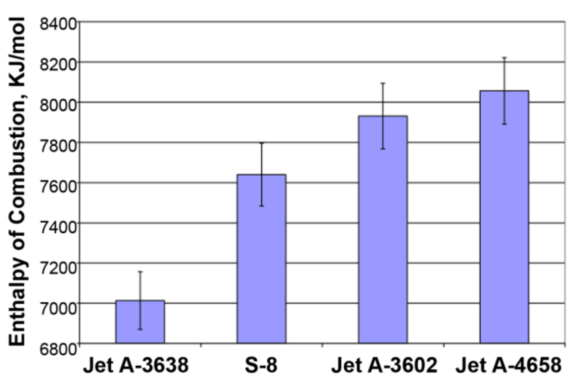


Apply the Copper Strip Corrosion Test

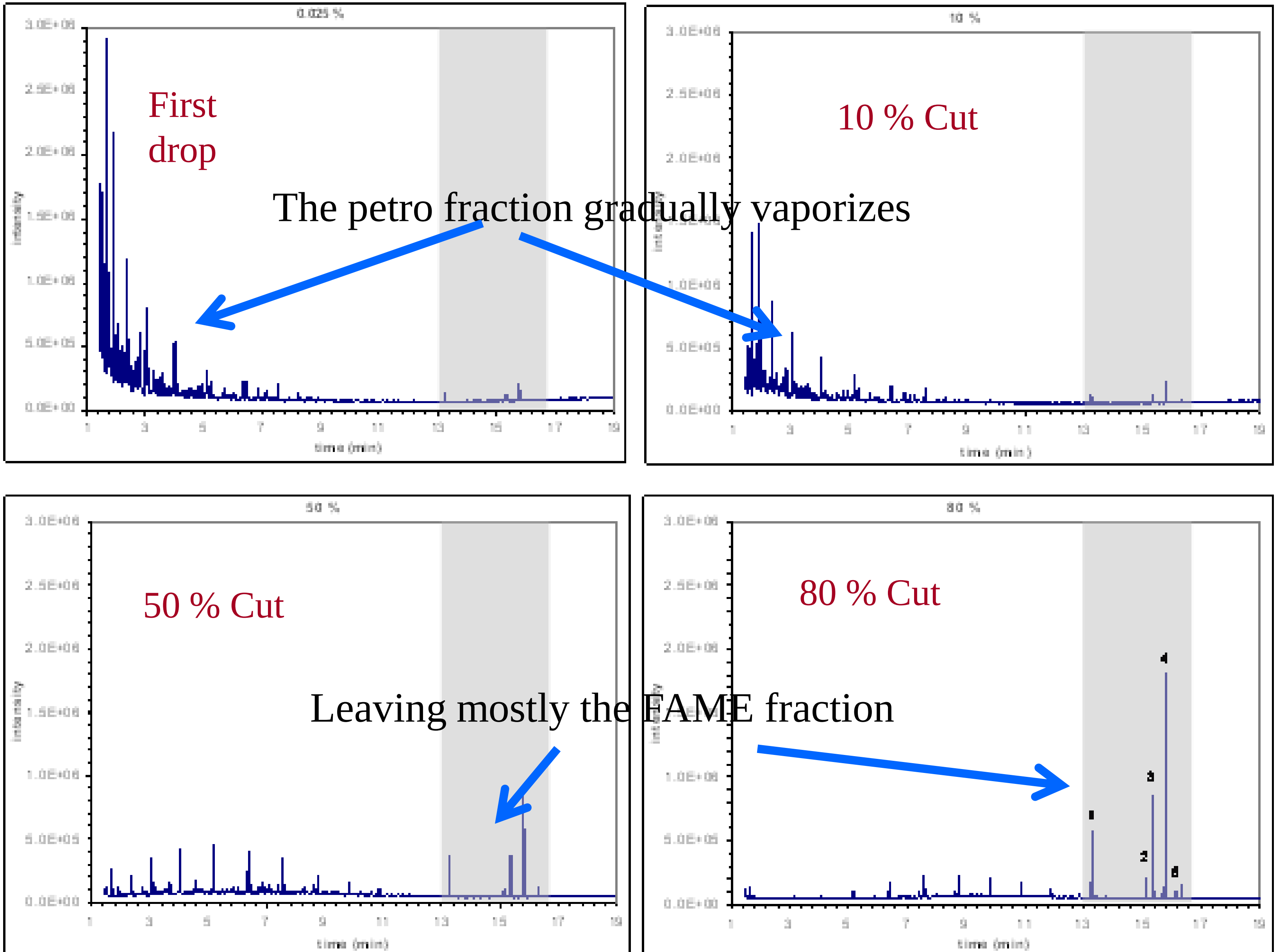
- Cu "coupons" instead of Cu strips
- Distillate is injected into GC autosampler vial
- Allows the use of automated chemical analysis
- Applicable to microscale samples
- Minimizes waste







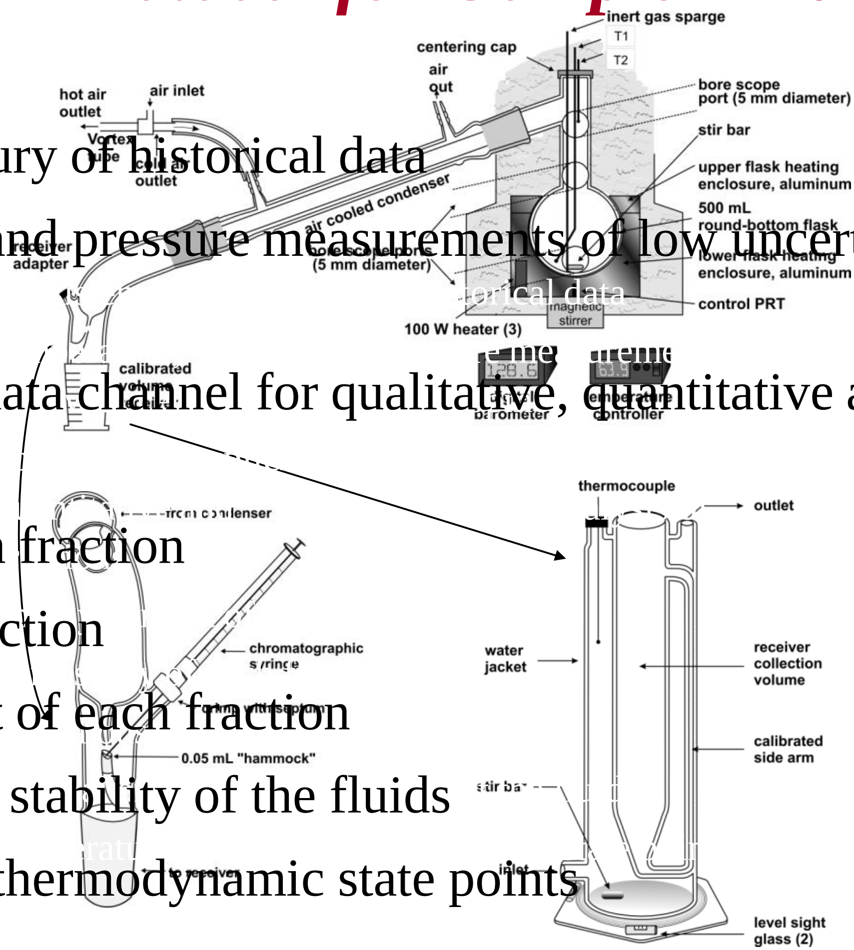
B20: Compositional Analysis (GC Traces)



Advanced Distillation Curve

Analytical Protocol for Complex Fluids

– Consistent with a century of historical data
– Temperature, volume and pressure measurements of low uncertainty – EOS development
– Composition explicit data channel for 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
– Temperatures are true thermodynamic state points



Bruno, T. J *et al.* **Anal. Chem.** 2010, 82, 777-783.

(February 2010 feature article)

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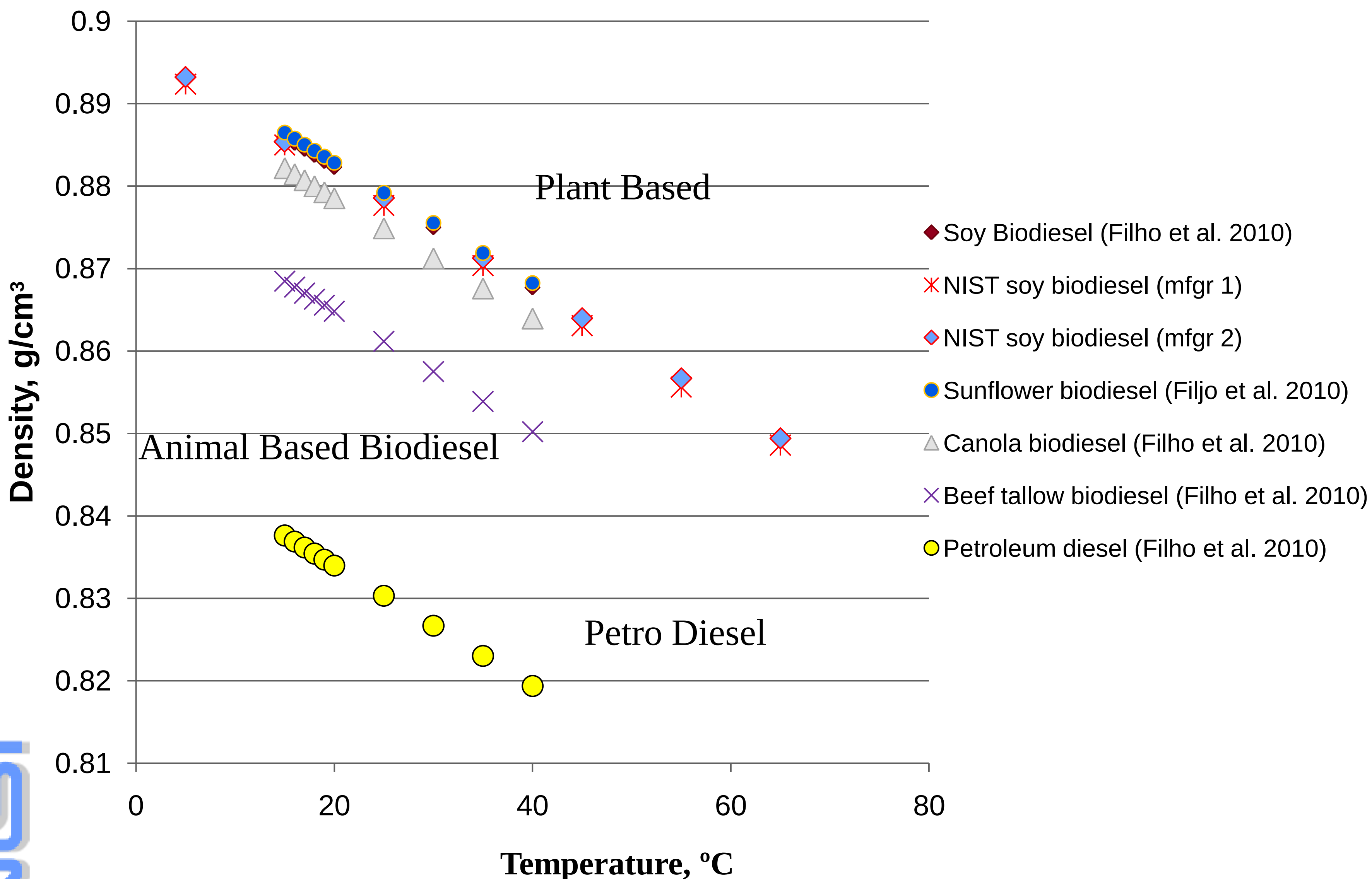
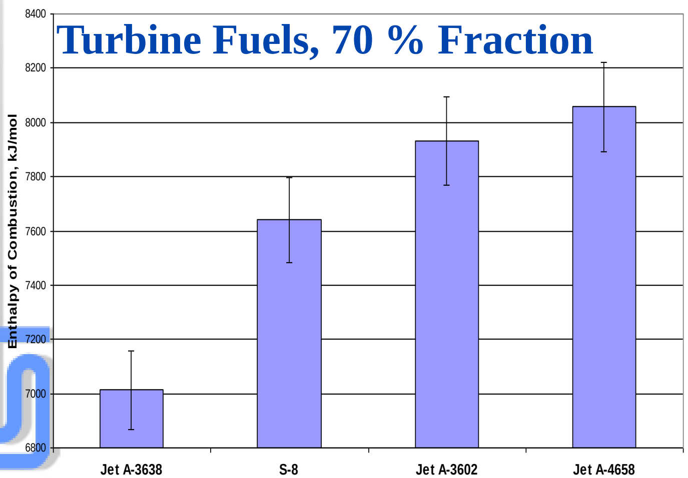
Biofuel Densities



Synthetic Fuels: Energy Content

Within-spec alternative fuels can have large differences in energy content!

Composite Enthalpy of Combustion (Aviation)			Basis
UL94 Petro-alternative	UL102 Bio-derived	100LL Standard	
4591 (229.6)	4501 (225.0)	4988 (249.4)	kJ/mol
43.7 (2.2)	42.0 (2.1)	44.4 (2.2)	kJ/g
31.4 (1.6)	33.6 (1.7)	30.7 (1.5)	kJ/mL

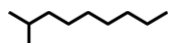
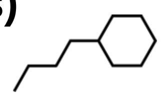
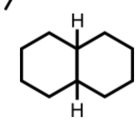


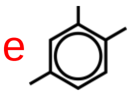
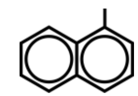
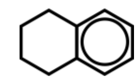
Composite Enthalpy of Combustion, -kJ/g (Biodiesels)

Distillate Volume Fraction (%)	SME Soy	CME Cuphea	B100 Retail
0.025	37 (1)	34(1)	36 (1)
10	37 (1)	34(1)	36 (1)
50	37 (1)	34(1)	36 (1)
80	37(1)	37(1)	37 (1)

How to Describe Fuels: *Surrogates*

Petroleum based diesel

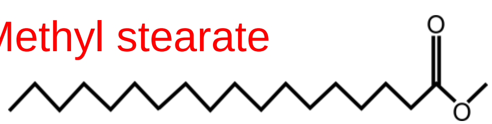
- **Alkanes**
  - n-hexadecane (straight chain) 
  - 2-methyltridecane (branched) 
- **Naphthenes (cycloalkanes)**
  - Butylcyclohexane (one-ring) 
  - Cis-decalin (two-ring) 

- **Aromatics**
  - 1,2,4-trimethylbenzene (one-ring) 
  - 1-methylnaphthalene (two-ring) 
- **Naphtho-aromatics**
  - tetralin 

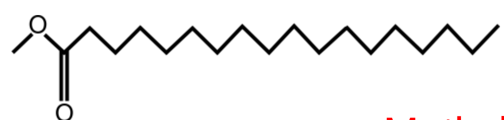
Soy-derived biodiesel

Fatty-acid methylesters

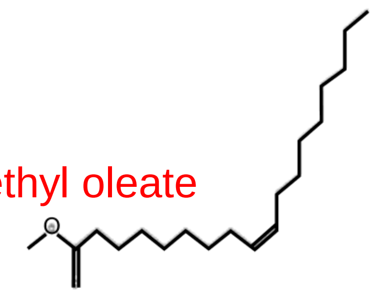
Methyl stearate



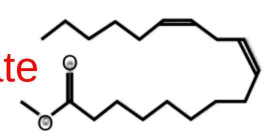
Methyl palmitate



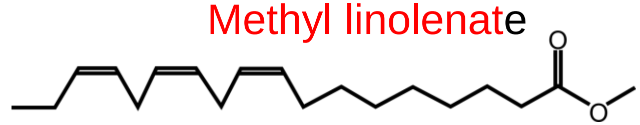
Methyl oleate



Methyl linoleate

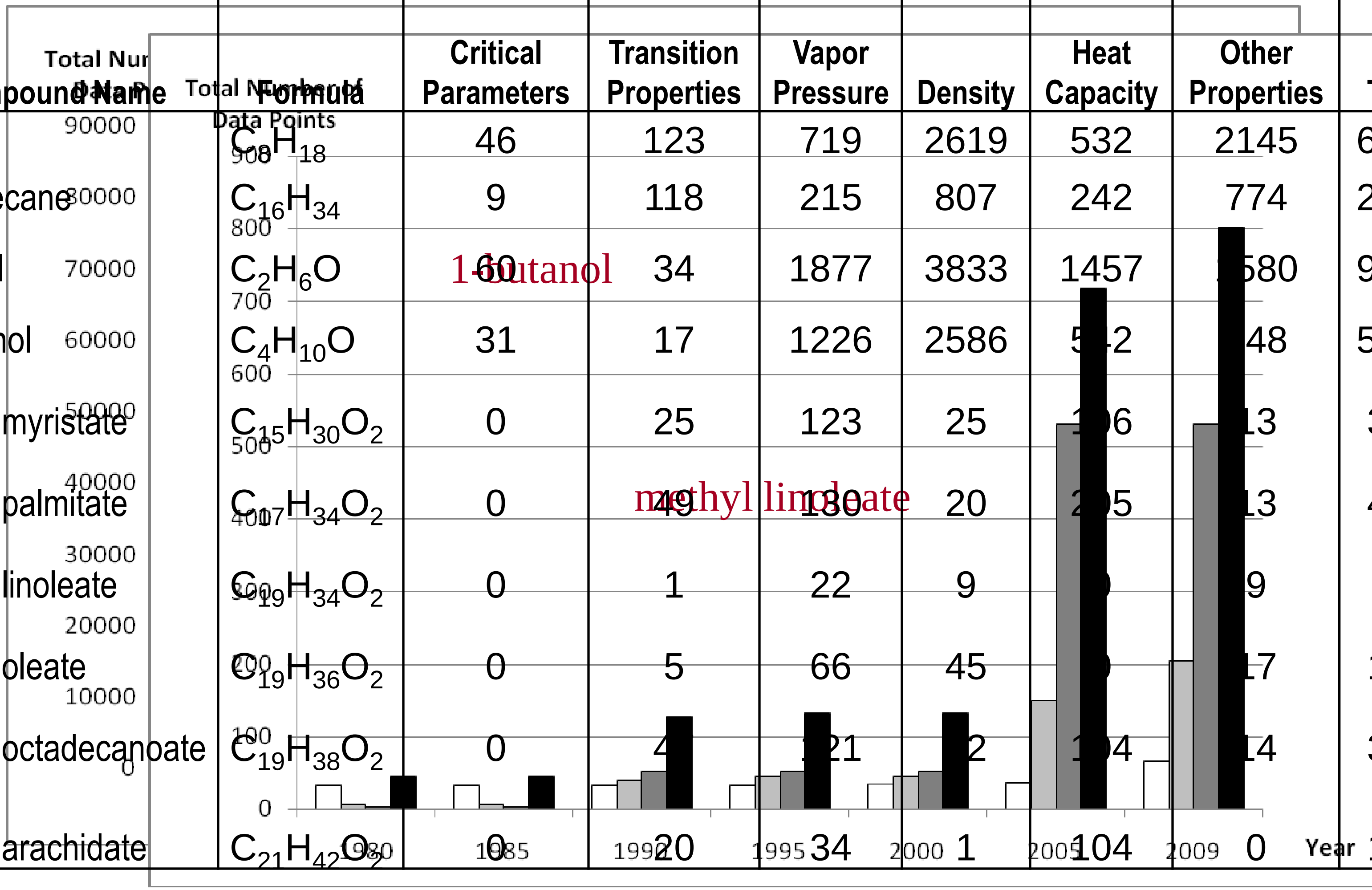


Methyl linolenate



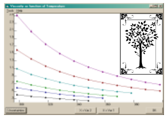
Are Adequate Data Available?

Compound Name	Formula	Critical Parameters	Transition Properties	Vapor Pressure	Density	Heat Capacity	Other Properties	Total
octane	C_8H_{18}	46	123	719	2619	532	2145	6184
hexadecane	$C_{16}H_{34}$	9	118	215	807	242	774	2165
ethanol	C_2H_6O	60	34	1877	3833	1457	[illegible]580	9823
1-butanol	$C_4H_{10}O$	31	17	1226	2586	[illegible]	[illegible]48	5768
methyl myristate	$C_{15}H_{30}O_2$	0	25	123	25	[illegible]	[illegible]13	331
methyl palmitate	$C_{17}H_{34}O_2$	0	49	130	20	[illegible]	[illegible]13	469
methyl linoleate	$C_{19}H_{34}O_2$	0	1	22	9	[illegible]	[illegible]9	66
methyl oleate	$C_{19}H_{36}O_2$	0	5	66	45	[illegible]	[illegible]17	179
methyl octadecanoate	$C_{19}H_{38}O_2$	0	4[illegible]	[illegible]21	[illegible]2	[illegible]	[illegible]14	362
methyl arachidate	$C_{21}H_{42}O_2$	0	20	34	1	104	0	175



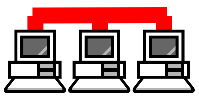
Experimental Thermophysical Property Data: Pures, Binaries, Ternaries, Total

How to Obtain Properties: "*Data on Demand* "



❑Software tools for mass-scale data capture

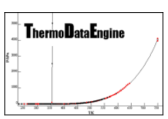
❑Comprehensive Data Storage Facility



❑Data Entry Facility

❑Data Communications Standard

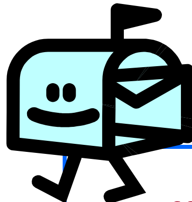
❑Data Reader Software



❑Software Expert Systems

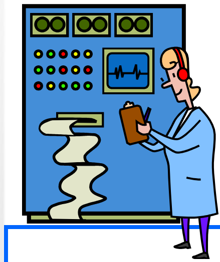
❑Web Communication Portal

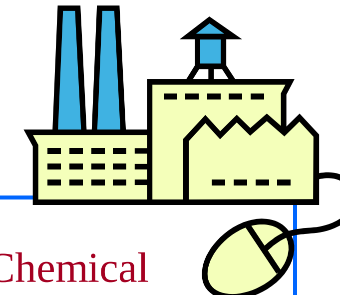
Global Data System



Efficiency of Information Delivery

Journal Publication Quality





Instrument Calibration & Validation

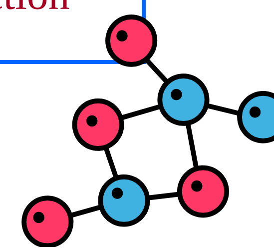
Global Information System In Thermodynamics

Chemical Process Design

Scientific Discovery Process

Strategic Experiment Planning

Molecular Modeling & Property Prediction



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Goals for Program on Biofuels Reference Data

To facilitate international trade in the technologies, innovation in design, optimization of plants and components, rational choices among alternatives, and transparency in the marketplace, we should strive for global consensus on fuel property data. This requires:

- **Standards for communicating data and models for fuels**
- **Comprehensive experimental data**
- **Property models for**
  - **constituents of biofuels (intermediates, waste streams, etc.)**
  - **finished fuels**
  - **blends of biofuels with conventional fuels**
  - **blended fuels with additives**

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The Path Forward: *What Must be Done?*

- Analysis of the properties most important for engine analysis, process design, pipeline transport, etc.
- Compilations of literature data
- Evaluations of data
- Experimental measurements
- Development of thermodynamic and transport property models
- Evaluation of thermodynamic and transport property models, leading to the declaration of international standards

Proposal for Discussion: *Establish international working group to foster coordination and cooperation in these efforts.*

Acknowledgements

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- Michael Frenkel
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QUESTIONS???