Refinery Feedstocks & Products Properties & Specifications

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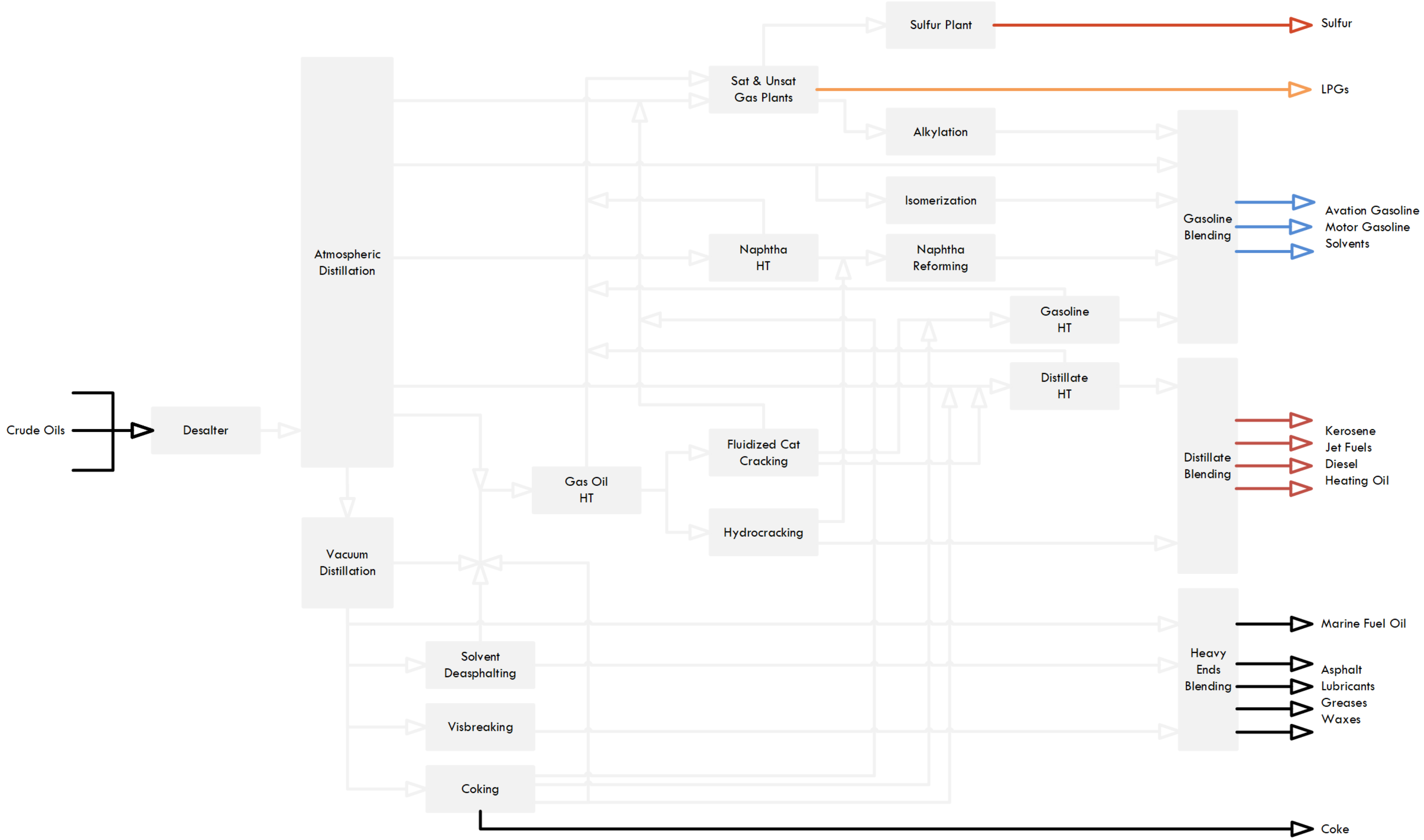
Petroleum Refinery Block Flow Diagram



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Topics

Quantity & Quality

- Chemical composition
- Distillation analyses
- Properties of distillation fractions

Products as defined by their properties & specifications

- Composition, boiling point ranges, and/or volatility
- Properties specific for certain distillation fractions
  - Autoignition tendency – octane & cetane number

Quantity & Quality

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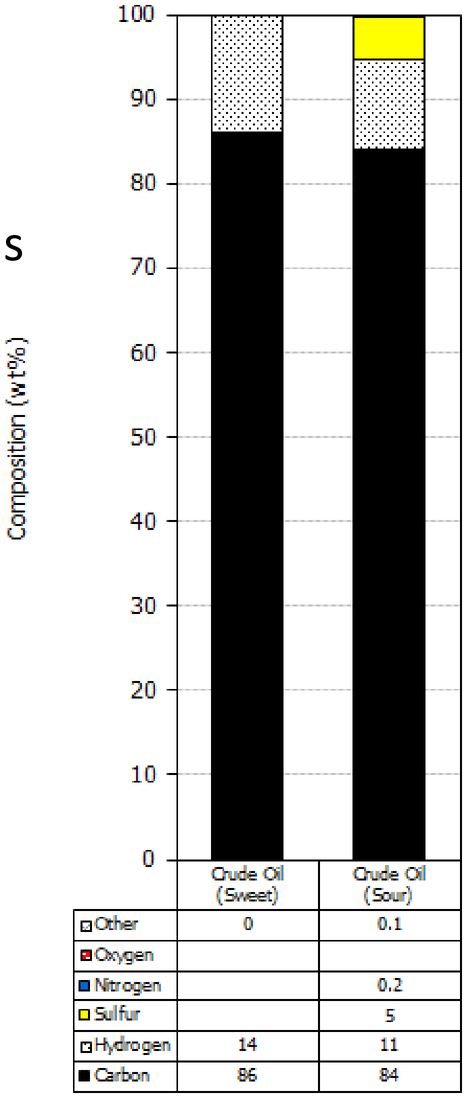
Crude Oil as Refinery Feedstock

Crude Oil

- Complex mixture of hydrocarbons & heterocompounds
- Dissolved gases to non-volatiles (1000°F+ boiling material)
- C_1 to C_{90}^{+}

Composition surprisingly uniform

Element	Wt%
Carbon	84 - 87
Hydrogen	11 - 14
Sulfur	0 - 5
Nitrogen	0 - 0.2
Other elements	0 - 0.1



	Crude Oil (Sweet)	Crude Oil (Sour)
▨ Other	0	0.1
🟥 Oxygen		
🟦 Nitrogen		0.2
🟨 Sulfur		5
▨ Hydrogen	14	11
■ Carbon	86	84

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Primary Hydrocarbon Molecular Types

Paraffins

- Carbon atoms inter-connected by single bond
- Other bonds saturated with hydrogen

Naphthenes

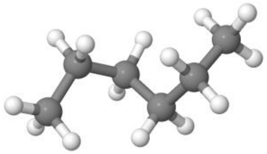
- Ringed paraffins (cycloparaffins)
- All other bonds saturated with hydrogen

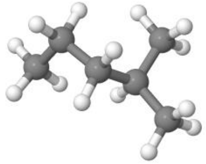
Aromatics

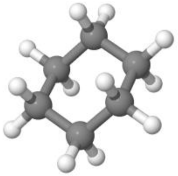
- Six carbon ring (multiple bonding)
- Bonds in ring(s) are unsaturated

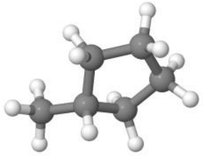
Olefins

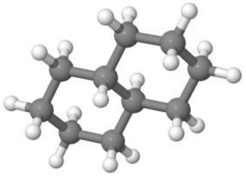
- Usually not in crude oil
- Formed during processing
- At least two carbon atoms inter-connected by (unsaturated) double bond

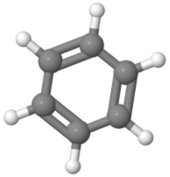

n-Hexane

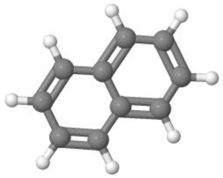

i-Hexane

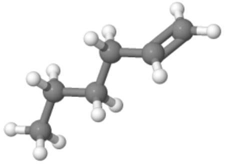

Cyclohexane

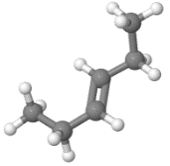

Methylcyclopentane

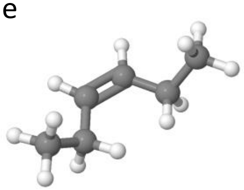

Decalin


Benzene


Naphthalene


1-Hexene


trans-3-Hexene


cis-3-Hexene

Drawings from NIST Chemistry WebBook, http://webbook.nist.gov/chemistry/

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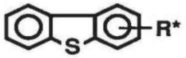
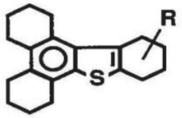
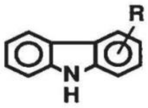
Example Heterocompounds



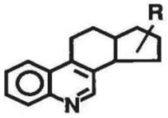
$C_nH_{2n-16}S$
Dibenzothiophenes



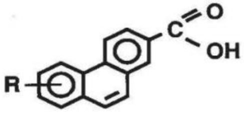
$C_nH_{2n-16}S$
Trinaphthenobenzothiophenes



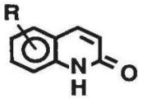
$C_nH_{2n-15}N$
Carbazoles



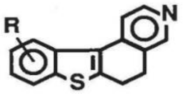
$C_nH_{2n-15}N$
Dinaphthenoquinolines



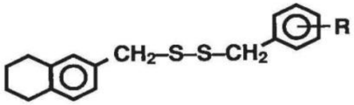
$C_nH_{2n-20}O_2$
Carboxylic Acids



$C_nH_{2n-11}NO$
Amides

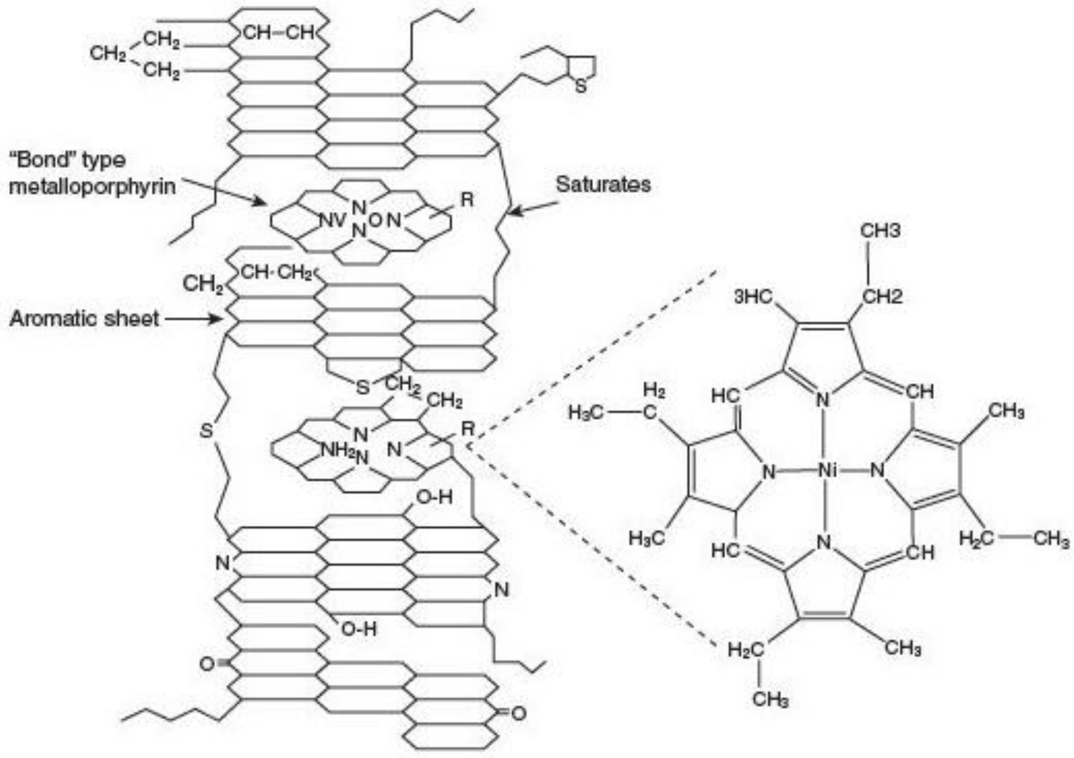


$C_nH_{2n-19}NS$
Azathiophenes



$C_nH_{2n-16}S_2$
Disulfides

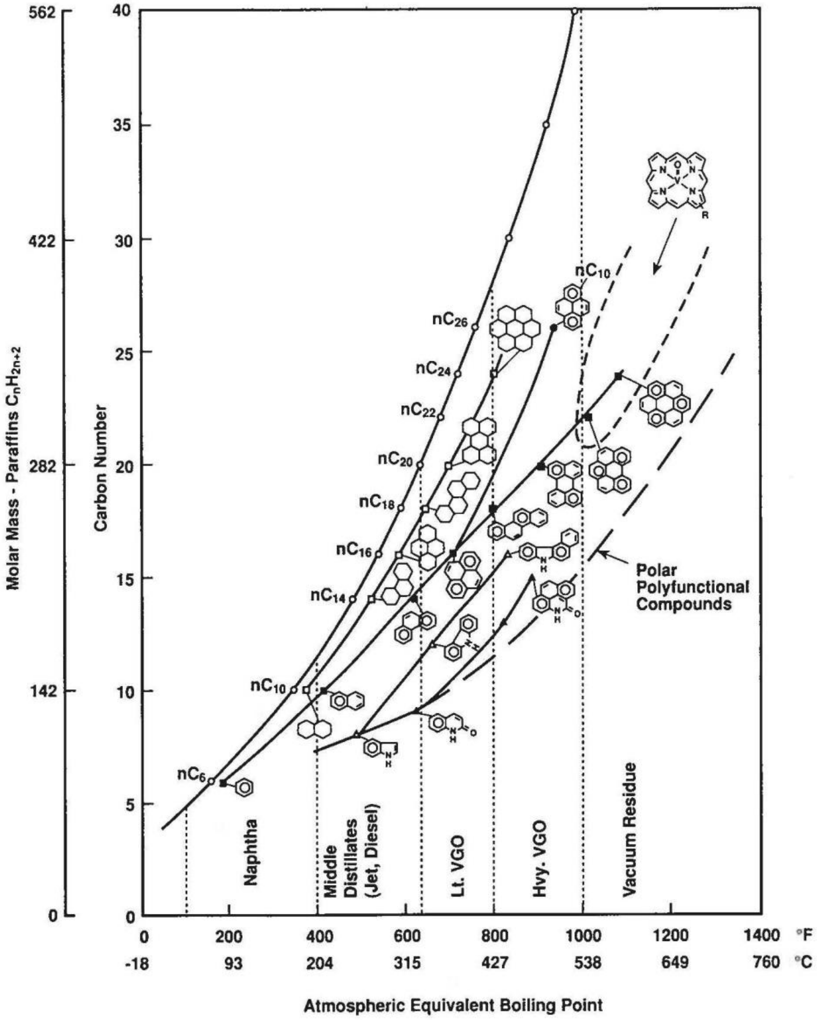
Composition & Analysis of Heavy Petroleum Fractions
K.H. Altgelt & M.M. Boduszynski
Marcel Dekker, Inc., 1994, pg. 16



Modeling and Simulation of Catalytic Reactors for Petroleum Refining.
by Jorge Ancheyta, John Wiley & Sons, 2011

Distribution of Compounds

Carbon No.	Boiling Point °C	Boiling Point °F	Paraffin Isomers	Examples
5	36	97	3	Gasoline
8	126	259	18	
10	174	345	75	
12	216	421	355	
15	271	520	4347	Diesel & jet fuels, middle distillates
20	344	651	3.66E+05	Vacuum gas oil
25	402	756	3.67E+07	Atmospheric residue
30	449	840	4.11E+09	
35	489	912	4.93E+11	
40	522	972	6.24E+13	
45	550	1022	8.22E+15	
60	615	1139	2.21E+22	Vacuum residue
80	672	1242	1.06E+31	
100	708	1306	5.92E+39	Nondistillable residue



Composition & Analysis of Heavy Petroleum Fractions
K.H. Altgelt & M.M. Boduszynski
Marcel Dekker, Inc., 1994, pp. 23 & 45

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Crude Oil Assay

Indicates distribution quantity & quality of crude oil feedstock

Definitions based upon boiling point temperature ranges

- Represents ***expected*** products from crude & vacuum distillation

Completeness of data depends upon source

Quality measures

- Specific / API gravity
- Sulfur content
- Octane number
- Cetane number
- Viscosity
- Carbon residue

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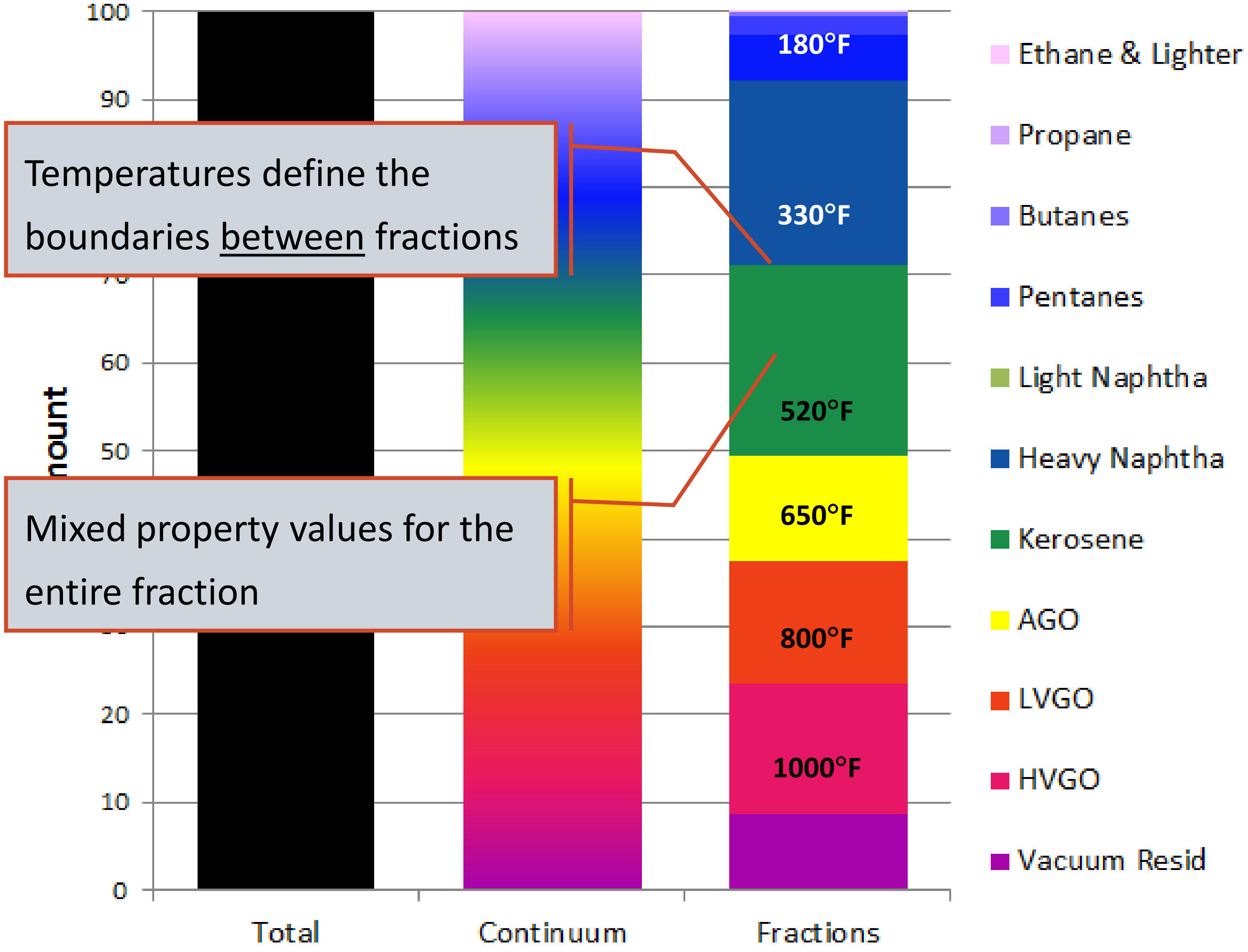
Crude Oil Assay Depiction



Temperatures define the boundaries between fractions

Mixed property values for the entire fraction

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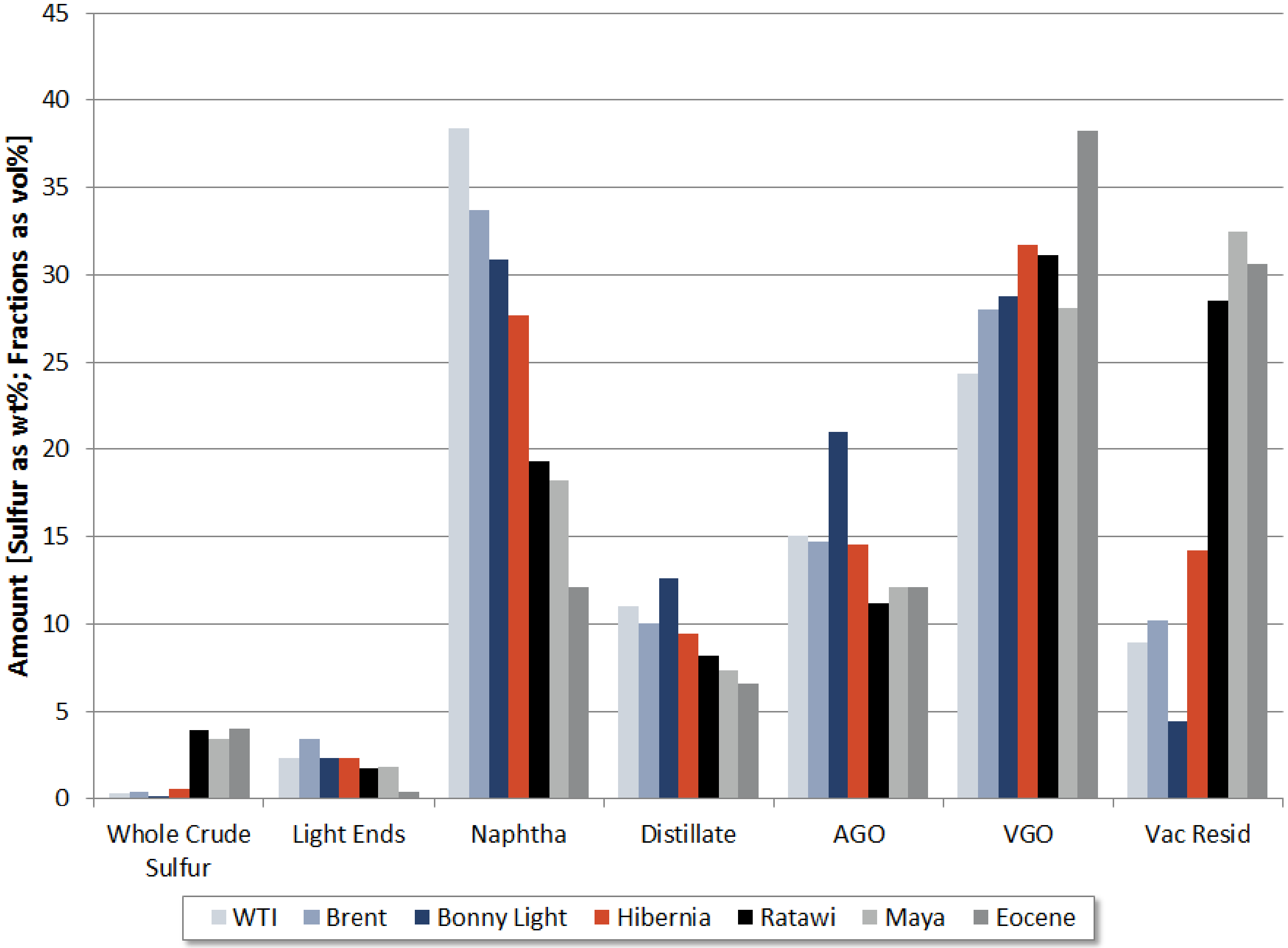
Crude Oils Are Not Created Equal



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Crude Oil Properties

Distillation analysis / Boiling point range

- Amount collected from batch distillation at the indicated temperature
- Standardized tests — ASTM 2892 (TBP), D86, D1160, …
  - Most useful is TBP (True Boiling Point)

Specific gravity, γ_o – ratio liquid density @ 60°F & 1 atm to that of water @ 60°F & 1 atm

- Air saturated: 8.32828 lb/gal
- Pure Water: 999.016 kg/m³ = 8.33719 lb/gal

API gravity

Higher density → lower °API

$$°\text{API} = \frac{141.5}{\gamma_o} - 131.5 \quad \Rightarrow \quad \gamma_o = \frac{141.5}{131.5 + °\text{API}}$$

Watson characterization factor

12 – 13 (paraffinic) to 10 (aromatic)

$$K_W = \frac{\sqrt[3]{T_b}}{\gamma_o} \qquad T_b \text{ in units of °R}$$

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Crude Oil Properties

Classification based on gravity

Light	API > 38°
Medium	38° > API > 29°
Heavy	29° > API > 8.5°
Very heavy	API < 8.5°

Sulfur, nitrogen, & metals content

- All can "poison" catalysts
- Sulfur
  - "Sour" vs. "sweet" — ~0.5 wt% cutoff
  - Restrictions on sulfur in final products
- Nitrogen
  - Usually tolerate up to 0.25 wt%
- Nickel, vanadium, copper
  - Tend to be in the largest molecules/highest boiling fractions

Properties appropriate for certain boiling point ranges

- Octane number
- Cetane number
- Viscosities
- Carbon residue

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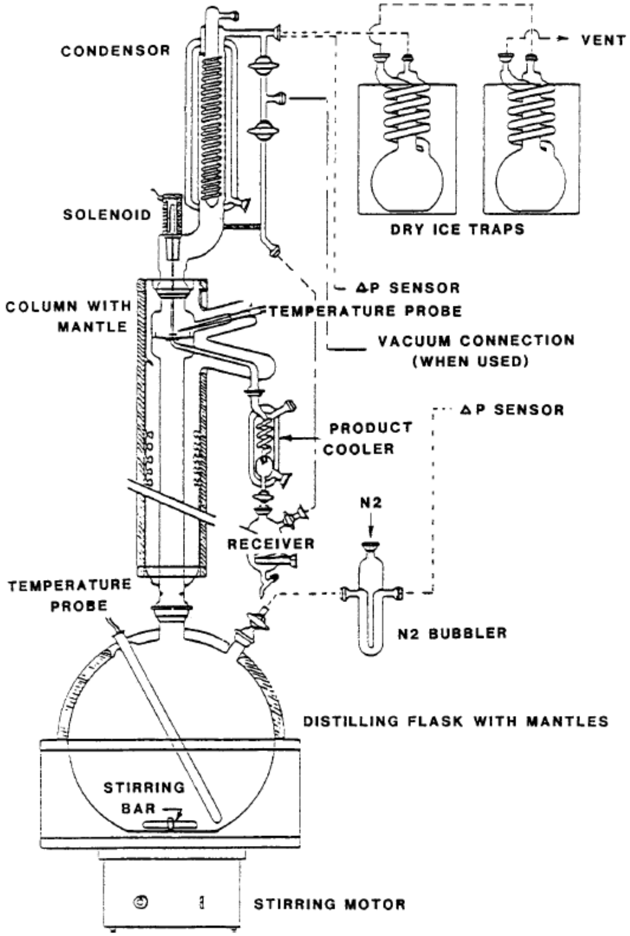
Distillation Analysis Types

True Boiling Point (TBP) – ASTM D2892

- 14 to 18 theoretical stages
- Near infinite reflux (5:1 reflux ratio min)
- No hotter than 650°F to minimize cracking
  - Max vapor temperature 410°F
- Pressure levels
  - 760 mmHg (1 atm)
  - 100 mmHg
  - 2 mmHg (min)

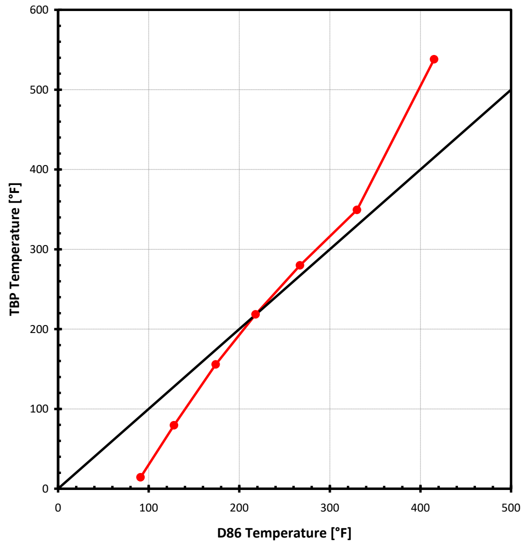


ASTM D 2892-13, Standard Test Method for Distillation of Crude Petroleum (15-Theoretical Plate Column)

Distillation Analysis Types

ASTM D86

- Low resolution — no packing, reflux from heat losses
- 1 atm; no hotter than 650°F — minimize cracking
- Correlations to correct to TBP basis



http://www.koehlerinstrument.com/products/K45601.html

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Distillation Analysis Types

ASTM D1160

- Used on resids (650°F+)
- Relatively low resolution
- Vacuum conditions — 10 to 40 mmHg; no hotter than 1000°F AEBP
- Correlations to correct to atmospheric pressure & TBP basis

https://www.labindia.com/labindia_instrument/iludest.html
Downloaded June 23, 2019

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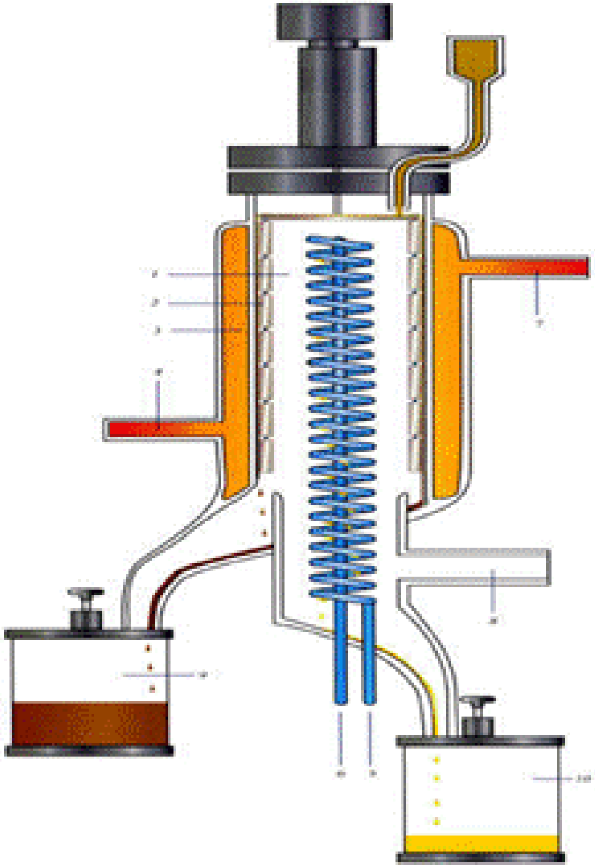
Distillation Analysis Types

Short Path Distillation

- Single stage flash
- Extremely low pressures — 0.1 mmHg or less
- Characterize deep cut resids

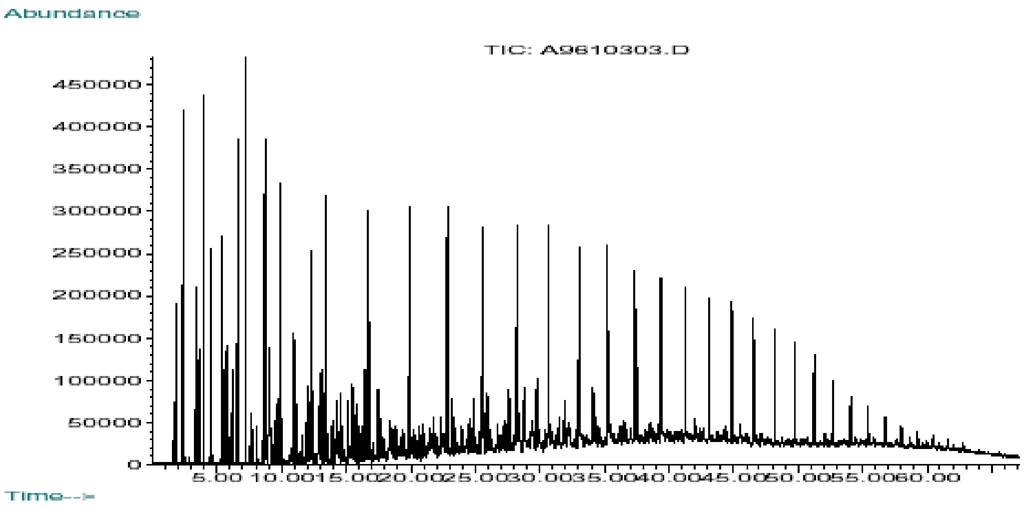


http://www.chemtechservicesinc.com/short-path-distillation.html

Distillation Analysis Types

Simulated Distillation – ASTM D 2887, D 6352, D 7169

- Relatively low resolution gas chromatography
  - Several thousand theoretical stages
- Essentially TBP temperatures — wt% basis
  - Temperatures inferred from elution times
  - Calibrated with n-paraffin mixture



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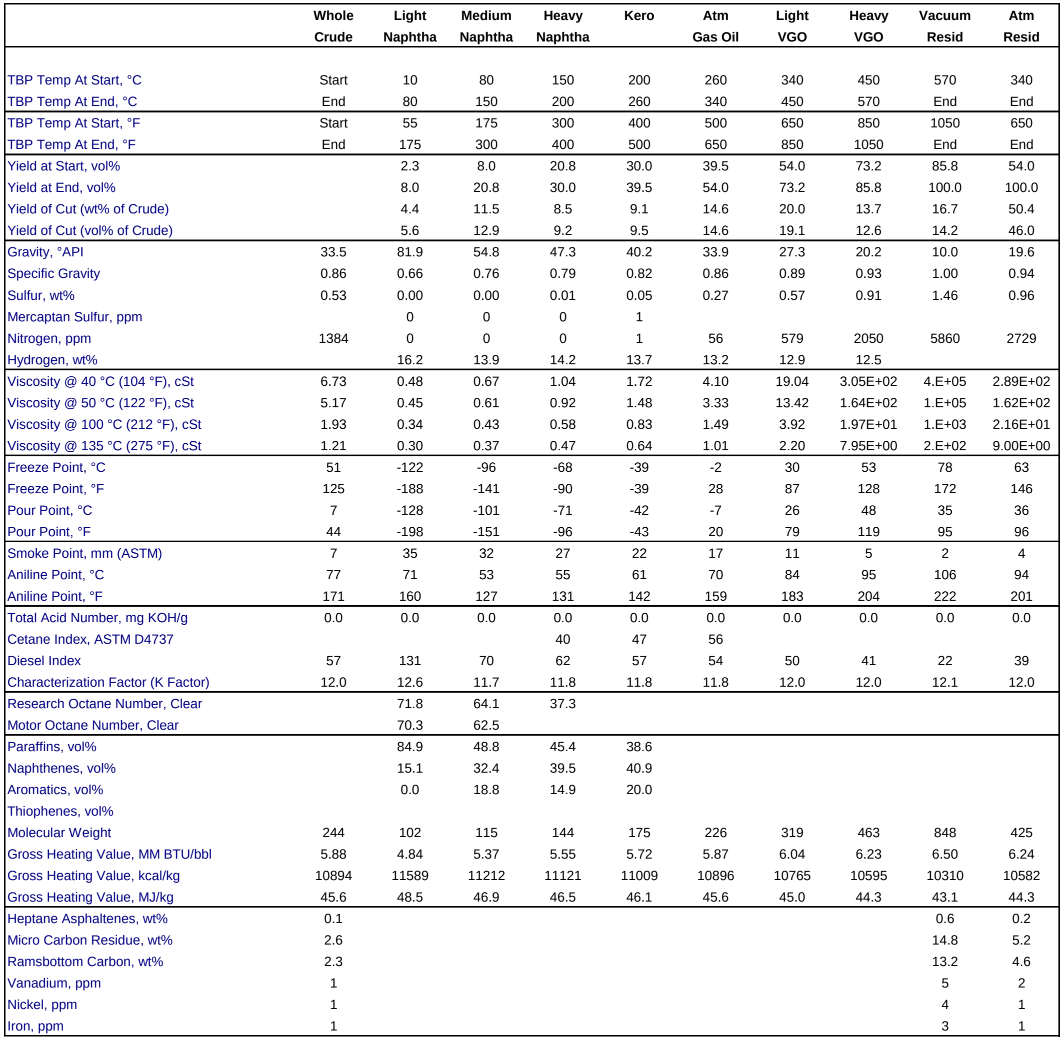
Crude Oil Assay – Hibernia (Chevron)



	Whole Crude	Light Naphtha	Medium Naphtha	Heavy Naphtha	Kero	Atm Gas Oil	Light VGO	Heavy VGO	Vacuum Resid	Atm Resid
TBP Temp At Start, °C	Start	10	80	150	200	260	340	450	570	340
TBP Temp At End, °C	End	80	150	200	260	340	450	570	End	End
TBP Temp At Start, °F	Start	55	175	300	400	500	650	850	1050	650
TBP Temp At End, °F	End	175	300	400	500	650	850	1050	End	End
Yield at Start, vol%		2.3	8.0	20.8	30.0	39.5	54.0	73.2	85.8	54.0
Yield at End, vol%		8.0	20.8	30.0	39.5	54.0	73.2	85.8	100.0	100.0
Yield of Cut (wt% of Crude)		4.4	11.5	8.5	9.1	14.6	20.0	13.7	16.7	50.4
Yield of Cut (vol% of Crude)		5.6	12.9	9.2	9.5	14.6	19.1	12.6	14.2	46.0
Gravity, °API	33.5	81.9	54.8	47.3	40.2	33.9	27.3	20.2	10.0	19.6
Specific Gravity	0.86	0.66	0.76	0.79	0.82	0.86	0.89	0.93	1.00	0.94
Sulfur, wt%	0.53	0.00	0.00	0.01	0.05	0.27	0.57	0.91	1.46	0.96
Mercaptan Sulfur, ppm		0	0	0	1					
Nitrogen, ppm	1384	0	0	0	1	56	579	2050	5860	2729
Hydrogen, wt%		16.2	13.9	14.2	13.7	13.2	12.9	12.5		
Viscosity @ 40 °C (104 °F), cSt	6.73	0.48	0.67	1.04	1.72	4.10	19.04	3.05E+02	4.E+05	2.89E+02
Viscosity @ 50 °C (122 °F), cSt	5.17	0.45	0.61	0.92	1.48	3.33	13.42	1.64E+02	1.E+05	1.62E+02
Viscosity @ 100 °C (212 °F), cSt	1.93	0.34	0.43	0.58	0.83	1.49	3.92	1.97E+01	1.E+03	2.16E+01
Viscosity @ 135 °C (275 °F), cSt	1.21	0.30	0.37	0.47	0.64	1.01	2.20	7.95E+00	2.E+02	9.00E+00
Freeze Point, °C	51	-122	-96	-68	-39	-2	30	53	78	63
Freeze Point, °F	125	-188	-141	-90	-39	28	87	128	172	146
Pour Point, °C	7	-128	-101	-71	-42	-7	26	48	35	36
Pour Point, °F	44	-198	-151	-96	-43	20	79	119	95	96
Smoke Point, mm (ASTM)	7	35	32	27	22	17	11	5	2	4
Aniline Point, °C	77	71	53	55	61	70	84	95	106	94
Aniline Point, °F	171	160	127	131	142	159	183	204	222	201
Total Acid Number, mg KOH/g	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Cetane Index, ASTM D4737				40	47	56				
Diesel Index	57	131	70	62	57	54	50	41	22	39
Characterization Factor (K Factor)	12.0	12.6	11.7	11.8	11.8	11.8	12.0	12.0	12.1	12.0
Research Octane Number, Clear		71.8	64.1	37.3						
Motor Octane Number, Clear		70.3	62.5							
Paraffins, vol%		84.9	48.8	45.4	38.6					
Naphthenes, vol%		15.1	32.4	39.5	40.9					
Aromatics, vol%		0.0	18.8	14.9	20.0					
Thiophenes, vol%										
Molecular Weight	244	102	115	144	175	226	319	463	848	425
Gross Heating Value, MM BTU/bbl	5.88	4.84	5.37	5.55	5.72	5.87	6.04	6.23	6.50	6.24
Gross Heating Value, kcal/kg	10894	11589	11212	11121	11009	10896	10765	10595	10310	10582
Gross Heating Value, MJ/kg	45.6	48.5	46.9	46.5	46.1	45.6	45.0	44.3	43.1	44.3
Heptane Asphaltenes, wt%	0.1								0.6	0.2
Micro Carbon Residue, wt%	2.6								14.8	5.2
Ramsbottom Carbon, wt%	2.3								13.2	4.6
Vanadium, ppm	1								5	2
Nickel, ppm	1								4	1
Iron, ppm	1								3	1

Simple analysis

http://crudemarketing.chevron.com/crude/north_american/hibernia.aspx

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Crude Oil Assay – Hibernia (ExxonMobil)

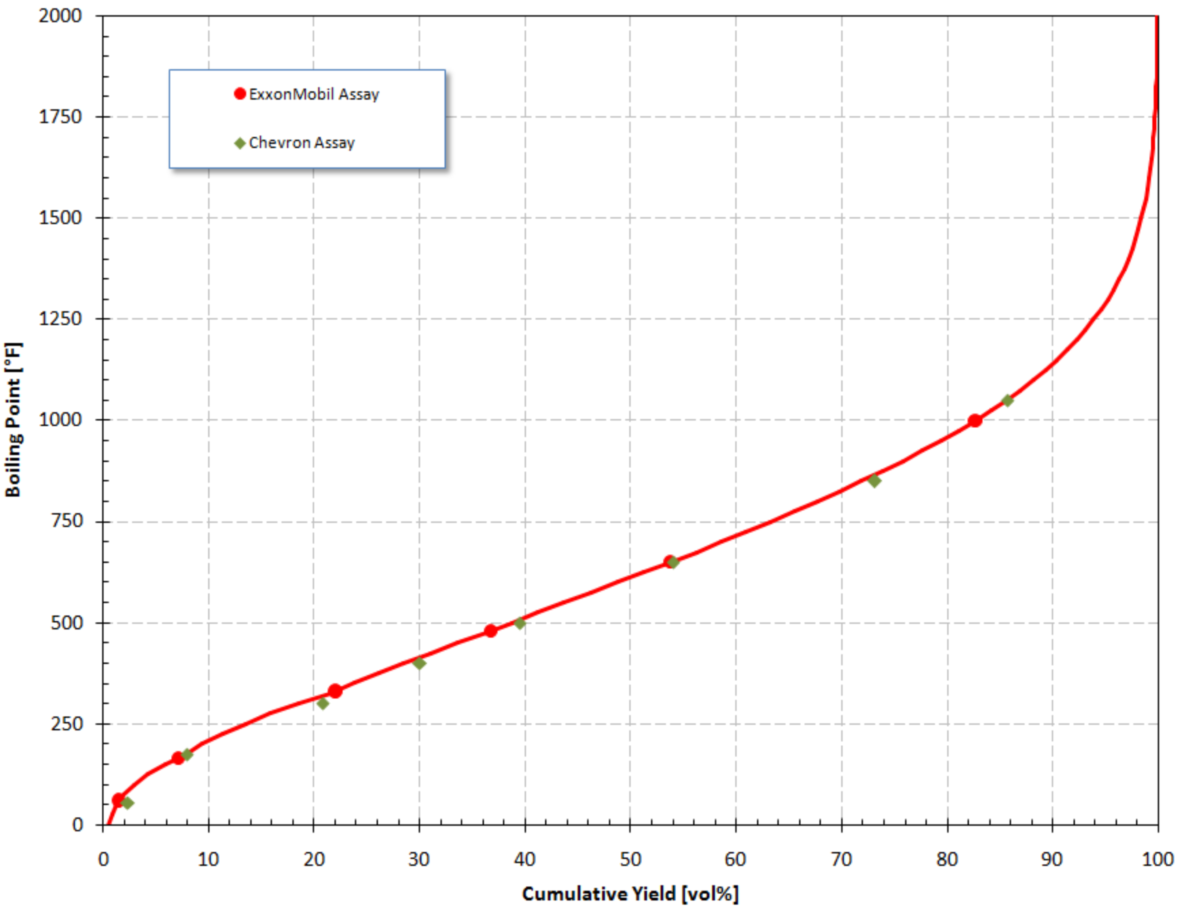
HIBER11Z	Whole crude - 200 to 1499	Butane and Lighter - 200 to 60	Lt. Naphtha C5- 165F 60 to 165	Hvy Naphtha 165 - 330F 165 to 330	Kerosene 330 - 480F 330 to 480	Diesel 480 - 650F 480 to 650	Vacuum Gas Oil 650 - 1000F 650 to 1000	Vacuum Residue 1000F+ 1000 to 1499
Cut volume, %	100	1.51	5.68	14.83	14.76	17.03	28.89	17.29
API Gravity,	33.9	121.42	81.02	54.91	43.1	34.04	24.71	12.65
Specific Gravity (60/60F),	0.8555	0.5595	0.6658	0.7591	0.8104	0.8548	0.9058	0.9816
Carbon, wt %		82.43	83.95	85.88	86.21	86.51	86.39	
Hydrogen, wt %		17.57	16.05	14.12	13.77	13.23	12.81	
Pour point, F	37				-62	17	103	103
Neutralization number (TAN), MG/GM	0.095					0.054	0.116	0.212
Sulfur, wt%	0.54			0.0011	0.0213	0.2431	0.6814	1.4428
Viscosity at 20C/68F, cSt	12.49	0.35	0.41	0.75	1.79	6.88	120.83	472934.04
Viscosity at 40C/104F, cSt	6.21	0.3	0.35	0.62	1.31	3.96	40.48	34316.32
Viscosity at 50C/122F, cSt	4.7	0.28	0.32	0.56	1.15	3.16	26.22	11920.94
Mercaptan sulfur, ppm	1			1.5	2.1			
Nitrogen, ppm	1350	0	0	0	0.2	88.5	1196.1	4868
CCR, wt%	2.45					0	0.26	11.9
N-Heptane Insolubles (C7 Asphaltenes), wt%								0.3
Nickel, ppm	1.3					0	0	6.5
Vanadium, ppm	0.7					0	0	3.5
Calcium, ppm	0.5							
Reid Vapor Pressure (RVP) Whole Crude, psi	3.4							
Heat of Combustion (Gross), BTU/lb	19429							
Heat of Combustion (Net), BTU/lb	18222	19288	18852	18626	18567			
Hydrogen Sulfide (dissolved), ppm	0							
Salt content, ptb	0.1							
Paraffins, vol %		100	84.28	51.64	47.08	41.83	26.36	
Naphthenes, vol %		0	14.13	31.88	32.71	34.07	37.12	
Aromatics (FIA), vol %				16.48	16.9			
Distillation type, D-	1160	86	86	86	86	86	1160	1160
ASTM IBP, F	17.9	-127.8	95.9	208.1	363.8	506	690.6	1038.8
5 vol%, F	135.3	-94.6	101.4	213.7	368.2	510.8	695.2	1043.4
10 vol%, F	201.5	-52.1	106	216.6	370.4	512.9	706.3	1055.3
20 vol%, F	306.9	10.5	110.9	223.6	375.5	518.9	728.3	1081.3
30 vol%, F	403.1	29.8	114.6	231.7	381.8	526.3	752.6	1111.3
40 vol%, F	497.7	35.9	117.1	240.8	389.1	535.3	778.5	1145.4
50 vol%, F	597	35.8	121.9	249.1	396.4	543.8	806.4	1183.7
60 vol%, F	705	38.8	129	258.8	405.1	553.8	835.7	1228.7
70 vol%, F	806.7	43.7	134.1	269	414	564.5	865.7	1277.3
80 vol%, F	925.9	47.3	139.3	279.9	423.8	576	897.7	1330.3
90 vol%, F	1082.4	46.1	141.8	291.1	434	587.8	929	1385.2
95 vol%, F	1213.2	46.1	144.4	297.4	439.8	594.4	947.8	1419.1
ASTM EP, F	1401.5	47.2	147	302.5	444.5	605	969.7	1458
Freeze point, F					-48.2	29		
Smoke point, mm					21.3			
Naphthalenes (D1840), vol%					4.4			
Viscosity at 100C/212F, cSt	1.81	0.21	0.23	0.38	0.69	1.44	5.97	316.71
Viscosity at 150C/302F, cSt	1.03	0.17	0.18	0.28	0.47	0.88	2.58	42.23
Cetane Index 1990 (D4737),	33.1	152.4	44.1	29.4	43.8	54.1	56.9	45.5
Cloud point, F					-54	24		
Aniline pt, F					138.2	161.3	191.7	

Simple analysis & comparison

http://www.exxonmobil.com/crudeoil/about_crudes_hibernia.aspx

Comparison of Chevron & ExxonMobil Assays

	ExxonMobil	Chevron
API Gravity	33.9	33.53
Specific Gravity (60/60F)	0.8555	0.8574
Sulfur, wt%	0.54	0.53
Viscosity, cSt at 40°C (104°F)	6.21	6.73
Viscosity, cSt at 50°C (122°F)	4.7	5.17
Vanadium, ppm	0.7	0.87
Nickel, ppm	1.3	0.74
CCR / MCR, wt%	2.45	2.61



Updated: July 1, 2019

Comparison of Chevron & ExxonMobil Assays

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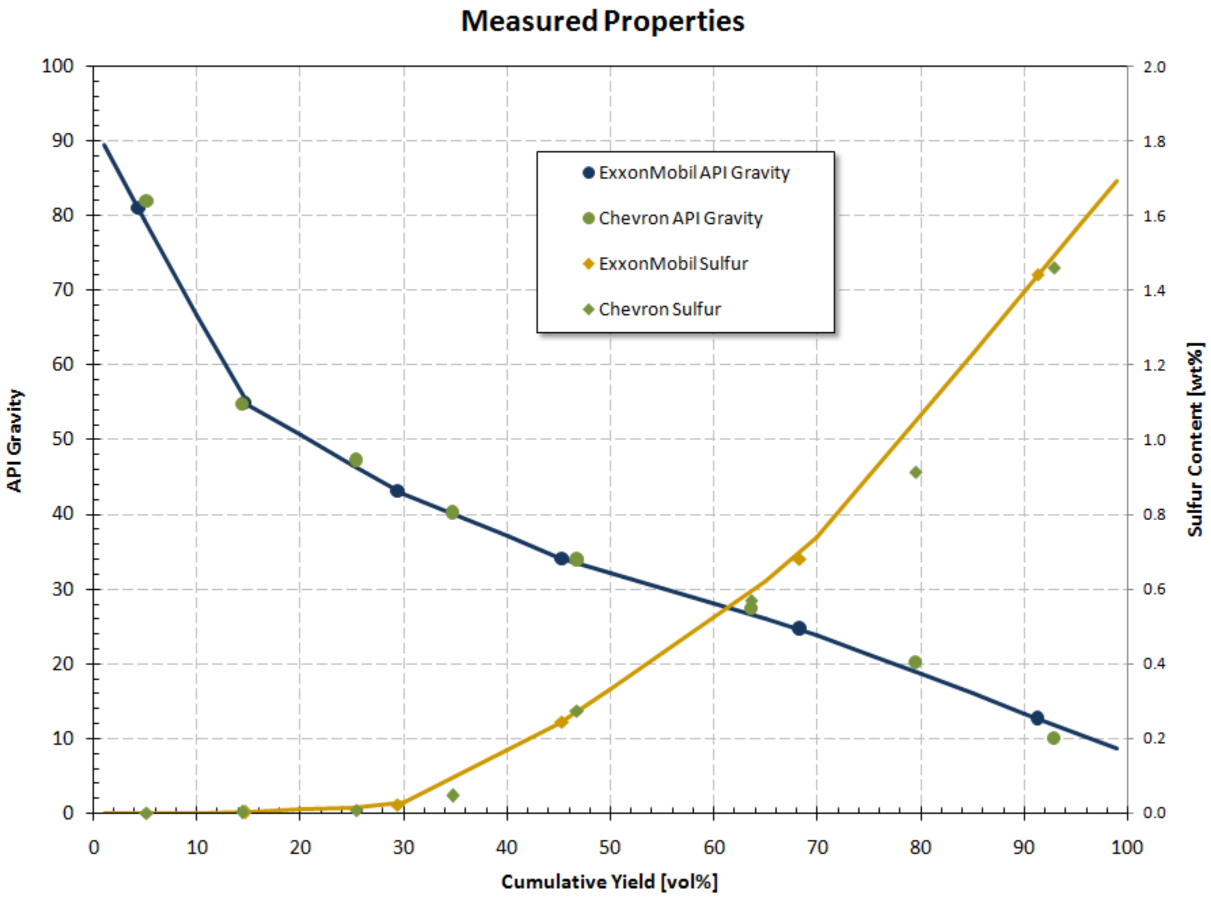
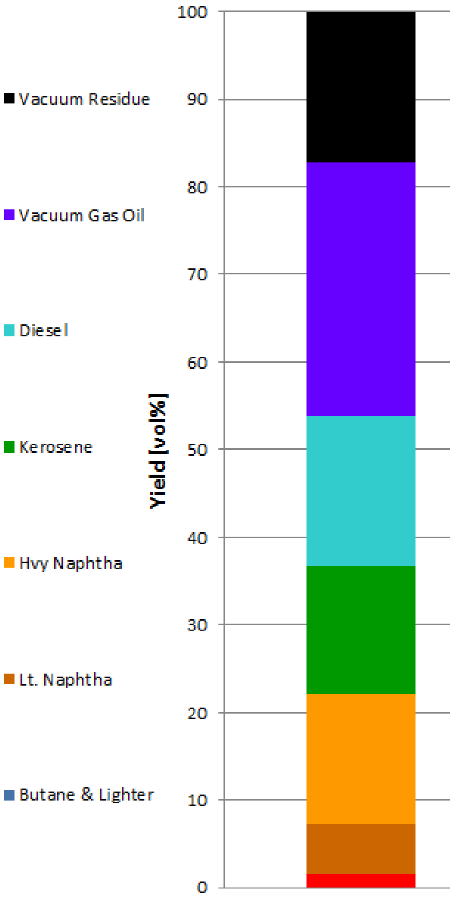
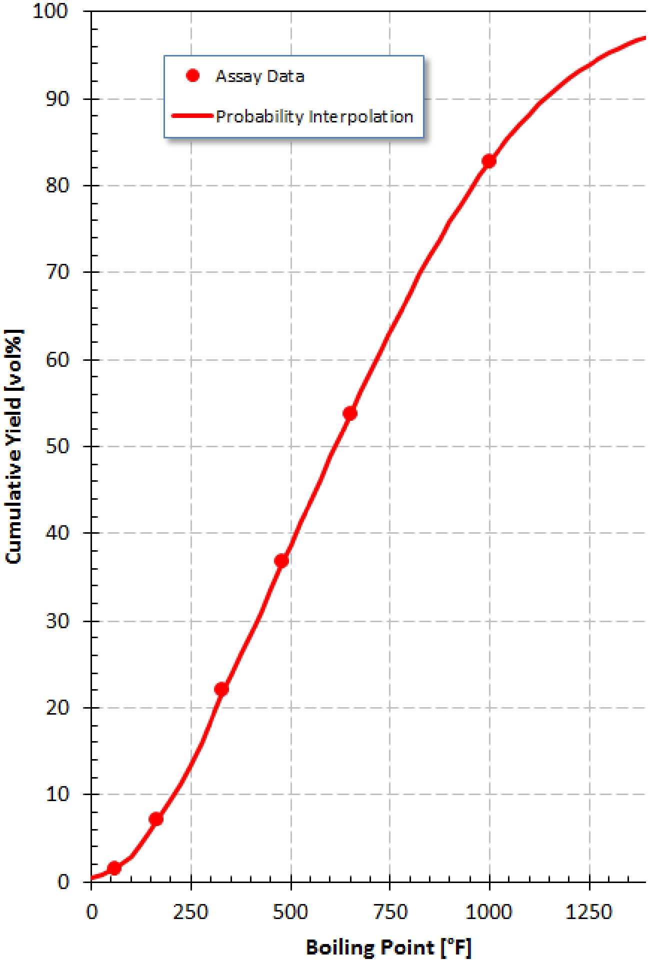
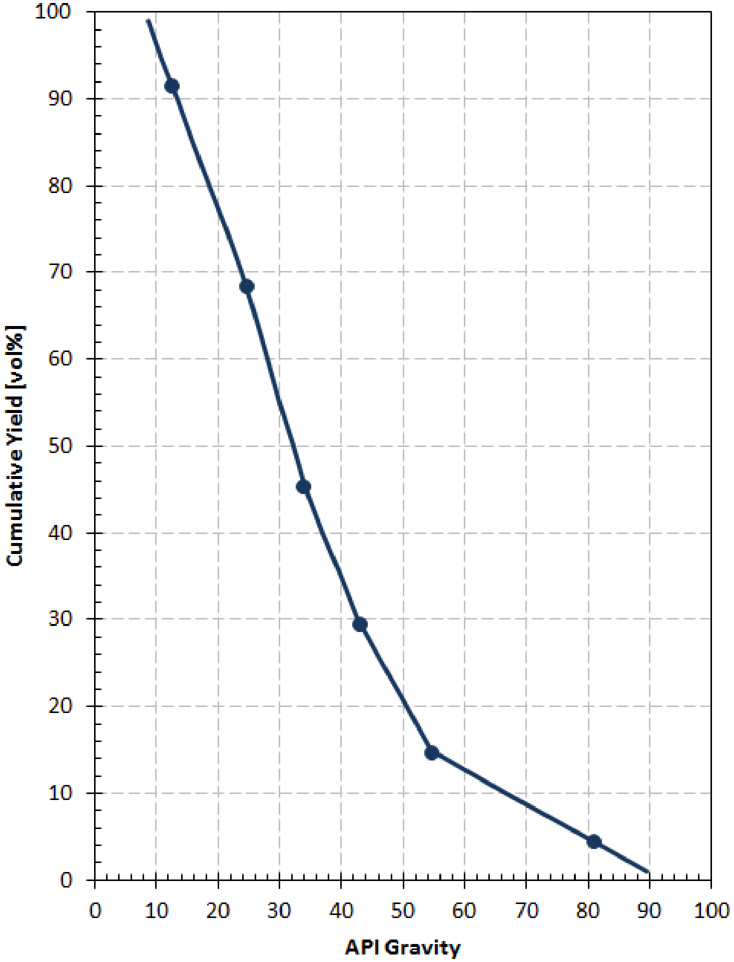


Updated: July 1, 2019

Comparison & Use of Yield Values

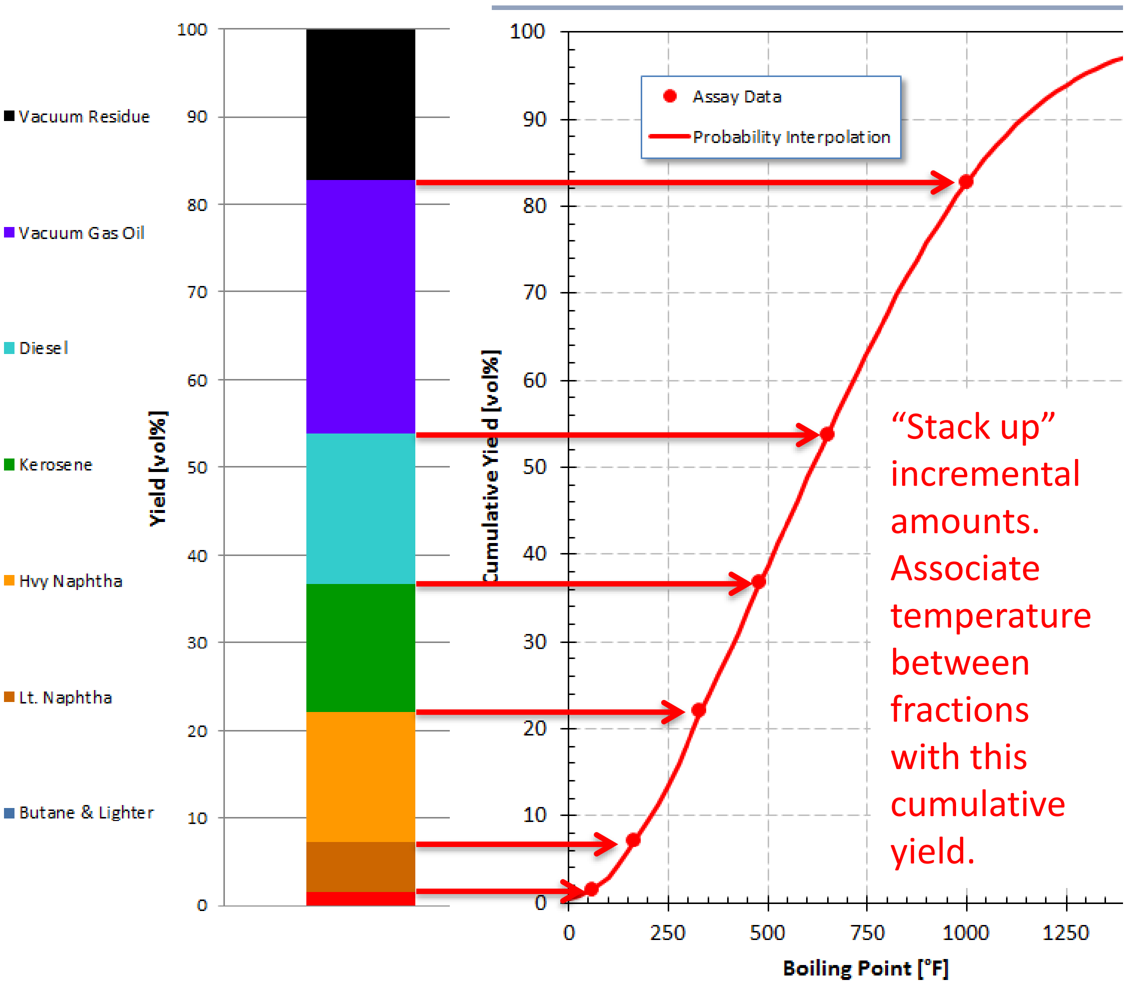




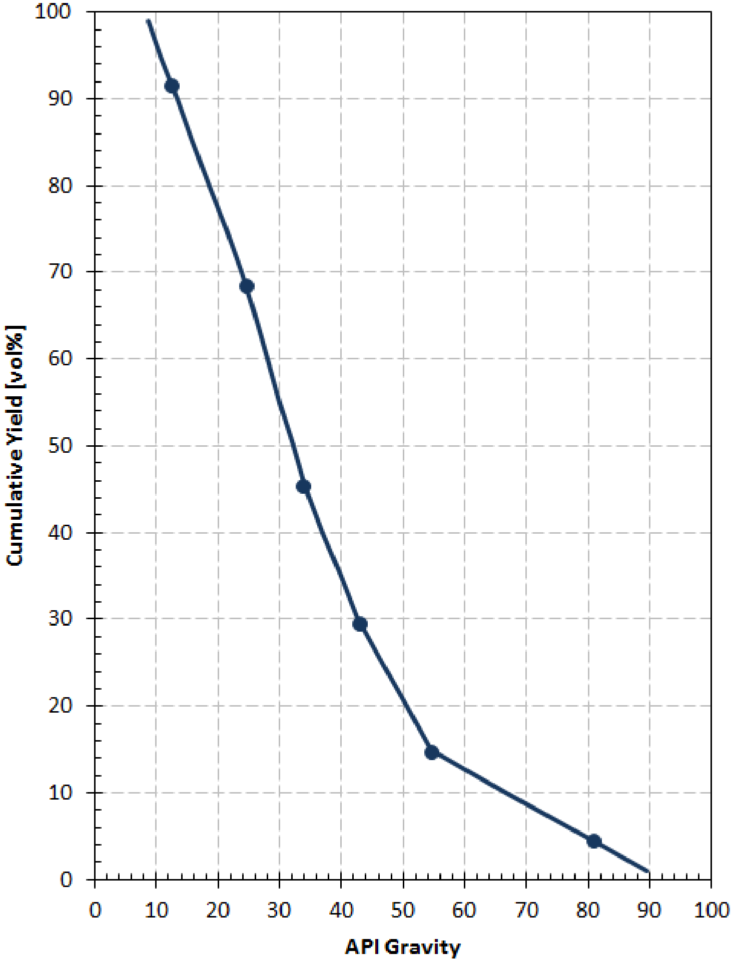


Updated: July 1, 2019

Comparison & Use of Yield Values

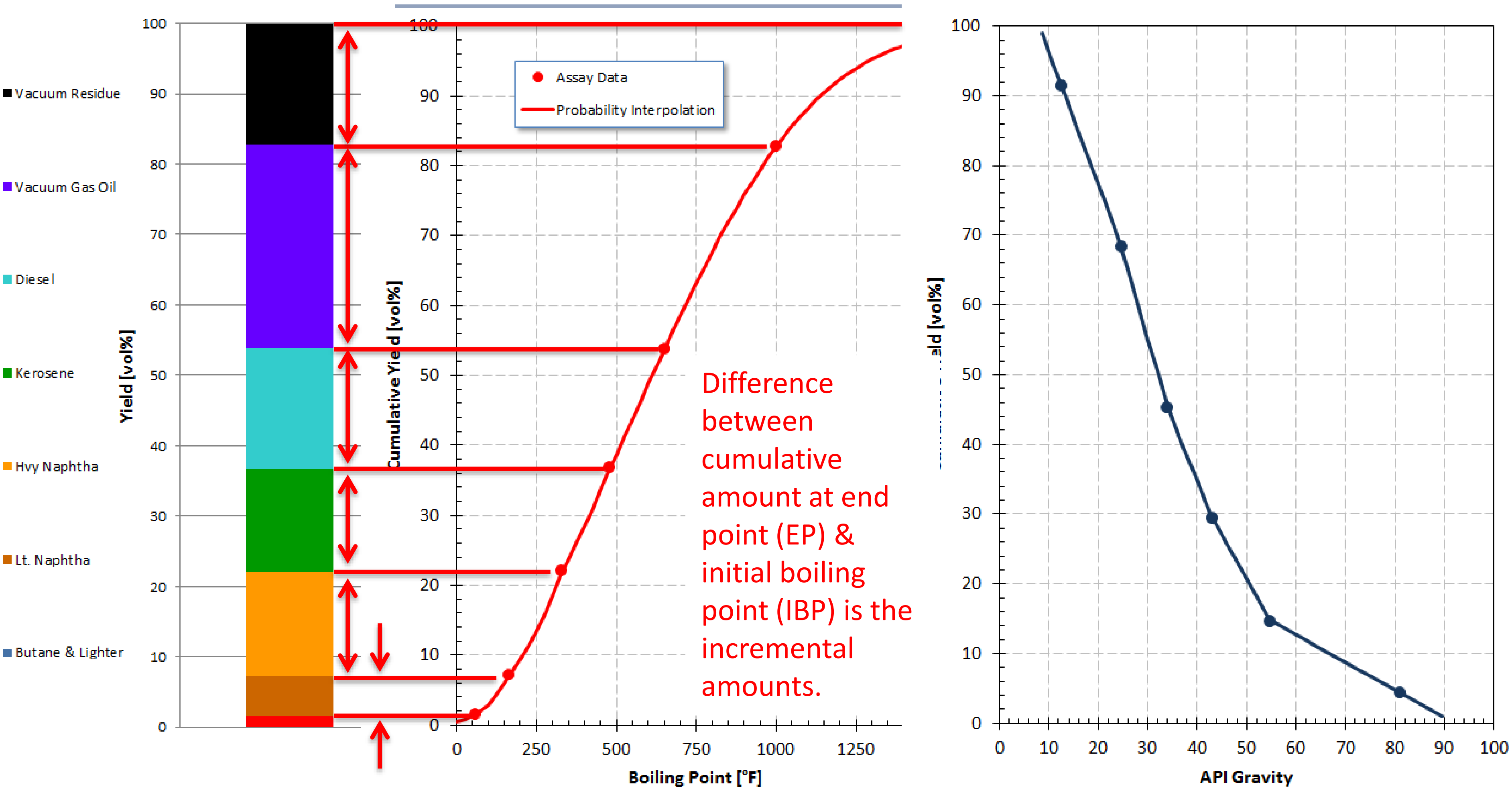


"Stack up" incremental amounts. Associate temperature between fractions with this cumulative yield.



Updated: July 1, 2019

Comparison & Use of Yield Values



Difference between cumulative amount at end point (EP) & initial boiling point (IBP) is the incremental amounts.

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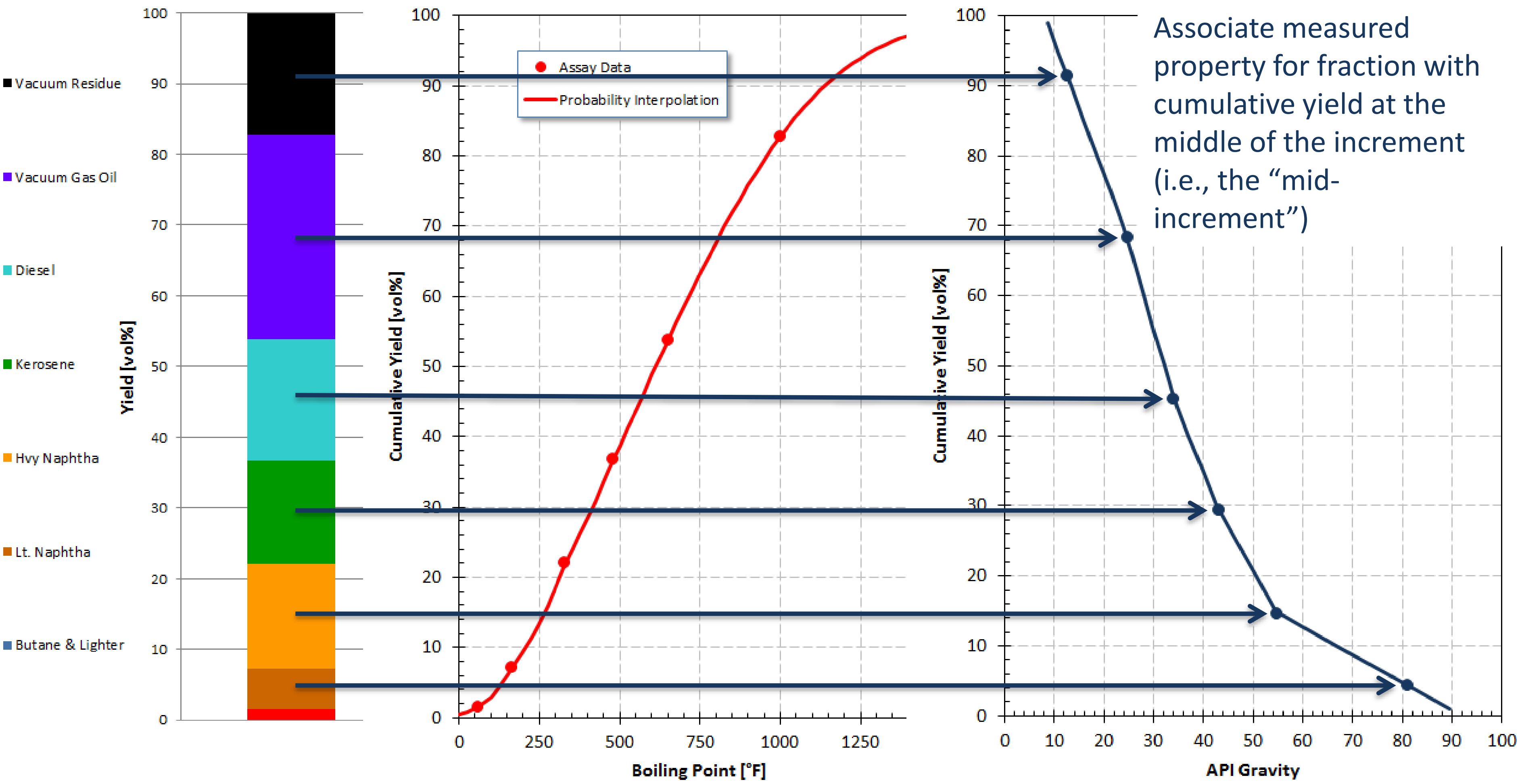
Comparison & Use of Yield Values



Associate measured property for fraction with cumulative yield at the middle of the increment (i.e., the "mid-increment")

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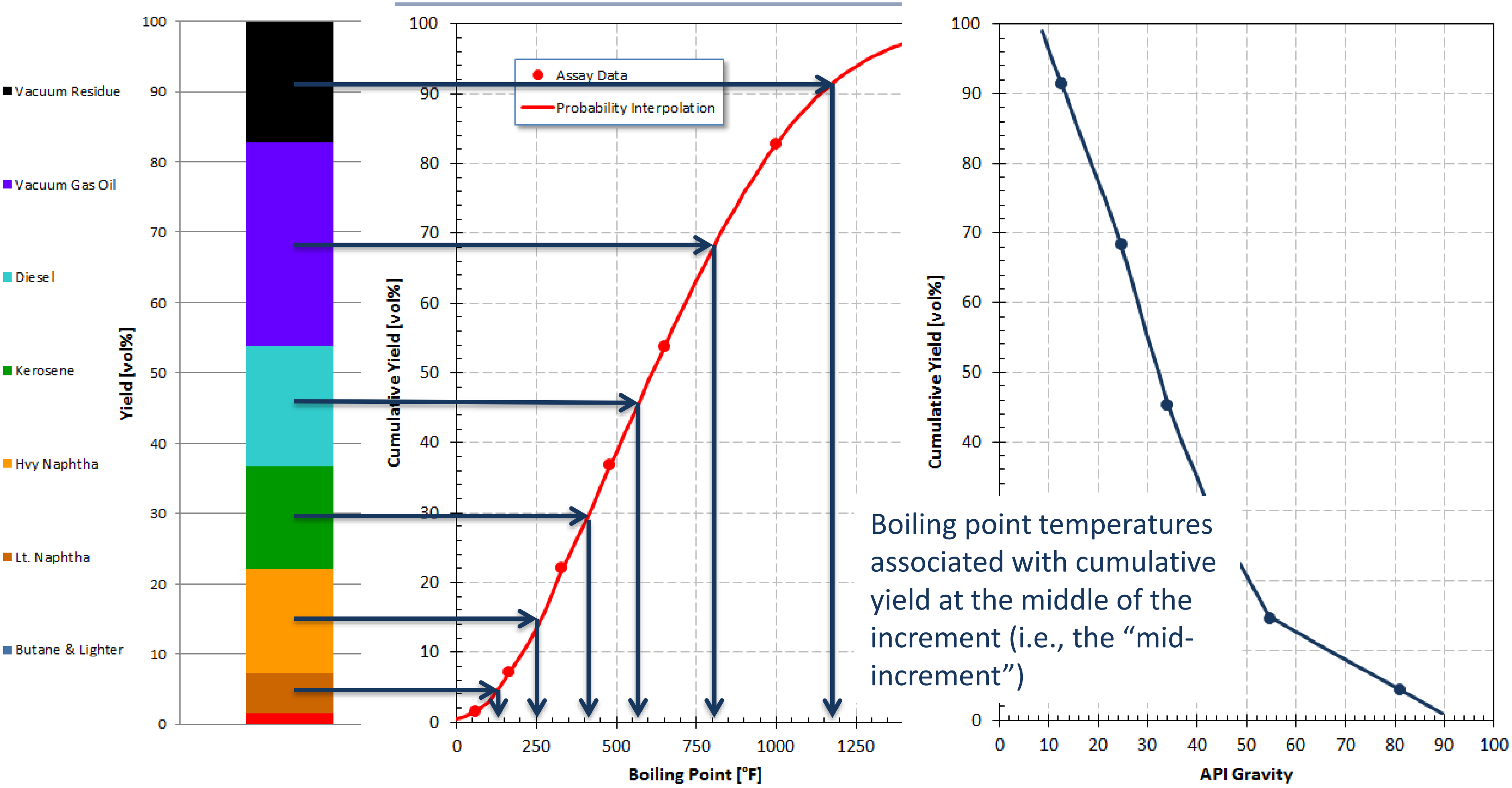
Comparison & Use of Yield Values



Boiling point temperatures associated with cumulative yield at the middle of the increment (i.e., the "mid-increment")

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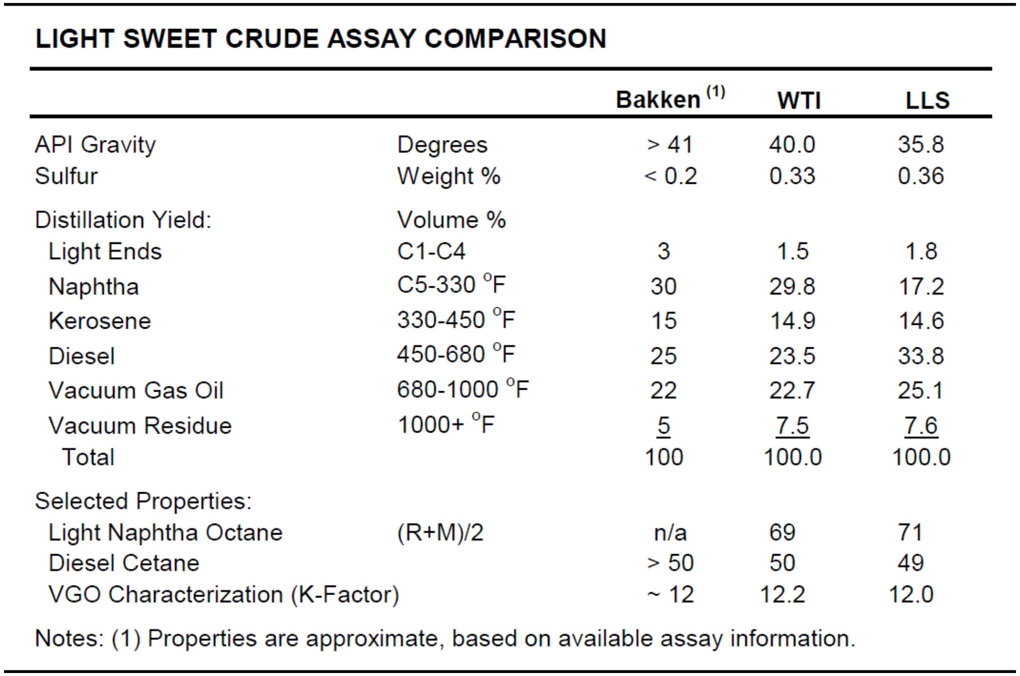
Other Crude Oil Assays – Light Crudes

Property	**Bakken**	**WTI**
API Gravity	41	39
Sulfur, wt%	0.2	0.32
Distillation Yield, volume %		
Lt Ends C1-C4	3.5	3.4
Naphtha C5-360 °F	36.3	32.1
Kerosene 360-500 °F	14.7	13.8
Diesel 500-650 °F	14.3	14.1
Vacuum Gas Oil 650-1050 °F	26.1	27.1
Vacuum Residue 1050+ °F	5.2	9.4
Bottoms Quality -- Vacuum Resid 1050+°F		
Yield, Vol. %	5.2	9.4
API Gravity	14	11.4
Sulfur, Wt. %	0.75	1.09
Vanadium, ppm	2	87
Nickel, ppm	7	41
Concarbon, Wt. %	11.3	18.2



LIGHT SWEET CRUDE ASSAY COMPARISON

		Bakken [(1)]	**WTI**	**LLS**
API Gravity	Degrees	> 41	40.0	35.8
Sulfur	Weight %	< 0.2	0.33	0.36
Distillation Yield:	Volume %			
Light Ends	C1-C4	3	1.5	1.8
Naphtha	C5-330 °F	30	29.8	17.2
Kerosene	330-450 °F	15	14.9	14.6
Diesel	450-680 °F	25	23.5	33.8
Vacuum Gas Oil	680-1000 °F	22	22.7	25.1
Vacuum Residue	1000+ °F	5	7.5	7.6
Total		100	100.0	100.0
Selected Properties:				
Light Naphtha Octane	(R+M)/2	n/a	69	71
Diesel Cetane		> 50	50	49
VGO Characterization (K-Factor)		~ 12	12.2	12.0

Notes: (1) Properties are approximate, based on available assay information.

http://www.turnermason.com/Publications/petroleum-publications_assets/Bakken-Crude.pdf

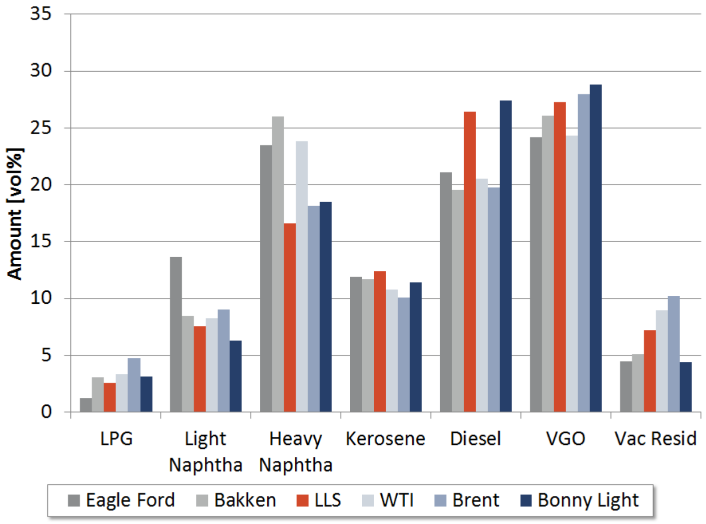
Hill, D., et.al.
North Dakota Refining Capacity Study, Final Technical Report
DOE Award No. DE-FE0000516, January 5, 2011

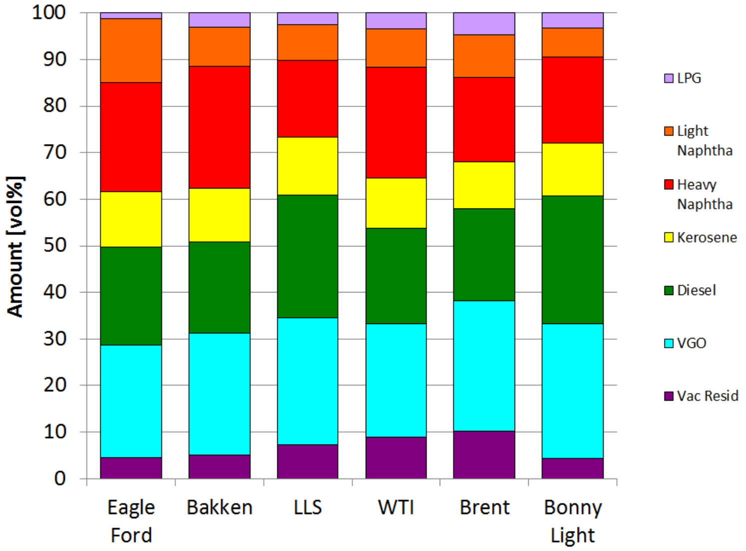
Updated: July 1, 2019

Other Crude Oil Assays – Light Crudes

Product	Temperature [°F]	Yield [vol%] Eagle Ford (Pool Value)	LLS
LPG (C1-C4)	< 85	1.13	2.54
Light Naphtha (C5+)	85 - 200	13.63	7.58
Heavy Naphtha	200 - 350	23.47	16.58
Kerosene	350 - 450	11.93	12.40
Diesel	450 - 650	21.08	26.40
VGO	650 - 1050	24.21	27.30
Residual Fuel Oil	1050+	4.47	7.20
Total		99.92	100.00

METHODOLOGY AND SPECIFICATIONS GUIDE
The Eagle Ford Marker: Rationale and methodology
Platts, McGraw Hill Financial
October 2012
https://www.platts.com/IM.Platts.Content/MethodologyReferences/MethodologySpecs/eaglefordmarker.pdf





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COLORADO SCHOOL OF MINES
EARTH • ENERGY • ENVIRONMENT

Products as defined by their properties & specifications

Updated: July 1, 2019

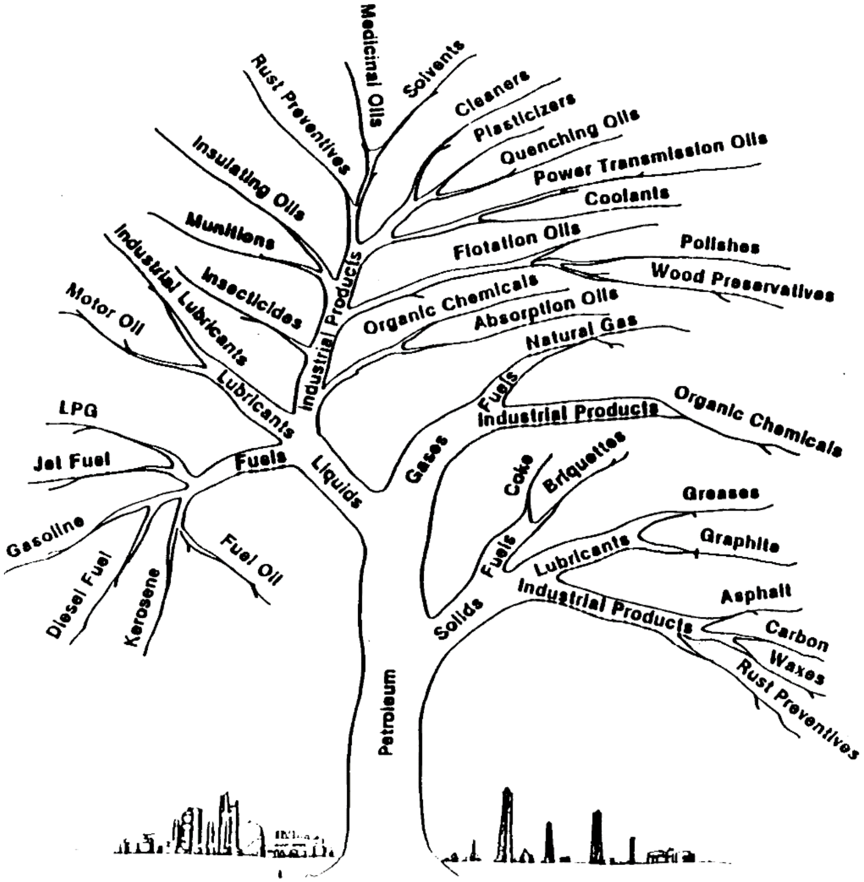
Petroleum Products

There are specifications for over 2,000 individual refinery products

- Took a full century to develop markets for all fractions of crude oil

Intermediate feedstocks can be routed to various units to produce different blend stocks

- Highly dependent on economics specific to that refinery & contractual limitations



Ref: Unknown origin. Possibly Socony-Vacuum Oil Company, Inc. (1943)

Petroleum Products

Refinery Fuel Gas (Still Gas)

Liquefied Petroleum Gas (LPG)
- Ethane & Ethane-Rich Streams
- Propanes
- Butanes

Gasoline
- Naphtha

Middle Distillates
- Kerosene
- Jet Fuel
- Diesel, Home Heating, & Fuel Oil

Gas Oil & Town Gas

Asphalt & Road Oil

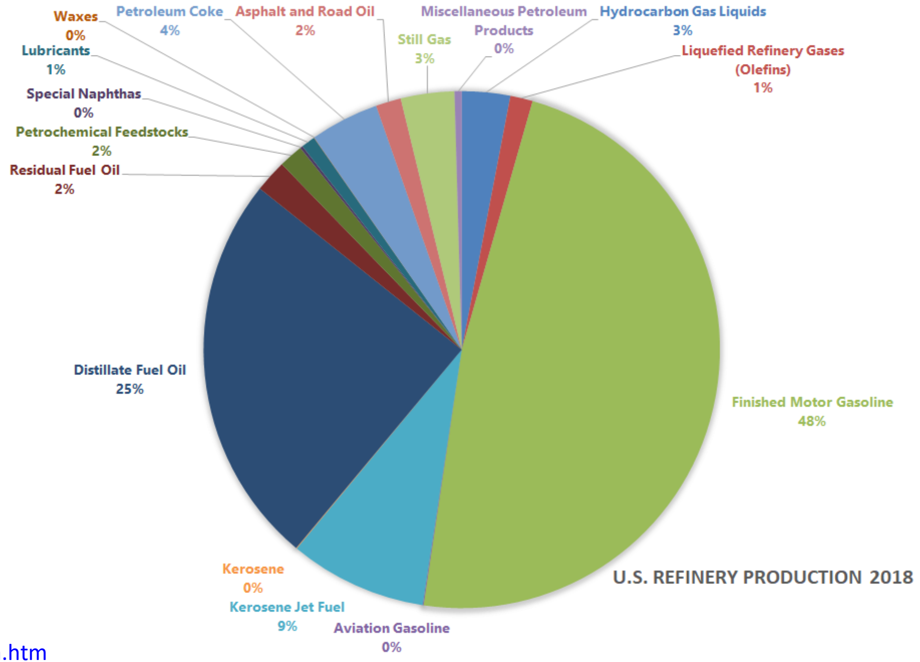
Petroleum Coke

Lubricants

Wax

Petrochemicals

Sulfur



EIA, refinery yield data – updated June 7, 2019
http://tonto.eia.doe.gov/dnav/pet/pet_pnp_pct_dc_nus_pct_m.htm

Updated: July 1, 2019

Sources of Product Specifications

State & Federal regulatory agencies

- Environmental laws
- Reflect need to reduce pollution in manufacturing & use of fuels

ASTM (American Society for Testing and Materials) Specifications & associated test procedures

- Specifications drafted considering positions of industry & regulatory agencies

Industry associations

- American Petroleum Institute
- Gas Processors Association
- Asphalt Institute

Between companies based on "typical" specs

- Negotiated
- Deviations have predetermined price adjustments

What Makes Gasoline Gasoline? What Makes Diesel Diesel?

<u>**Gasoline**</u>

Must be a good fuel in a spark-ignited internal combustion engine

- Proper atomization & vaporization when mixed with combustion air
- Boiling points of chemical species
- Boiling point range of mixture
- Ability to compress & not ignite prior to spark-ignition
  - Measured as octane number
- Minimal combustion byproducts – want complete combustion

Minimize environmental unfriendliness

- Volatility in storage tanks
  - RVP – Reid Vapor Pressure
- Individual chemical species
  - Sulfur content
  - Benzene

<u>**Diesel**</u>

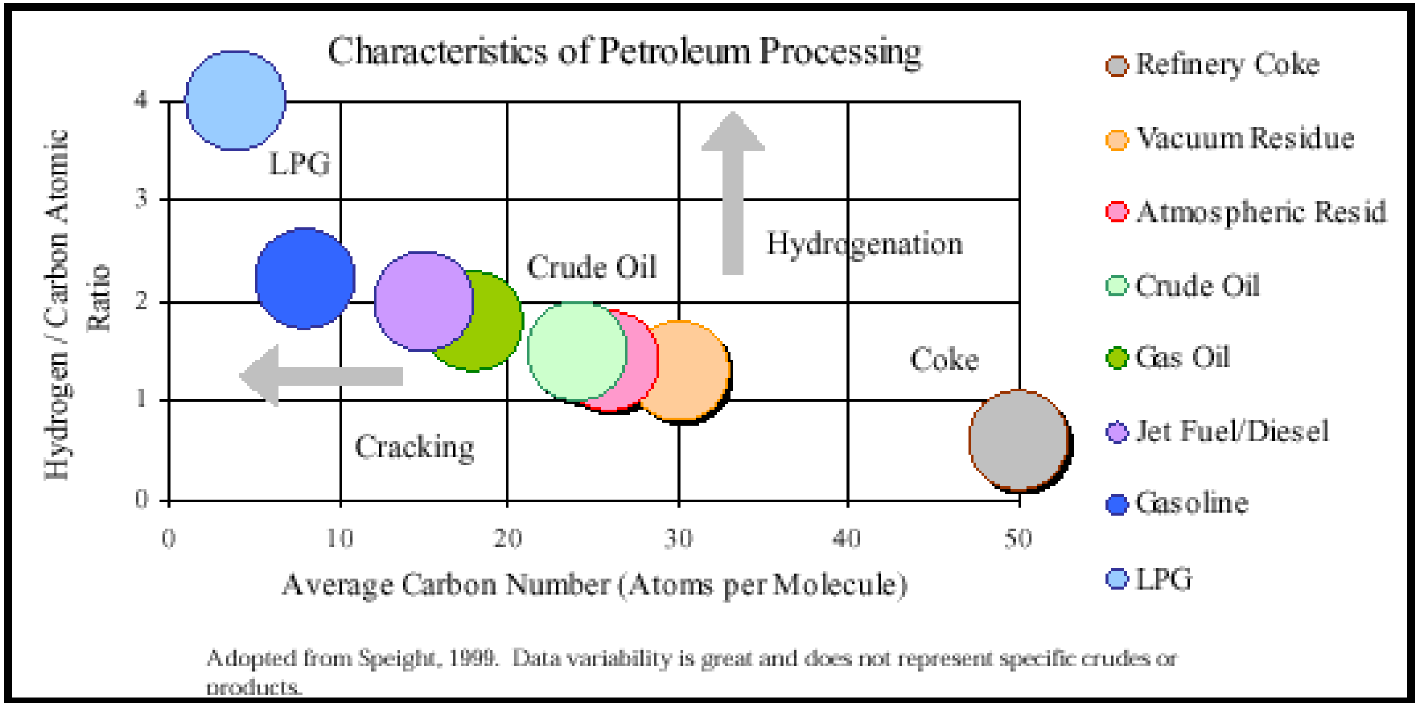
Must be a good fuel in a non-spark-ignited fuel-injected internal combustion engine

- Proper atomization when injected into compressed air
- Boiling point range of mixture
- Ability to ignite when injected into compressed air
  - Measured as cetane number
- Minimal combustion byproducts – want complete combustion

Minimize environmental unfriendliness

- Volatility in storage tanks
  - Flash point
- Individual chemical species
  - Sulfur content

Characteristics of Petroleum Products



Adopted from Speight, 1999. Data variability is great and does not represent specific crudes or products.

Refining Overview – Petroleum Processes & Products,
by Freeman Self, Ed Ekholm, & Keith Bowers, AIChE CD-ROM, 2000

Fuel Gas Specifications

Parameter	Specification
Temperature Range	40°F to 120°F
Pressure	500 to 1,000 psig
Gross Heating Value	950 – 1150 BTU/scf
Hydrocarbon Dew Point[1]	10°F – 20°F
Water	4 or 7 lbs/million scf
Total Sulfur	5 to 20 grains/100 scf
Hydrogen Sulfide H_2S	4 to 16 ppmv
Mercaptans	1 to 5 grains/100 scf
Total Nitrogen & CO_2	4 mol%
CO_2 (also Total N_2 + CO_2)	2 to 3 mol%
Oxygen	0.1 to 0.4 mole %

[1] At pipeline pressure

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Liquefied Petroleum Gas (LPG)

Characteristic	Commercial Propane	Commercial Butane	ASTM Test
	C3 & C3=	C4 & C4=	D1267-02
Vapor Pressure @ 100°F	208	70	D1267-02
95 vol%@ max °F	-37°F	+36°F	D1837-64
C4+ max	2.5%		D2163-77
C5+max		2.0%	D2163-77

Vapor pressure "spec" is actually an approximate guideline for defining the light ends content of the LPG mixture.

Natural Gasoline Specifications

Characteristic	GPA Specifications	ASTM Test
Reid Vapor Pressure	10 to 34 psig	D-323
Evaporation at 140°F	25 to 85 %	D-216
Evaporation at 275°F	> 90 %	D-216
End Point		D-216

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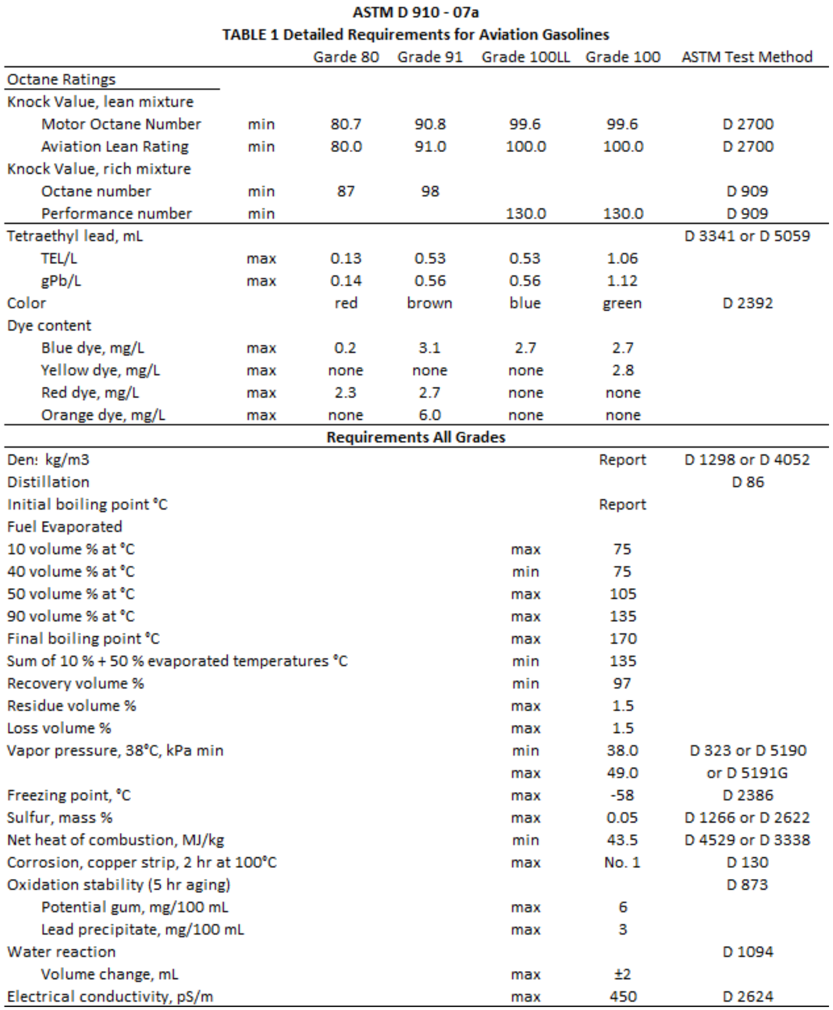
Aviation Gasoline Specifications



ASTM D 910 - 07a

TABLE 1 Detailed Requirements for Aviation Gasolines

		Garde 80	Grade 91	Grade 100LL	Grade 100	ASTM Test Method
Octane Ratings						
Knock Value, lean mixture						
Motor Octane Number	min	80.7	90.8	99.6	99.6	D 2700
Aviation Lean Rating	min	80.0	91.0	100.0	100.0	D 2700
Knock Value, rich mixture						
Octane number	min	87	98			D 909
Performance number	min			130.0	130.0	D 909
Tetraethyl lead, mL						D 3341 or D 5059
TEL/L	max	0.13	0.53	0.53	1.06	
gPb/L	max	0.14	0.56	0.56	1.12	
Color		red	brown	blue	green	D 2392
Dye content						
Blue dye, mg/L	max	0.2	3.1	2.7	2.7	
Yellow dye, mg/L	max	none	none	none	2.8	
Red dye, mg/L	max	2.3	2.7	none	none	
Orange dye, mg/L	max	none	6.0	none	none	
Requirements All Grades						
Den: kg/m3					Report	D 1298 or D 4052
Distillation						D 86
Initial boiling point °C					Report	
Fuel Evaporated						
10 volume % at °C				max	75	
40 volume % at °C				min	75	
50 volume % at °C				max	105	
90 volume % at °C				max	135	
Final boiling point °C				max	170	
Sum of 10 % + 50 % evaporated temperatures °C				min	135	
Recovery volume %				min	97	
Residue volume %				max	1.5	
Loss volume %				max	1.5	
Vapor pressure, 38°C, kPa min				min	38.0	D 323 or D 5190
				max	49.0	or D 5191G
Freezing point, °C				max	-58	D 2386
Sulfur, mass %				max	0.05	D 1266 or D 2622
Net heat of combustion, MJ/kg				min	43.5	D 4529 or D 3338
Corrosion, copper strip, 2 hr at 100°C				max	No. 1	D 130
Oxidation stability (5 hr aging)						D 873
Potential gum, mg/100 mL				max	6	
Lead precipitate, mg/100 mL				max	3	
Water reaction						D 1094
Volume change, mL				max	±2	
Electrical conductivity, pS/m				max	450	D 2624

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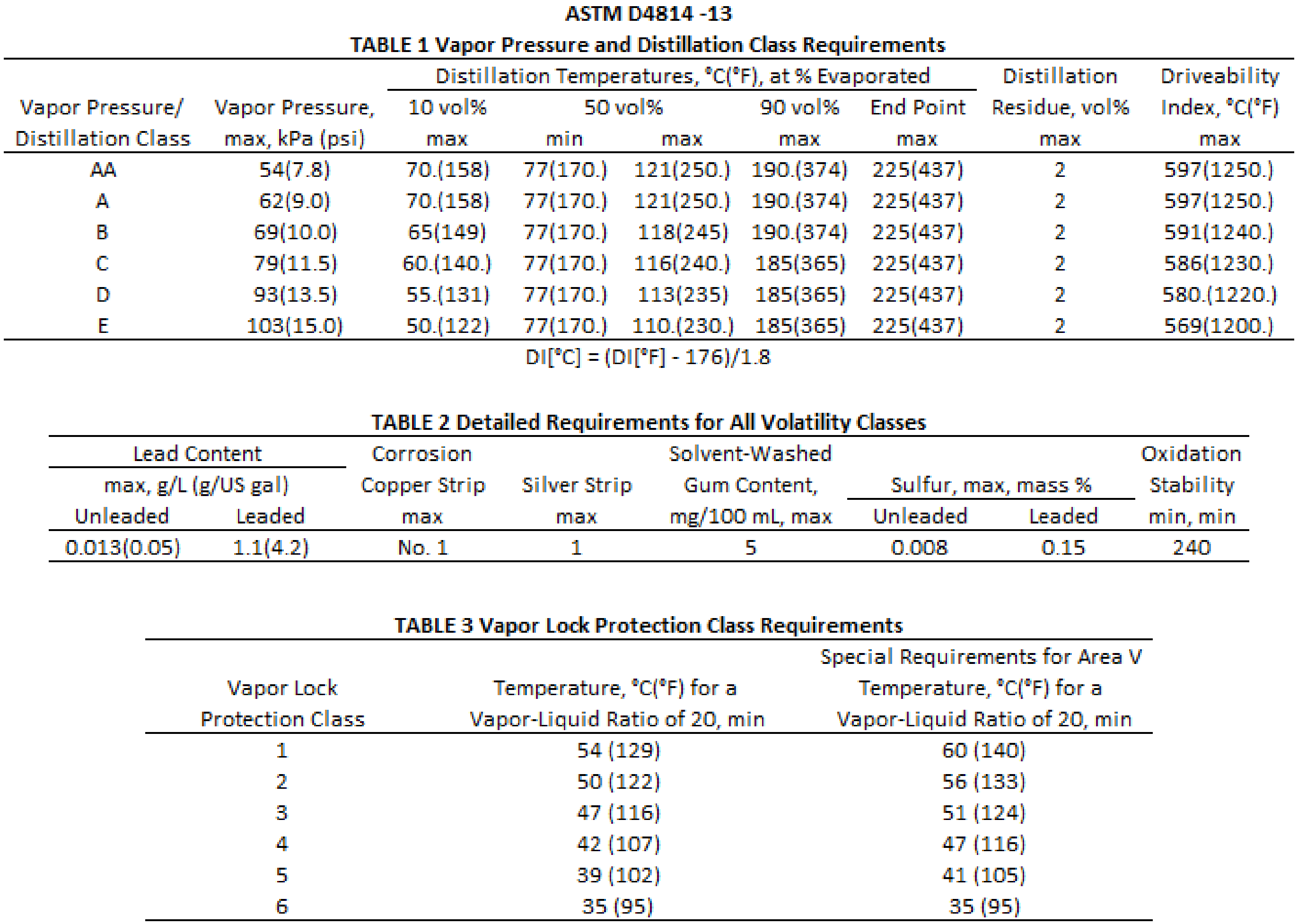
Motor Gasoline Specifications



ASTM D4814 -13

TABLE 1 Vapor Pressure and Distillation Class Requirements

		Distillation Temperatures, °C(°F), at % Evaporated					Distillation	Driveability
Vapor Pressure/ Distillation Class	Vapor Pressure, max, kPa (psi)	10 vol% max	50 vol% min	50 vol% max	90 vol% max	End Point max	Residue, vol% max	Index, °C(°F) max
AA	54(7.8)	70.(158)	77(170.)	121(250.)	190.(374)	225(437)	2	597(1250.)
A	62(9.0)	70.(158)	77(170.)	121(250.)	190.(374)	225(437)	2	597(1250.)
B	69(10.0)	65(149)	77(170.)	118(245)	190.(374)	225(437)	2	591(1240.)
C	79(11.5)	60.(140.)	77(170.)	116(240.)	185(365)	225(437)	2	586(1230.)
D	93(13.5)	55.(131)	77(170.)	113(235)	185(365)	225(437)	2	580.(1220.)
E	103(15.0)	50.(122)	77(170.)	110.(230.)	185(365)	225(437)	2	569(1200.)

DI[°C] = (DI[°F] - 176)/1.8

TABLE 2 Detailed Requirements for All Volatility Classes

Lead Content max, g/L (g/US gal)		Corrosion Copper Strip	Silver Strip	Solvent-Washed Gum Content,	Sulfur, max, mass %		Oxidation Stability
Unleaded	Leaded	max	max	mg/100 mL, max	Unleaded	Leaded	min, min
0.013(0.05)	1.1(4.2)	No. 1	1	5	0.008	0.15	240

TABLE 3 Vapor Lock Protection Class Requirements

Vapor Lock Protection Class	Temperature, °C(°F) for a Vapor-Liquid Ratio of 20, min	Special Requirements for Area V Temperature, °C(°F) for a Vapor-Liquid Ratio of 20, min
1	54 (129)	60 (140)
2	50 (122)	56 (133)
3	47 (116)	51 (124)
4	42 (107)	47 (116)
5	39 (102)	41 (105)
6	35 (95)	35 (95)

Motor Gasoline Volatility Classes (ASTM D 4814-13)

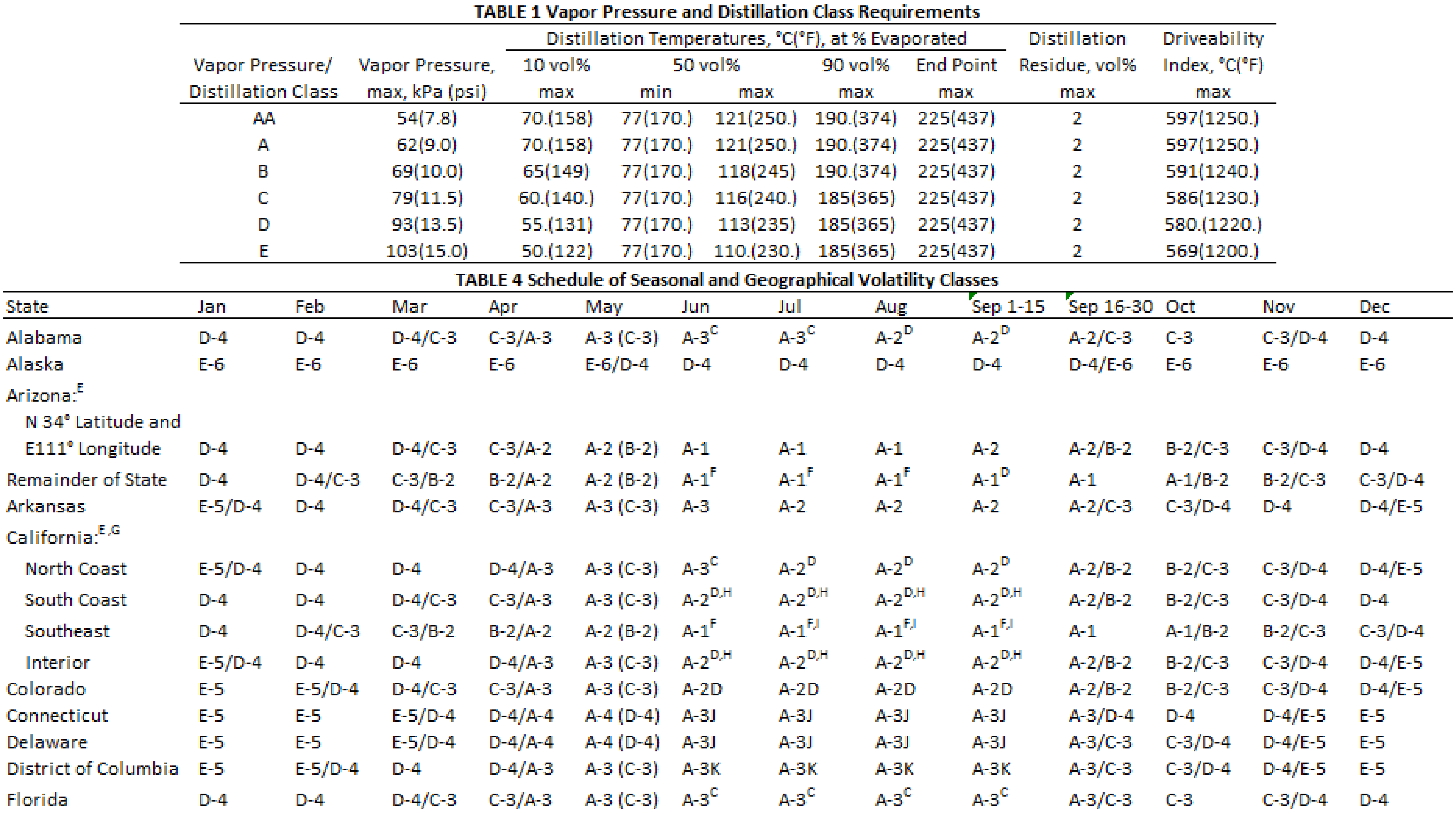


TABLE 1 Vapor Pressure and Distillation Class Requirements

Vapor Pressure/ Distillation Class	Vapor Pressure, max, kPa (psi)	Distillation Temperatures, °C(°F), at % Evaporated					Distillation Residue, vol% max	Driveability Index, °C(°F) max
		10 vol% max	50 vol% min	50 vol% max	90 vol% max	End Point max		
AA	54(7.8)	70.(158)	77(170.)	121(250.)	190.(374)	225(437)	2	597(1250.)
A	62(9.0)	70.(158)	77(170.)	121(250.)	190.(374)	225(437)	2	597(1250.)
B	69(10.0)	65(149)	77(170.)	118(245)	190.(374)	225(437)	2	591(1240.)
C	79(11.5)	60.(140.)	77(170.)	116(240.)	185(365)	225(437)	2	586(1230.)
D	93(13.5)	55.(131)	77(170.)	113(235)	185(365)	225(437)	2	580.(1220.)
E	103(15.0)	50.(122)	77(170.)	110.(230.)	185(365)	225(437)	2	569(1200.)

TABLE 4 Schedule of Seasonal and Geographical Volatility Classes

State	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep 1-15	Sep 16-30	Oct	Nov	Dec
Alabama	D-4	D-4	D-4/C-3	C-3/A-3	A-3 (C-3)	A-3[C]	A-3[C]	A-2[D]	A-2[D]	A-2/C-3	C-3	C-3/D-4	D-4
Alaska	E-6	E-6	E-6	E-6	E-6/D-4	D-4	D-4	D-4	D-4	D-4/E-6	E-6	E-6	E-6
Arizona:[E]													
N 34° Latitude and E111° Longitude	D-4	D-4	D-4/C-3	C-3/A-2	A-2 (B-2)	A-1	A-1	A-1	A-2	A-2/B-2	B-2/C-3	C-3/D-4	D-4
Remainder of State	D-4	D-4/C-3	C-3/B-2	B-2/A-2	A-2 (B-2)	A-1[F]	A-1[F]	A-1[F]	A-1[D]	A-1	A-1/B-2	B-2/C-3	C-3/D-4
Arkansas	E-5/D-4	D-4	D-4/C-3	C-3/A-3	A-3 (C-3)	A-3	A-2	A-2	A-2	A-2/C-3	C-3/D-4	D-4	D-4/E-5
California:[E,G]													
North Coast	E-5/D-4	D-4	D-4	D-4/A-3	A-3 (C-3)	A-3[C]	A-2[D]	A-2[D]	A-2[D]	A-2/B-2	B-2/C-3	C-3/D-4	D-4/E-5
South Coast	D-4	D-4	D-4/C-3	C-3/A-3	A-3 (C-3)	A-2[D,H]	A-2[D,H]	A-2[D,H]	A-2[D,H]	A-2/B-2	B-2/C-3	C-3/D-4	D-4
Southeast	D-4	D-4/C-3	C-3/B-2	B-2/A-2	A-2 (B-2)	A-1[F]	A-1[F,J]	A-1[F,J]	A-1[F,J]	A-1	A-1/B-2	B-2/C-3	C-3/D-4
Interior	E-5/D-4	D-4	D-4	D-4/A-3	A-3 (C-3)	A-2[D,H]	A-2[D,H]	A-2[D,H]	A-2[D,H]	A-2/B-2	B-2/C-3	C-3/D-4	D-4/E-5
Colorado	E-5	E-5/D-4	D-4/C-3	C-3/A-3	A-3 (C-3)	A-2D	A-2D	A-2D	A-2D	A-2/B-2	B-2/C-3	C-3/D-4	D-4/E-5
Connecticut	E-5	E-5	E-5/D-4	D-4/A-4	A-4 (D-4)	A-3J	A-3J	A-3J	A-3J	A-3/D-4	D-4	D-4/E-5	E-5
Delaware	E-5	E-5	E-5/D-4	D-4/A-4	A-4 (D-4)	A-3J	A-3J	A-3J	A-3J	A-3/C-3	C-3/D-4	D-4/E-5	E-5
District of Columbia	E-5	E-5/D-4	D-4	D-4/A-3	A-3 (C-3)	A-3K	A-3K	A-3K	A-3K	A-3/C-3	C-3/D-4	D-4/E-5	E-5
Florida	D-4	D-4	D-4/C-3	C-3/A-3	A-3 (C-3)	A-3[C]	A-3[C]	A-3[C]	A-3[C]	A-3/C-3	C-3	C-3/D-4	D-4

Updated: July 1, 2019

Other Gasoline Considerations

Reformulated gasoline (RFG) blended to burn cleaner by reducing smog-forming and toxic pollutants

- Clean Air Act requires RFG used in cities with the worst smog pollution
- Clean Air Act required RFG to contain 2 wt% oxygen
  - MTBE & ethanol were the two most commonly used substances
  - MTBE legislated out of use because of health concerns
  - Oxygenate content regulation superceeded by the Renewable Fuel Standard

RBOB – Reformulated Blendstock for Oxygenate Blending

- Lower RVP to account for 1.5 psi increase due to 10 vol% ethanol

Benzene content

- Conventional gasoline could have 1.0 vol% benzene (max) pre-2011
- New regulations Jan 1, 2011 reduced benzene in all US gasoline to 0.62 vol%
- Had been proposed by EPA under Mobile Sources Air Toxics (MSAT) Phase 2
- Credit system for refiners that could not meet the 0.62% limit

Sulfur content

- EPA calling for ultra low sulfur gasoline by 2017 – from 30 ppmw (Tier 2) to 10 ppmw (Tier 3)

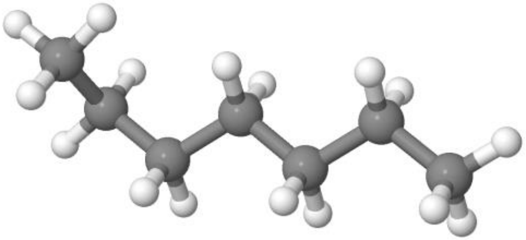
What are Octane Numbers?

Tendency for auto-ignition upon compression

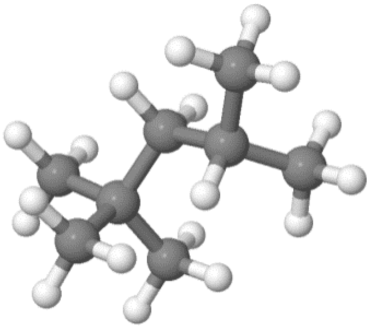
- Gasoline — bad
- Tendency of gasoline to cause “pinging” in engine
- Higher octane number needed for higher
  compression ratios

Different types (typically RON > MON)

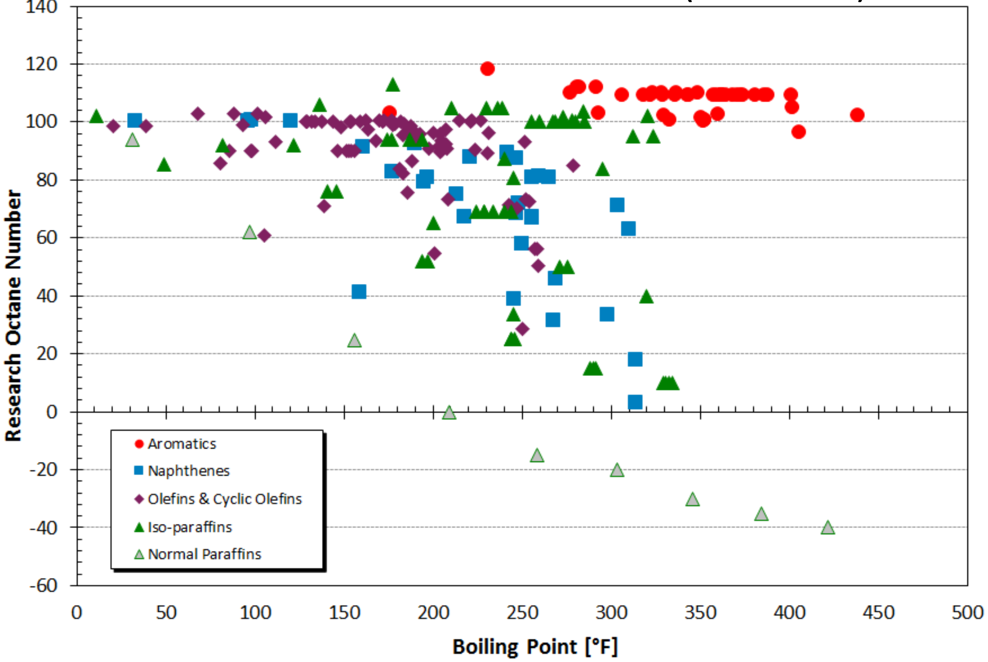
- RON — Research Octane Number
  - Part throttle knock problems
- MON — Motor Octane Number
  - More severe — high speed & high load conditions
- (R+M)/2 – Road Octane Number
  - Also known as AKI (Anti-Knock Index)
  - Reported at the pump in the U.S.



n-Heptane → 0



2,2,4-trimethylpentane → 100 (issoctane)



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What is Reid Vapor Pressure (RVP)?

Specific test to measure volatility at 100°F (37.8°C)

Pressure at 100°F when liquid in contact with air at volume ratio of 1:4

- Related to the true vapor pressure
- Similar to vapor formation in an automobile's gasoline tank

Usually just reported as "psi"

- Actually gauge pressure measured – subtract off the contribution of the atmospheric pressure

Relatively easy to measure

- Direct pressure measurement instead of observation of bubble formation

Procedures controlled by ASTM standards (ASTM D 323)

- A: Low volatility (RVP less than 26 psi / 180 kPa)
- B: Low volatility – horizontal bath
- C: High volatility (RVP greater than 26 psi / 180 kPa)
- D: Aviation gasoline (RVP approximately 7 psi / 50 kPa)

What are alternate RVP-like tests?

ASTM D 5191 – *Standard Test Method for Vapor Pressure of Petroleum Products (Mini Method)*

- Expand liquid from 32°F to 5 times its volume (4:1 volume ratio) at 100°F without adding air
- Referred to as the DVPE (Dry Vapor Pressure Equivalent) & calculated from measured pressure value:

DVPE [psi] = 0.965 (Measured Vapor Pressure [psi]) – 0.548 [psi]

ASTM D 6378 – *Standard Test Method for Determination of Vapor Pressure (VPX) of Petroleum Products, Hydrocarbons, and Hydrocarbon-Oxygenate Mixtures (Triple Expansion Method))*

- Expand liquid to three different volume ratios
- No chilling of initial sample – sample of known volume introduced to chamber at 20°C (76°F) or higher
- Three expansions at a controlled temperature – 100°F equivalent to ASTM D5190
  - Allows for the removal of the partial pressure effects from dissolved air
- RVPE (Reid Vapor Pressure Equivalent) calculated from correlation to measured pressure minus dissolved air effects

Middle Distillates

General classifications

- Kerosene
- Jet fuel
- Distillate fuel oil
  - Diesel
  - Heating oil

Properties

- Flash point
- Cloud point / Pour point
- Aniline point
- Cetane number
- Viscosity
- Water & sediment

Updated: July 1, 2019

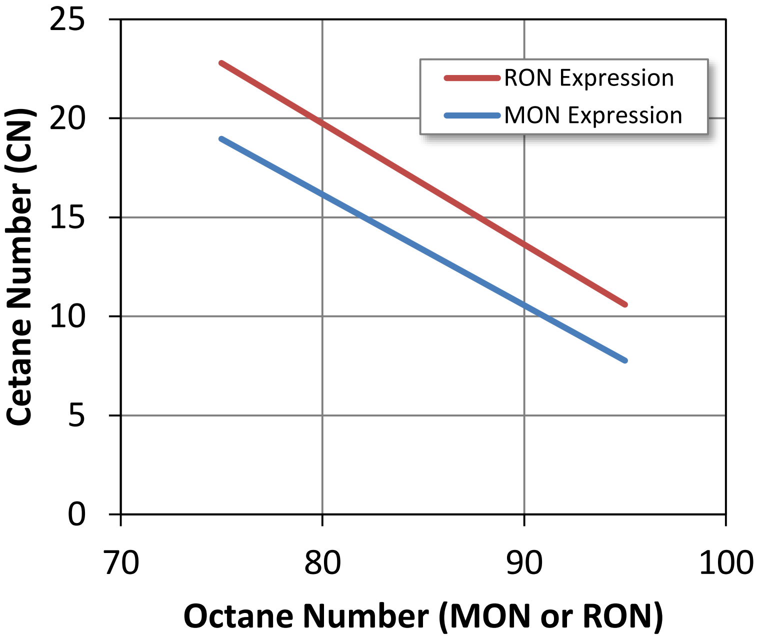
Diesel Cetane Number

One key to diesel quality

- Measures the ability for auto-ignition (essentially the opposite of octane number)
- References:
  - n-hexadecane (cetane) → 100
  - Isocetane (2,2,4,4,6,8,8-heptamethylnonane) → 15
- May be measured by test engine but frequently approximated
  - ASTM D 976 — *Standard Test Methods for Calculated Cetane Index of Distillate Fuels*
  - ASTM D 4737 — *Standard Test Method for Calculated Cetane Index by Four Variable Equation*

Trends

- Cetane number had declined since the middle 1970s – heavier crudes with higher aromatic content
- Trend starting to reverse because of tight oil from shale formations
- More stringent emissions requirements necessitate higher cetane numbers



Bowden, Johnston, & Russell, “Octane-Cetane Relationship”,
Final Report AFLRL No. 33, March 1974,
Prepared by U.S. Army Fuels & Lubricants Research Lab & Southwest Research Institute

Updated: July 1, 2019

What is Flash Point?

"… lowest temperature corrected to a pressure of 101.3 kPa (760 mm Hg) at which application of an ignition source causes the vapors of a specimen of the sample to ignite under specified conditions…"

Procedure strictly controlled by ASTM standards

- D 56 —Tag Closed Tester
- D 92 —Cleveland Open Cup
- D 93 —Pensky-Martens Closed Cup Tester
- D 1310 — Tag Open-Cup Apparatus
- D 3143 — Cutback Asphalt with Tag Open-Cup Apparatus
- D 3278 —Closed-Cup Apparatus
- D 3828 — Small Scale Closed Tester
- D 3941 — Equilibrium Method with Closed-Cup Apparatus

OSHA Flammable Liquid Definitions

GHS (Globally Harmonized System)			Flammable and Combustible Liquids Standard (29 CFR 1910.106)		
Category	**Flash Point °C (°F)**	**Boiling Point °C (°F)**	**Class**	**Flash Point °C (°F)**	**Boiling Point °C (°F)**
Flammable 1	< 23 (73.4)	≤ 35 (95)	Flammable Class IA	< 22.8 (73)	< 37.8 (100)
Flammable 2	< 23 (73.4)	> 35 (95)	Flammable Class IB	< 22.8 (73)	≥ 37.8 (100)
Flammable 3	≥ 23 (73.4) & < 60 (140)		Flammable Class IC	≥ 22.8 (73) & 37.8 (100)	
			Combustile Class II	≥ 37.8 (100) & < 60 (140)	
Flammable 4	> 60 (140) & ≤ 93 (199.4)		Combustile Class IIIA	≥ 60 (140) & < 93.3 (200)	
None			Combustile Class IIIB	≥ 93.3 (200)	

Source: OHSA RIN1218-AC20
https://www.federalregister.gov/articles/2012/03/26/2012-4826/hazard-communication#t-8

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What are Cloud & Pour Points?

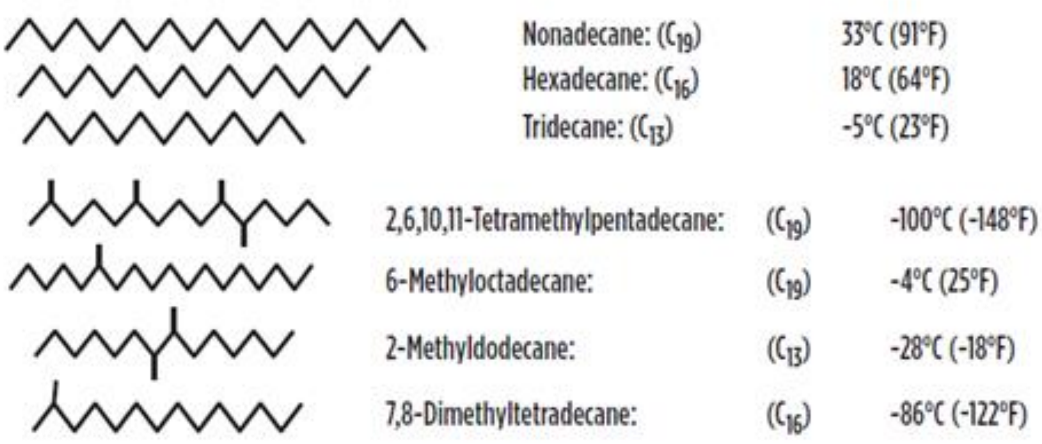
Indicate the tendency to form solids at low temperatures – the higher the temperature the higher the content of solid forming compounds (usually waxes)

Cloud Point

- Temperature at which solids ***start to precipitate*** & give a cloudy appearance
- Tendency to plug filters at cold operating temperatures

Pour Point

- Temperature at which the oil ***becomes a gel*** & cannot flow



Nonadecane:	(C_{19})	33°C (91°F)
Hexadecane:	(C_{16})	18°C (64°F)
Tridecane:	(C_{13})	-5°C (23°F)
2,6,10,11-Tetramethylpentadecane:	(C_{19})	-100°C (-148°F)
6-Methyloctadecane:	(C_{19})	-4°C (25°F)
2-Methyldodecane:	(C_{13})	-28°C (-18°F)
7,8-Dimethyltetradecane:	(C_{16})	-86°C (-122°F)

Melting Points of selected long-chain normal & iso paraffins typically found in middle distillates

Solidification of diesel fuel in a fuel-filtering device after sudden temperature drop
"Consider catalytic dewaxing as a tool to improve diesel cold-flow properties",
Rakoczy & Morse, *Hydrocarbon Processing*, July 2013

Updated: July 1, 2019

Additional Specifications

Sulfur

- Control of sulfur oxides upon combustion
- Three levels, reduction for the traditional five categories

Aniline Point

- Minimum temperature at which equal volumes of aniline ($C_6H_5NH_2$) and the oil are miscible
- The lower the aniline point the greater the aromatic content

Viscosity

- Fluidity during storage at lower temperatures

Sediment & water content

- Controlling contamination

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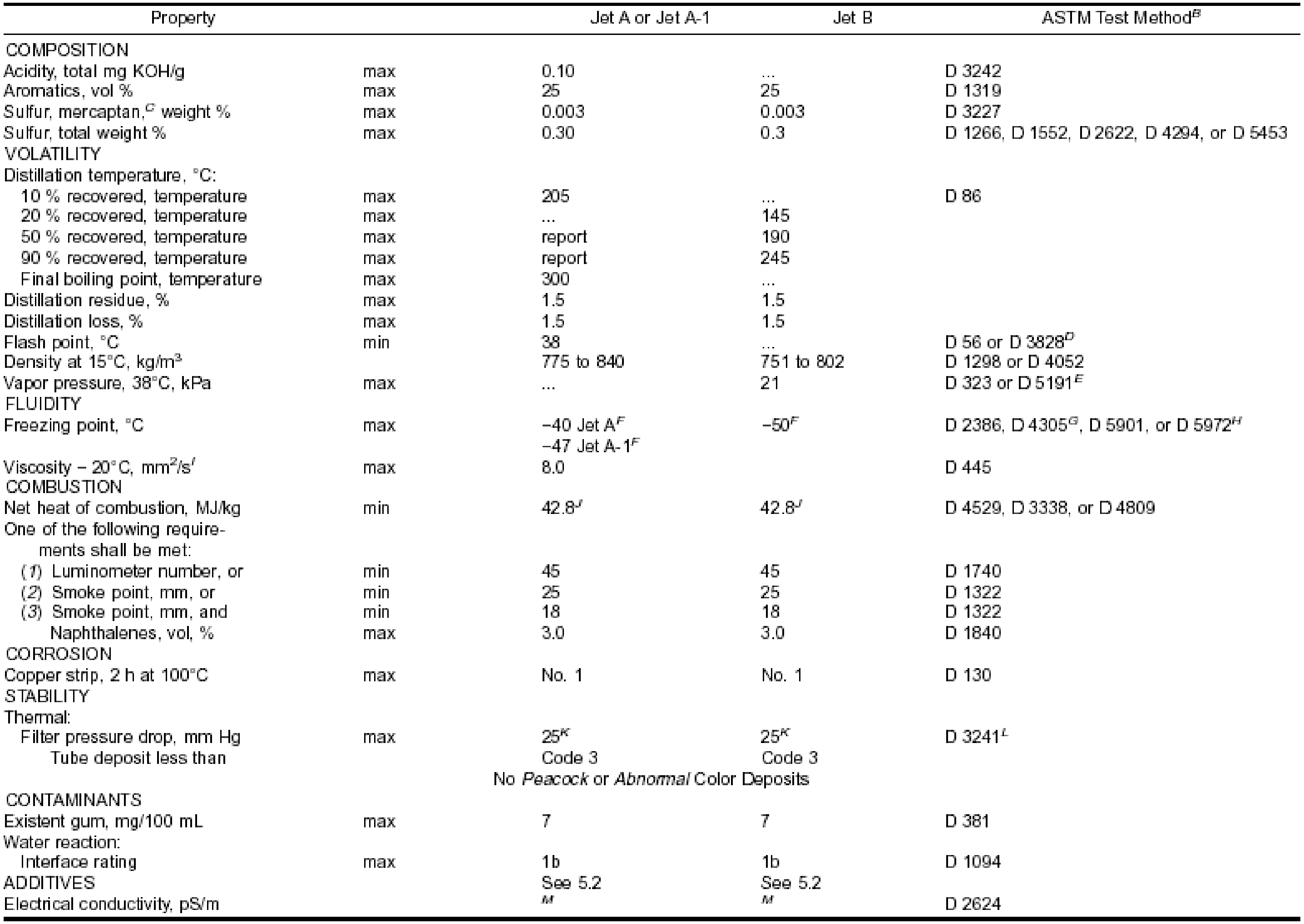
Kerosene Specifications

Parameter	Specification	ASTM Test Method
Flash Point	100°F	ASTM D-56
10% distilled, max	401°F	ASTM D-86
Final Boiling Point	572°F	ASTM D-86
No. 1 sulfur, max	0.04% (No. 1) 0.30% (No. 2)	ASTM D-1266
Burn quality	pass	ASTM D-187

Updated: July 1, 2019

Jet Fuel Specifications



Property		Jet A or Jet A-1	Jet B	ASTM Test Method[B]
COMPOSITION				
Acidity, total mg KOH/g	max	0.10	...	D 3242
Aromatics, vol %	max	25	25	D 1319
Sulfur, mercaptan,[C] weight %	max	0.003	0.003	D 3227
Sulfur, total weight %	max	0.30	0.3	D 1266, D 1552, D 2622, D 4294, or D 5453
VOLATILITY				
Distillation temperature, °C:				
10 % recovered, temperature	max	205	...	D 86
20 % recovered, temperature	max	...	145	
50 % recovered, temperature	max	report	190	
90 % recovered, temperature	max	report	245	
Final boiling point, temperature	max	300	...	
Distillation residue, %	max	1.5	1.5	
Distillation loss, %	max	1.5	1.5	
Flash point, °C	min	38	...	D 56 or D 3828[D]
Density at 15°C, kg/m^3		775 to 840	751 to 802	D 1298 or D 4052
Vapor pressure, 38°C, kPa	max	...	21	D 323 or D 5191[E]
FLUIDITY				
Freezing point, °C	max	−40 Jet A[F] −47 Jet A-1[F]	−50[F]	D 2386, D 4305[G], D 5901, or D 5972[H]
Viscosity − 20°C, mm^2/s[I]	max	8.0		D 445
COMBUSTION				
Net heat of combustion, MJ/kg	min	42.8[J]	42.8[J]	D 4529, D 3338, or D 4809
One of the following requirements shall be met:				
(*1*) Luminometer number, or	min	45	45	D 1740
(*2*) Smoke point, mm, or	min	25	25	D 1322
(*3*) Smoke point, mm, and	min	18	18	D 1322
Naphthalenes, vol, %	max	3.0	3.0	D 1840
CORROSION				
Copper strip, 2 h at 100°C	max	No. 1	No. 1	D 130
STABILITY				
Thermal:				
Filter pressure drop, mm Hg	max	25[K]	25[K]	D 3241[L]
Tube deposit less than		Code 3	Code 3	
		No *Peacock* or *Abnormal* Color Deposits		
CONTAMINANTS				
Existent gum, mg/100 mL	max	7	7	D 381
Water reaction:				
Interface rating	max	1b	1b	D 1094
ADDITIVES		See 5.2	See 5.2	
Electrical conductivity, pS/m		[M]	[M]	D 2624

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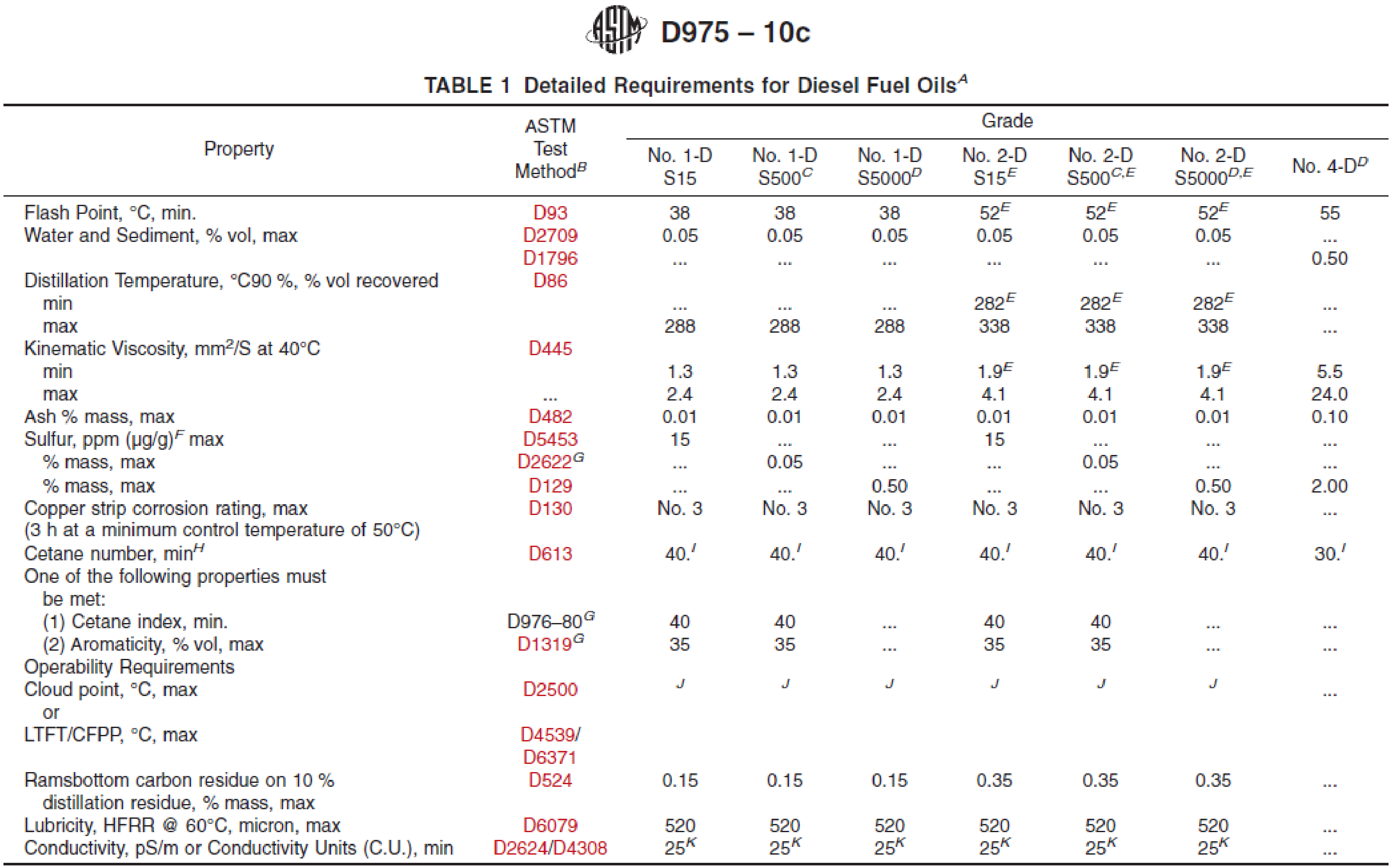
Stationary Turbine Fuel & Diesel Classes

0-GT	Includes naphtha, jet fuel B & other volatile hydrocarbons
1-GT	Approximates No. 1 Fuel Oil (D 396) & 1-D diesel (D 975)
2-GT	Approximates No. 2 Fuel Oil (D 396) & 2-D diesel (D 975)
3-GT	Approximates No. 4 & No. 5 fuel oils
4-GT	Approximates No. 4 & No. 5 fuel oils

No. 1	Mostly from virgin stock. "Superdiesel." Used for autos & high-speed engines.
No.2	Wider boiling & contains cracked stocks. Very similar to home heating fuel (w/o additives).
No.4	Traditionally largest volume produced. Used for marine, railroads, & other low to medium speed power plants

Diesel Specifications



D975 – 10c

TABLE 1 Detailed Requirements for Diesel Fuel Oils[A]

Property	ASTM Test Method[B]	Grade No. 1-D S15	No. 1-D S500[C]	No. 1-D S5000[D]	No. 2-D S15[E]	No. 2-D S500[C,E]	No. 2-D S5000[D,E]	No. 4-D[D]
Flash Point, °C, min.	D93	38	38	38	52[E]	52[E]	52[E]	55
Water and Sediment, % vol, max	D2709	0.05	0.05	0.05	0.05	0.05	0.05	...
	D1796	...	...	...	...	...	...	0.50
Distillation Temperature, °C90 %, % vol recovered	D86							
min		...	...	...	282[E]	282[E]	282[E]	...
max		288	288	288	338	338	338	...
Kinematic Viscosity, mm^2/S at 40°C	D445							
min		1.3	1.3	1.3	1.9[E]	1.9[E]	1.9[E]	5.5
max	...	2.4	2.4	2.4	4.1	4.1	4.1	24.0
Ash % mass, max	D482	0.01	0.01	0.01	0.01	0.01	0.01	0.10
Sulfur, ppm (µg/g)[F] max	D5453	15	...	...	15	...	...	...
% mass, max	D2622[G]	...	0.05	...	...	0.05	...	...
% mass, max	D129	...	...	0.50	...	...	0.50	2.00
Copper strip corrosion rating, max (3 h at a minimum control temperature of 50°C)	D130	No. 3	No. 3	No. 3	No. 3	No. 3	No. 3	...
Cetane number, min[H]	D613	40.[I]	40.[I]	40.[I]	40.[I]	40.[I]	40.[I]	30.[I]
One of the following properties must be met:								
(1) Cetane index, min.	D976–80[G]	40	40	...	40	40	...	...
(2) Aromaticity, % vol, max	D1319[G]	35	35	...	35	35	...	...
Operability Requirements								
Cloud point, °C, max	D2500	[J]	[J]	[J]	[J]	[J]	[J]	...
or								
LTFT/CFPP, °C, max	D4539/ D6371							
Ramsbottom carbon residue on 10 % distillation residue, % mass, max	D524	0.15	0.15	0.15	0.35	0.35	0.35	...
Lubricity, HFRR @ 60°C, micron, max	D6079	520	520	520	520	520	520	...
Conductivity, pS/m or Conductivity Units (C.U.), min	D2624/D4308	25[K]	25[K]	25[K]	25[K]	25[K]	25[K]	...

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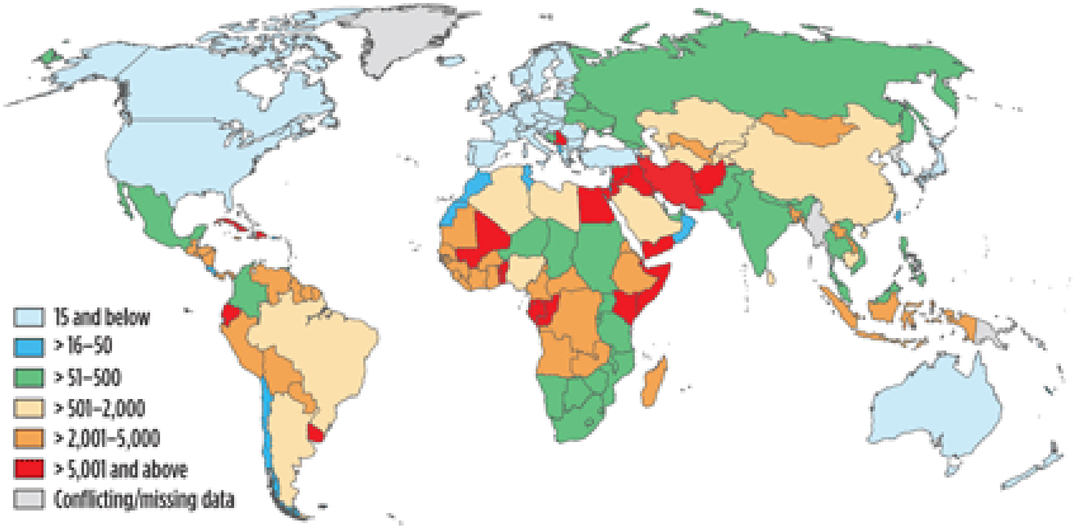
Diesel Sulfur Content

Sulfur levels dropping because of air quality regulations

- Since 1993 diesel fuel formulated with 85% less sulfur
- Low Sulfur Diesel had been 500 ppm sulfur
- ULSD 15 ppm & required for on-road usage since January 2007

Worldwide, sulfur specs continuing to drop to meet U.S. & European standards

- For example, Uruguay at 50 ppm since 2014.



Source: United Nations Environmental Programme (UNEP)

Global status of maximum allowable sulfur in diesel fuel, parts per million (June 2012)
"Saudi Arabia's plan for near-zero-sulfur fuels", *Hydrocarbon Processing*, March 2013

Distillate Fuel Oil

Only grades 1 and 2 have boiling range specs (max)

No. 1 Fuel Oil – minor product

No. 2 Fuel Oil — domestic heating oil

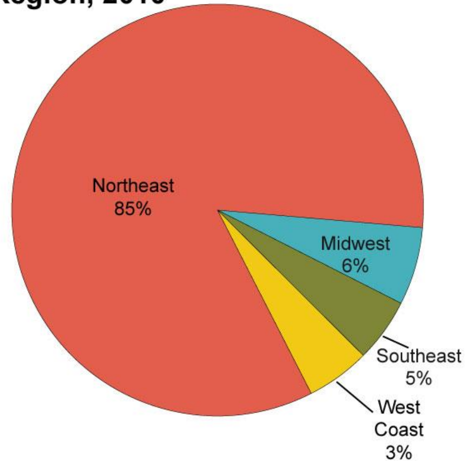
- Similar to medium quality diesel 2-D
- Made in the winter season in refineries when automotive fuel demand is lower.

No. 3 Fuel Oil — not produced since 1948

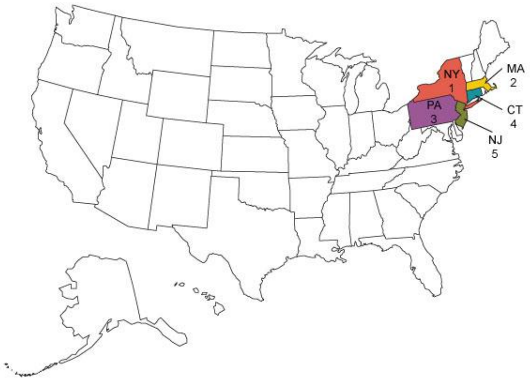
No. 4 Fuel Oil —for industrial burner installations with no preheat facility

- Sometimes a mixture of distillate & residual material
- Lower viscosity heating oil

Sales of Residential Heating Oil by Region, 2010



Top Five Heating Oil Consuming States, 2010



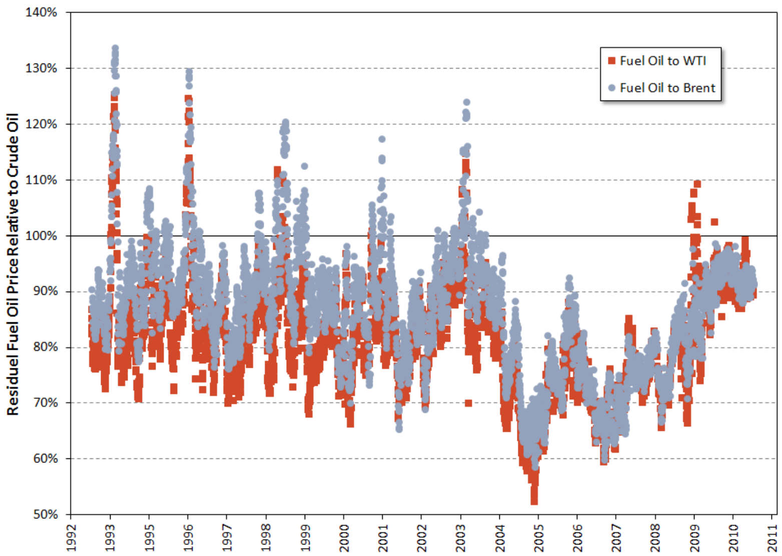
http://www.eia.gov/energyexplained/index.cfm?page=heating_oil_use

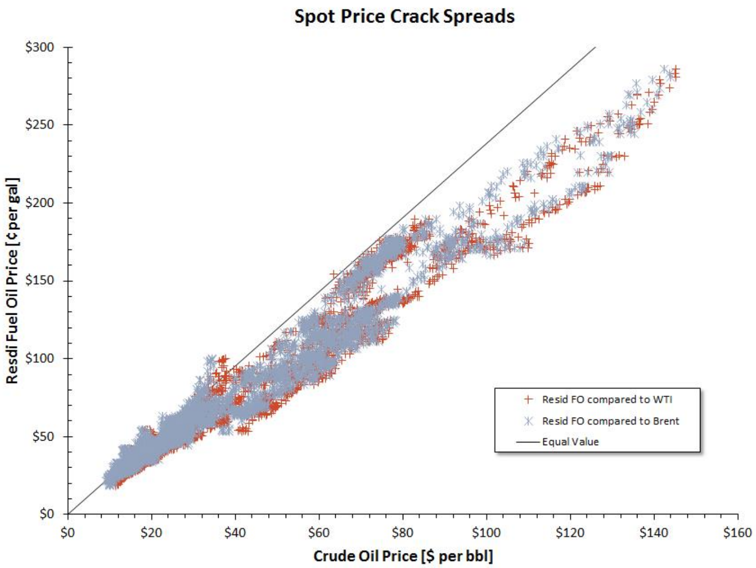
Residual Fuel Oils

No. 5 Fuel Oil — premium residual fuel oil of medium viscosity, rarely used

No. 6 Fuel Oil — heavy residual fuel oil

- Vacuum resid & cutter stock mix (to decrease viscosity)
- Common use
  - Boilers for steam turbines of stationary power plants
  - Marine boilers — variation of Bunker C
  - Industrial & commercial applications
- Least valued of all refinery products
  - Historically only liquid product worth less than raw crude





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Residual Fuel Oils

No. 6 Fuel Oil — Market has been declining in last 20 years

- More power plants use coal or natural gas
- Ships use diesel for marine diesels or gas turbines
- Environmental reductions in sulfur levels
- “Emission-control areas” (ECAs) will shift to low-sulfur (0.1 wt%) marine gasoil (MGO) or marine diesel oil (MDO) starting January 1, 2015 – U.S., Canada, Caribbean, & northern Europe
- Other option on-board emissions-scrubbing systems

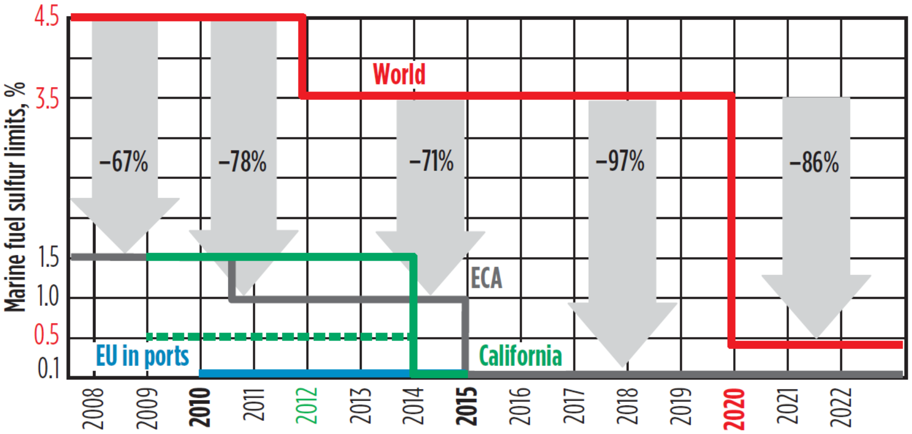
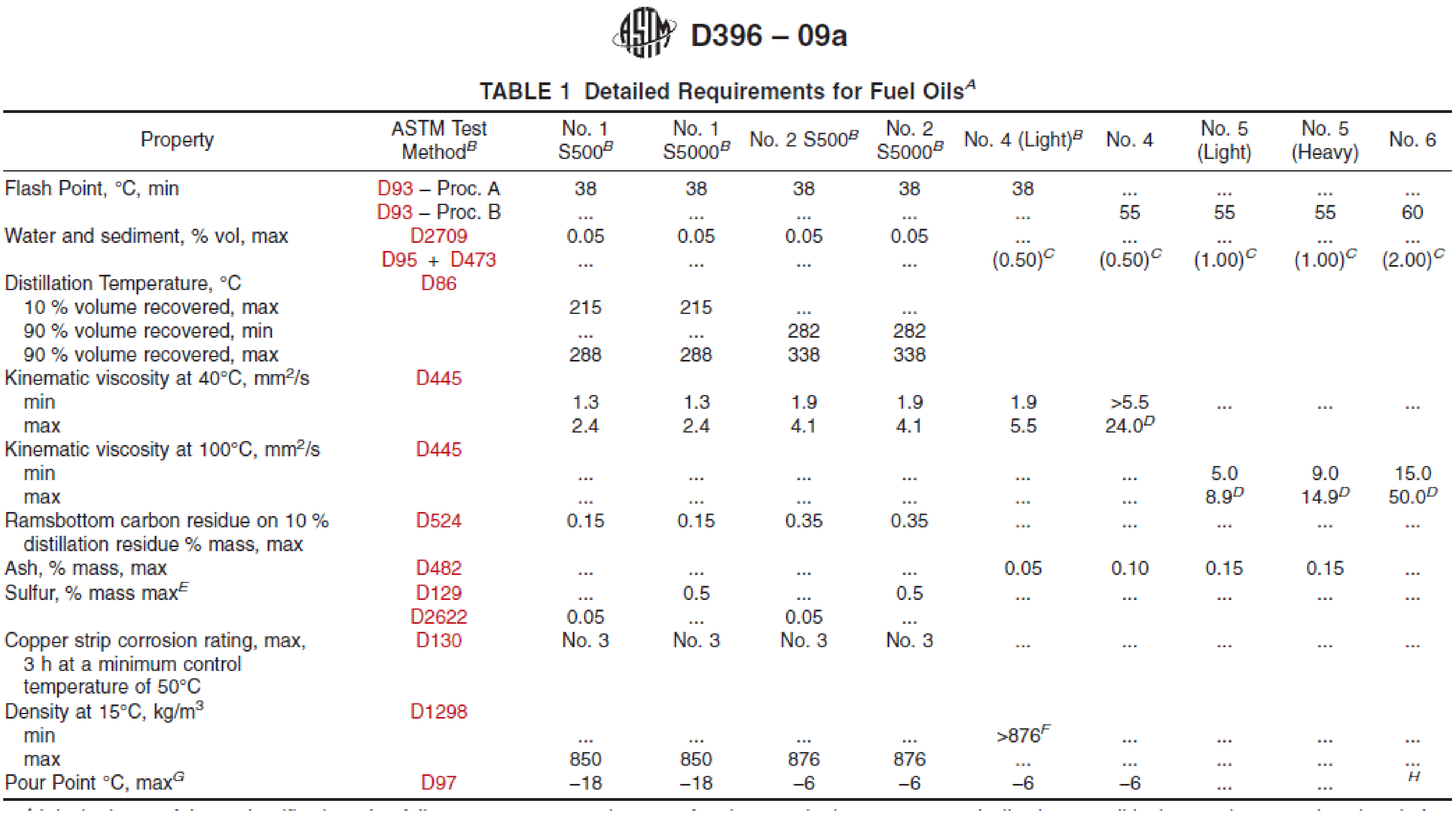


FIG. 1. New sulfur limits for marine fuels, 2008–2020.

“Methanol takes on LNG for future marine fuels”, *Hydrocarbon Processing*, May 2015

ASTM Fuel Oil Specs



D396 – 09a

TABLE 1 Detailed Requirements for Fuel Oils^{A}

Property	ASTM Test Method^{B}	No. 1 S500^{B}	No. 1 S5000^{B}	No. 2 S500^{B}	No. 2 S5000^{B}	No. 4 (Light)^{B}	No. 4	No. 5 (Light)	No. 5 (Heavy)	No. 6
Flash Point, °C, min	D93 – Proc. A	38	38	38	38	38	...	...	...	...
	D93 – Proc. B	...	...	...	...	...	55	55	55	60
Water and sediment, % vol, max	D2709	0.05	0.05	0.05	0.05	...	...	...	...	...
	D95 + D473	...	...	...	...	(0.50)^{C}	(0.50)^{C}	(1.00)^{C}	(1.00)^{C}	(2.00)^{C}
Distillation Temperature, °C	D86									
10 % volume recovered, max		215	215	...	...					
90 % volume recovered, min		...	...	282	282					
90 % volume recovered, max		288	288	338	338					
Kinematic viscosity at 40°C, mm^{2}/s	D445									
min		1.3	1.3	1.9	1.9	1.9	>5.5	...	...	...
max		2.4	2.4	4.1	4.1	5.5	24.0^{D}			
Kinematic viscosity at 100°C, mm^{2}/s	D445									
min		...	...	...	...	...	...	5.0	9.0	15.0
max		...	...	...	...	...	...	8.9^{D}	14.9^{D}	50.0^{D}
Ramsbottom carbon residue on 10 % distillation residue % mass, max	D524	0.15	0.15	0.35	0.35	...	...	...	...	...
Ash, % mass, max	D482	...	...	...	...	0.05	0.10	0.15	0.15	...
Sulfur, % mass max^{E}	D129	...	0.5	...	0.5	...	...	...	...	...
	D2622	0.05	...	0.05	...					
Copper strip corrosion rating, max, 3 h at a minimum control temperature of 50°C	D130	No. 3	No. 3	No. 3	No. 3	...	...	...	...	...
Density at 15°C, kg/m^{3}	D1298									
min		...	...	...	...	>876^{F}	...	...	...	...
max		850	850	876	876	...	...	...	...	...
Pour Point °C, max^{G}	D97	–18	–18	–6	–6	–6	–6	...	...	^{H}

Comparison Kerosene / Jet / Diesel / Heating Oil

ASTM Specifications for Middle Distillates

Property			No. 2 Kerosene	Jet-A	Jet-B	No. 2D S15	No. 2D S500	No. 2HO S500
Cetane Number		min				40	40	
Aromatics	[vol%]	max		25	25	35	35	
Sulfur	[wt%]	max	0.3	0.3	0.3	0.0015	0.05	0.05
Flash Point	[°C]		38			52	52	38
Distillation (D 86)								
T10	[°C]	max	205	205				
T20	[°C]	max			145			
T50	[°C]	max			190			
T90	[°C]	min				282	282	282
	[°C]	max			245	338	338	338
EP	[°C]	max	300	300				
Distillation Residue	[vol%]	max						
Distillation Loss	[vol%]	max						
Freezing Point	[°C]	max		-40	-50			
Pour Point	[°C]	max						-6
Carbon Residue	[wt%]					0.35	0.35	0.35
Kinematic Viscosity								
@ 40°C	mm^2/s	min				1.9	1.9	1.9
	mm^2/s	max				4.1	4.1	4.1

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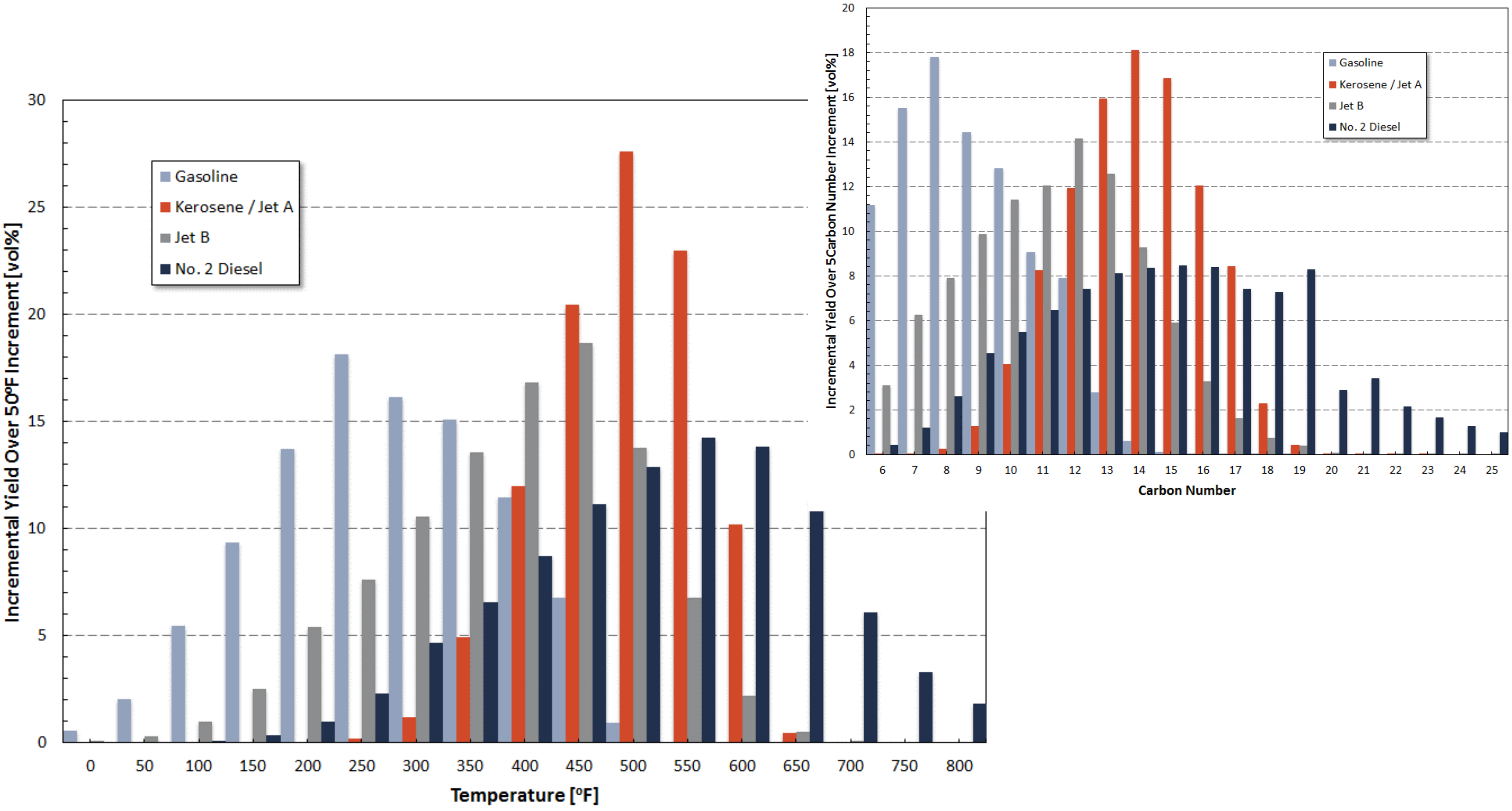
Comparison of Boiling Ranges



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Gas Oil & Town Gas

Historical usage

- Gas oils used to make town gas for illumination
- Decomposed over a heated checker-work
- Composed of carbon monoxide and carbon dioxide
  - Low heating value
  - Burned cleanly
  - Easily distributed for illumination fuel
- Displaced kerosene in the cities — electricity ultimately eliminated its use

Gas oil no longer a consumer product

- Traded between refineries
- Feedstock for catalytic cracking & hydrocracking

Lubricant Terminology

Phrase	Meaning
Lube basestock	Lube product that meets all specifications & is suitable for blending
Lube slate	Set of lube basestocks, usually 3 to 5
Neutral lubes	Obtained from a side cut of the vacuum distillation tower
Bright stock lubes	Processed of vacuum resid from the vacuum tower bottoms

Lubricants

Terminology based solely on the Viscosity Index — independent of the crude source or type of processing

- Paraffinic lubricants are all grades, both bright stock & neutral, with a finished viscosity Index more than 75
- Naphthenic lubricants are all grades with a viscosity Index less than 75

Important properties

- Kinematic viscosity (viscosity divided by mass density)
- Color
- Pour point for cold weather operation
- Flash point
- Volatility for reduced evaporation
- Oxidation stability
- Thermal stability

SAE Viscosity Specifications

Kinematic viscosity measured in centistokes but specifications are labeled in Saybolt Seconds (SUS)

Specifications are established by the Society of Automotive Engineers

- SAE viscosity well known motor oil specification (e.g., 10W-30)

Grade	Max Viscosity (SUS) @ 0°F	Max Viscosity (SUS) @ 210°F	Min Viscosity (SUS) @ 210°F
5W	6,000		
10W	12,000		
20W	48,000		
20		58	45
30		70	58
40		86	70
50		110	85

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Asphalt

Important product in the construction industry

- Comprise 20% of the “Other Products” category

Asphalt can only be made from crudes containing asphaltenic material

Numerous detailed specifications on the many asphalt products

- Asphalt Institute, Lexington Kentucky
  - Industry trade group for asphalt producers & affiliated businesses
- American Association of State Highway and Transportation Officials
  - Sponsors the AASHTO Materials Reference Laboratory (AMRL) at the National Institute of Standards and Technology (NIST)
- American Society of Testing and Materials (ASTM)

Petroleum Coke

	Green Coke	Calcined Coke
Fixed carbon	86% - 92%	99.5%
Moisture	6% - 14%	0.1%
Volatile matter	8% - 14%	0.5%
Sulfur	1% - 6%	1% - 6%
Ash	0.25%	0.40%
Silicon	0.02%	0.02%
Nickel	0.02%	0.03%
Vanadium	0.02%	0.03%
Iron	0.01%	0.02%

Sulfur Specifications

Purity	99.8 weight % sulfur, based on dry analysis
Ash	500 ppmw maximum
Carbon	1,000 ppm(weight) maximum
Color	"Bright yellow" when solidified. Sulfur recovered by liquid reduction-oxidation processes have color due to metals — some purchasers will include a requirement excluding sulphur recovered from these processes
H_2S	10 ppmw max (Important for international transport & sales)
State	Shipped as either liquid or solid. International transport specifies solid.

Summary

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Summary

Many of the properties are based upon distillation/evaporation specifications

- % Distilled at specified TBP temperature
- Temperature for specified % distilled
- Reid vapor pressure (RVP)

Many specifications are specific for certain products

- Octane number
- Cetane number

Overlap of boiling point ranges allows flexibility of routing intermediate streams to multiple products

Supplemental Slides

Updated: July 1, 2019

Standard Conditions (Temperature & Pressure)

"Standard conditions" may vary between countries, states within the US, & between different organizations

- Standard temperature – 60°F
  - Most other countries use 15°C (59°F)
  - Russia uses 20°C (68°F)
- Standard pressure – 1 atm (14.696 psia)
  - Other typical values are 14.73 psia (ANSI Z132.1) & 14.503 psia

"Normal conditions"

- Almost exclusively used with metric units (e.g., Nm^3)
- IUPAC: 0°C & 100 kPa (32°F & 14.50 psia)
- NIST: 0°C & 1 atm (32°F & 14.696 psia)

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Standard Liquid Volume vs. Standard Gas Volume

Standard liquid volume – volume of a stream if it could exist in the liquid state at the standard conditions

- Mass flow rate converted to standard liquid volume flow rate using the specific gravity values
- U.S. customary flow rate units usually “bbl/day”, “bpd”, or “sbpd”

Standard/normal gas volume – volume of a stream if it could exist in the ideal gas state at the standard conditions

- Molar flow rate converted to standard ideal gas volume using molar volume at standard conditions
- U.S. customary flow rate units usually “scfd”
  Metric flow rate units usually “Nm^3/day”

Standard Liquid & Gas Volumetric Flow Rates

Standard liquid volume flow (sbpd):

$$\dot{V}_L = \frac{\dot{m}}{\gamma_o \rho_W^*} = \frac{100\ \frac{\text{lb}}{\text{hr}}}{(0.4941)\left(8.3372\ \frac{\text{lb}}{\text{gal}}\right)}$$

$$= 24.4\ \frac{\text{gal}}{\text{hr}}\left(24\ \frac{\text{hr}}{\text{day}}\right)\left(\frac{\text{bbl}}{42\ \text{gal}}\right)$$

$$= 13.9\ \frac{\text{bbl}}{\text{day}}$$

Compound	Mol Wt	Specific Gravity (60/60)	Rate [lb/hr]	Rate [lb.mol/hr]
Ethane	30.07	0.3562	19.0	0.632
Propane	44.10	0.5070	47.2	1.070
Isobutane	58.12	0.5629	4.3	0.074
N-Butane	58.12	0.5840	19.0	0.327
Isopentane	72.15	0.6247	2.1	0.029
N-Pentane	72.15	0.6311	8.4	0.116
Total	44.47	0.4919	100.0	2.249

Standard ideal gas volume flow (scfd):

$$\dot{V}_G = \dot{n}\tilde{V}_{IG}^* = \left(2.249\ \frac{\text{lb.mol}}{\text{hr}}\right)\left(379.5\ \frac{\text{ft}^3}{\text{lb.mol}}\right)\left(24\ \frac{\text{hr}}{\text{day}}\right)$$

$$= 20{,}480\ \frac{\text{ft}^3}{\text{day}}$$

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Crude Oil Assay – Ten Section Field (Text pg. 416)

			Increment	Cumulative		Corrected	Corrected	Mid-Cumulative	
Fraction	mm Hg	°F	vol%	vol%	SpGr	°F	Cumulative	Amount	°API
	756	82	IBP			82.3	1.8	0.9	
1	756	122	2.6	2.6	0.644	122.3	4.4	3.1	88.2
2	756	167	2.3	4.9	0.683	167.3	6.7	5.5	75.7
3	756	212	5.0	9.9	0.725	212.3	11.7	9.2	63.7
4	756	257	7.9	17.8	0.751	257.3	19.6	15.7	56.9
5	756	302	6.2	24.0	0.772	302.4	25.8	22.7	51.8
6	756	347	4.9	28.9	0.791	347.4	30.7	28.3	47.4
7	756	392	4.6	33.5	0.808	392.4	35.3	33.0	43.6
8	756	437	5.2	38.7	0.825	437.4	40.5	37.9	40.0
9	756	482	4.9	43.6	0.837	482.4	45.4	43.0	37.6
10	756	527	6.2	49.8	0.852	527.4	51.6	48.5	34.6
11	40	392	4.3	54.1	0.867	584.0	55.9	53.8	31.7
12	40	437	5.2	59.3	0.872	635.0	61.1	58.5	30.8
13	40	482	5.3	64.6	0.890	685.5	66.4	63.8	27.5
14	40	527	3.2	67.8	0.897	735.7	69.6	68.0	26.2
15	40	572	5.4	73.2	0.915	785.4	75.0	72.3	23.1
Residuum			25.0	98.2	0.984		100.0	87.5	12.3
Total			98.2		0.858				
Loss			1.8						
Reported					0.854				

Steps for this example

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Crude Oil Assay – WTI (from OGJ article)

	IBP	EP	Cumulative	Yields Increment		Mid-Inc	Specific Gravity	API Gravity	Sulfur
Fraction	°F	°F	vol%	vol%	wt%	vol%		°API	wt%
Whole Crude	IBP	FBP		100	100		0.8212	40.8	0.34
Primary Fractions									
Gas + LPG	IBP	68		2.71	4.35				
Naphtha	68	347	2.71	32.39	26.66	18.905	0.6758	77.9	0.0314
Kerosene	347	563	35.10	23.50	23.47	46.850	0.8201	41.0	0.110
AGO	563	650	58.60	8.10	8.41	62.650	0.8529	34.4	0.289
VGO	650	1049	66.70	24.30	26.51	78.850	0.8960	26.4	0.445
Vac Resid	1049	FBP	91.00	9.00	10.60	95.500	0.9672	14.8	1.408
Total				100.00	100.00				0.326
Other Fractions									
Atm Resid	650	FBP	66.70	33.3	37.12	83.350	0.9153	23.1	0.720
Vac Resid #2	761	FBP	74.70	25.3	28.55	87.350	0.9268	21.2	
Vac Resid #3	878	FBP	82.05	17.95	20.55	91.025	0.9403	19.0	
Expanded Assay									
Gas + LPG	IBP	68		2.71	4.35				
Naphtha	68	347	2.71	32.39	26.66	18.905	0.6758	77.9	0.0314
Kerosene	347	563	35.10	23.50	23.47	46.850	0.8201	41.0	0.11
AGO	563	650	58.60	8.10	8.41	62.650	0.8529	34.4	0.289
LVGO	650	761	66.70	8.00	8.56	70.700	0.8789	29.5	0.367
MVGO	761	878	74.70	7.35	8.00	78.375	0.8938	26.8	0.440
HVGO	878	1049	82.05	8.95	9.95	86.525	0.9132	23.4	0.889
Vac Resid	1049	FBP	91.00	9.00	10.60	95.500	0.9672	14.8	1.408
Total				100.00	100.00				

Steps

SAE 902098 Gasoline Blend Stock Analyses

Table 7 Analyses of Blending Components

Blending Component	Cat Cracked Naptha #1	Cat Cracked Naptha #2	Light Cat Cracked Naptha	Light Alkylate	Heavy Alkylate	Full Range Reformate	Light St Run Naptha	C6 Isomerate	Light Reformate	Mid Cut Reformate	Heavy Reformate
Gravity, °API	52.1	51.9	66.8	72.3	55.8	44.2	81.8	83.0	72.0	32.8	29.8
Aromatics, vol%	35.2	35.9	17.6	0.5	1.0	61.1	2.2	1.6	4.8	94.2	93.8
Olefins, vol%	32.6	25.4	44.9	0.2	0.9	1.0	0.9	0.1	1.5	0.6	1.9
Saturates, vol%	32.2	38.8	37.4	99.3	98.1	37.9	96.9	98.3	93.7	5.1	4.2
Benzene, vol%	1.06	1.23	1.24	0.00	0.01	1.17	0.73	0.00	4.01	0.00	0.00
Bromine Number	57.1	41.7	91.4	2.3	0.3	1.2	0.5	3.8	3.1	0.6	0.9
RVP, psi	4.3	4.6	8.7	4.6	0.3	3.2	10.8	8.0	3.8	1.0	0.3
Distillation, °F											
IBP	110	112	95	101	299	117	91	118	138	224	313
T05	143	142	117	144	318	168	106	131	169	231	326
T10	158	155	124	162	325	192	113	134	174	231	328
T20	174	171	130	181	332	224	117	135	179	231	331
T30	192	189	139	196	340	244	121	135	182	232	335
T40	215	212	149	205	345	258	126	136	185	233	339
T50	241	239	164	211	354	270	132	136	188	234	344
T60	270	269	181	215	362	280	139	137	190	235	350
T70	301	302	200	219	373	291	149	137	192	237	358
T80	336	337	224	225	391	304	163	138	194	240	370
T90	376	379	257	239	427	322	184	139	195	251	391
EP	431	434	337	315	517	393	258	146	218	316	485
RON	93.2	92.6	93.6	93.2	65.9	97.3	63.7	78.6	57.6	109.3	104.3
MON	81.0	82.1	79.4	91.2	74.5	86.7	61.2	80.5	58.5	100.4	92.4
(R+M)/2	87.1	87.4	86.5	92.2	70.2	92.0	62.4	79.5	58.0	104.9	98.4
Carbon, wt%	86.94	85.88	85.60	84.00	84.39	88.11	83.58	83.44	84.41	90.87	89.62
Hydrogen, wt%	13.00	13.56	14.20	16.09	15.54	11.60	16.29	16.49	15.54	9.32	10.34
Nitrogen, ppmw	46	37	27	0	0	0	0	0	0	0	0
Sulfur, ppmw	321	522	0	15	15	9	325	10	7	10	8
Heating Value, BTU/lb (net)	17300	17300	18700	18400	18100	16800	18400	18500	18200	15500	17300

Updated: July 1, 2019

SAE 902098 Gasoline Analyses

Table 10 Blended Fuel Analyses

Fuel	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	A	Z	ZZ
Code	Avg	Cert	2211	1122	2222	1111	2121	1221	2112	1212	2111	2122	1222	1211	2221	1121	1112	2212	M0	M85	M10
Gravity, °API	57.4	58.8	50.2	59.2	50.2	64.1	53.4	62.2	51.9	58.2	53.4	50.6	59.1	62.6	51.7	64.2	59.6	49.1	57.4	47.9	56.8
Aromatics, vol%	32.0	29.9	43.8	20.7	43.7	20.0	44.3	20.2	42.9	21.4	45.7	47.8	18.0	21.4	46.7	20.3	21.5	46.0	32.0	5.0	28.0
Olefins, vol%	9.2	4.6	3.3	22.3	17.2	3.2	17.4	20.2	4.1	4.0	4.9	17.7	21.8	5.7	19.3	18.3	4.8	4.0	9.2	1.0	6.8
Saturates, vol%	58.8	65.5	37.5	57.0	24.3	76.8	38.3	45.0	53.0	59.7	49.4	34.5	45.7	59.0	19.4	61.4	73.7	34.8	58.8	8.4	55.5
MTBE, vol%	0.00	0.00	15.40	0.00	14.80	0.00	0.00	14.60	0.00	14.90	0.00	0.00	14.50	13.90	14.60	0.00	0.00	15.20	0.00	0.00	0.00
Methanol, vol%	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	85.60	9.70
Benzene, vol%	1.53	0.52	1.33	1.49	1.38	1.52	1.42	1.52	1.30	1.28	1.45	1.42	1.51	1.44	1.38	1.53	1.47	1.41	1.53	0.42	1.16
Bromine Number	21.3	12.2	9.2	44.3	32.5	10.0	35.7	41.1	11.5	10.0	13.3	38.7	42.6	16.2	35.0	38.9	12.2	10.8	21.3	3.0	18.6
RVP, psi	8.7	8.7	8.7	8.5	8.7	8.8	8.8	8.5	8.9	8.6	8.8	8.5	8.7	8.8	8.6	8.5	8.6	8.4	8.7	8.8	12.0
Distillation, °F																					
IBP	91	87	89	87	90	89	92	93	87	89	90	89	91	93	92	90	92	89	91	110	89
T05	114	112	118	111	113	110	116	116	110	112	114	110	111	114	116	113	117	114	114	134	105
T10	128	127	136	128	128	125	130	125	127	125	127	127	125	124	130	126	134	129	128	141	113
T20	151	152	165	153	151	144	153	135	156	143	146	152	139	134	151	140	161	151	151	145	122
T30	174	180	185	176	172	162	175	143	182	159	166	178	152	142	168	155	186	170	174	146	129
T40	196	205	200	197	192	180	196	154	208	178	188	205	170	152	185	171	209	192	196	147	139
T50	218	220	213	218	220	197	214	168	239	208	208	236	193	164	204	190	234	225	218	147	202
T60	243	230	226	238	253	212	228	186	266	259	226	263	233	181	223	208	260	263	243	147	232
T70	267	242	236	265	281	227	240	214	291	294	238	294	283	211	237	227	289	293	267	147	259
T80	295	262	250	307	318	245	254	247	324	322	253	328	323	253	250	248	321	326	295	148	287
T90	330	300	288	357	357	279	286	286	353	356	294	357	356	292	283	284	357	354	330	148	324
EP	415	410	399	430	429	370	386	367	437	447	404	436	436	374	397	361	442	428	415	347	405
RON	92.0	96.7	100.0	93.7	98.9	90.5	96.9	95.4	97.1	92.7	93.5	97.1	96.6	91.5	100.4	92.7	90.2	99.4	92.0	107.1	95.7
MON	82.6	87.5	88.0	83.2	85.6	84.2	84.6	83.9	86.9	85.1	83.1	84.5	85.0	83.6	86.0	82.7	83.8	87.5	82.6	103.1	84.4
(R+M)/2	87.3	92.1	94.0	88.4	92.3	87.4	90.8	89.6	92.0	88.9	88.3	90.8	90.9	87.6	93.2	87.7	87.0	93.4	87.3	105.1	90.1
Carbon, wt%	86.74	86.64	85.34	86.29	85.09	85.05	87.79	83.53	87.71	83.51	87.88	87.87	83.65	83.36	85.44	86.11	85.85	85.50	86.74	44.25	81.48
Hydrogen, wt%	13.22	13.35	11.92	13.73	12.20	14.12	12.17	13.56	12.26	13.70	12.10	12.07	13.60	13.92	11.94	13.82	14.08	11.84	13.22	12.61	13.17
Nitrogen, ppmw	29	12	1	46	31	4	15	10	3	12	1	26	16	6	9	13	8	11	29	2	25
Sulfur, ppmw	339	119	284	316	267	290	317	312	261	297	318	266	301	294	288	333	310	279	339	27	242
Oxygen, wt%	0.00	0.00	2.72	0.00	2.69	0.00	0.00	2.88	0.00	2.76	0.00	0.00	2.67	2.68	2.60	0.00	0.00	2.63	0.00	43.13	5.33
Heating Value, BTU/lb (net)	18300	18300	17500	18300	17800	18500	18100	17900	18200	17900	17500	17600	17700	18100	17100	18600	18100	17000	18300	9600	17400

ASTM D 323 RVP Procedures

Procedure "A" (Atmospherically Stable Liquids)

Apparatus	Liquid & vapor chambers. Vapor chamber 4.0 ± 0.2 times size of liquid chamber
Liquid Preparation	1 L sample container filled 70-80% with test liquid sample. Sample container cooled in a cold bath at 0 - 1°C (32 - 34°F). Sample container opened, allowing air to enter container. Container shaken vigorously (to saturate the liquid with air) & returned to cold bath.
Liquid Transfer	The liquid chamber cooled in the same cold bath. Cold liquid sample transferred to the cold liquid chamber, entirely filling liquid chamber.
Air Preparation	Vapor chamber full of air is placed in a hot bath at 37.8 ± 0.1°C (100 ± 0.2°F).
Assembly	Vapor chamber removed from hot bath & coupled to liquid chamber. The coupled apparatus is inverted, shaken, & put into hot bath.
Pressure Measurement	Apparatus should remain in hot bath for at least 5 minutes before the apparatus is removed from bath, shaken, & returned to hot bath. Shaking procedure should be repeated at least 5 times with no less than 2 minutes in between. Shaking procedure should be repeated until 2 consecutive pressure readings indicate equilibrium has occurred. Pressure measured as gauge but reported with reference to "gauge" or "absolute".

ASTM D 323 RVP Procedures

Procedure “C” (Volatile Liquids)

Liquid Preparation	Sample container of about 0.5 L capacity cooled in a cold bath at 0 - 4.5°C (32 - 40°F). ***This sample container is not opened & contacted with air.***
Liquid Transfer	Liquid chamber is cooled in the same cold bath. Cold liquid sample transferred to the cold liquid chamber, similar to Procedure A. However, since this liquid is under pressure, extra care must be taken to ensure that gas is not flashed off and lost and that the liquid chamber is actually completely filled with the liquid.

ASTM D 56 Flash Point by Tag Closed Tester Flash Points Below 60°C (140°F)

Apparatus	*Tag Close Tester* — test cup, lid with ignition source, & liquid bath.
Preparation	Transfers should not be made unless sample is at least 10°C (18°F) below the expected flash point. Do not store samples in gas-permeable containers since volatile materials may diffuse through the walls of the enclosure. At least 50 mL sample required for each test.
Manual Procedure	1. Temperature of liquid in bath shall be at least 10°C (18°F) below expected flash point at the time of introduction of the sample into test cup. Measure 50 ± 0.5 mL sample into cup, both sample & graduated cylinder being precooled, when necessary, so that specimen temperature at time of measurement will be 27 ± 5°C (80 ± 10°F) or at least 10°C (18°F) below the expected flash point, whichever is lower. 2. Apply test flame —size of the small bead on the cover & operate by introducing the ignition source into vapor space of cup & immediately up again. Full operation should be 1 sec with equal time for introduction & return. 3. Adjust heat so temperature rise 1°C (2°F)/min ± 6 s. When temperature of specimen in is 5°C (10°F) below its expected flash point, apply the ignition source. Repeat application of ignition source after each 0.5°C (1°F) rise in temperature of the specimen.

Linear Blending Rules

Values for individual blend stocks averaged either with volume fractions or mass fractions

- Some properties blend best with mole fractions, but molar amounts not typically known

Units on the quality measure may give an indication as to volume or mass blending.

Volume blending

- Specific gravity (essentially mass per unit volume)
- Aromatics & olefins content (vol%)

$$X_{mix} = \sum v_i X_i = \frac{\sum V_i X_i}{\sum V_i}$$

Mass blending:

- Sulfur & nitrogen content (wt% or ppm)
- Nickel & vanadium (ppm)

$$X_{mix} = \sum w_i X_i = \frac{\sum m_i X_i}{\sum m_i} = \frac{\sum v_i \gamma_{oi} X_i}{\sum v_i \gamma_{oi}}$$

Updated: July 1, 2019

How Do We Blend Specific Gravities?

Assume ideal liquid mixing — volumes are additive

- "Shrinkage" correlations available, mostly used for custody transfer

Liquid densities at fixed conditions blend linearly with volume

- Mass & volumes are additive

$$\gamma_{o,mix} = \frac{\sum V_i \gamma_{o,i}}{\sum V_i} = \frac{\sum V_i \gamma_{o,i}}{V} = \sum v_i \gamma_{o,i}$$

Can also blend with mass & molar amounts

- Volumes are additive

$$\frac{1}{\gamma_{o,mix}} = \sum \frac{w_i}{\gamma_{o,i}} \quad \Rightarrow \quad \frac{M}{\gamma_{o,mix}} = \sum \frac{x_i M_i}{\gamma_{o,i}}$$

Density adjustments

- Corrections needed for temperature & pressure effects

Updated: July 1, 2019

How Do We Blend API Gravities?

Specific gravity is blended & API gravity is back-calculated.

- May have to calculate individual specific gravities from given API gravities

Example

- Incorrect value from direct volume blending of API gravities

Blend Stock	Given Volume	Given API Gravity	Calculated Specific Gravity	Calculated API Gravity
A	25	60	0.7389	
B	20	50	0.7796	
C	15	30	0.8762	
D	40	10	1.0000	
Mix	100		0.8721	30.8
INCORRECT			**0.8576**	**33.5**

Updated: July 1, 2019

Temperature Corrections to Specific Gravity

O'Donnell method[1]

$$\gamma_T^2 = \gamma_o^2 - 0.000601\left(T_{^\circ F} - 60\right)$$

API Volume Correction Tables

$$\gamma_T = \gamma_o \cdot \exp\left[-\alpha_{60}\left(T_{^\circ F} - 60\right)\left(1 + 0.8\alpha_{60}\left(T_{^\circ F} - 60\right)\right)\right]$$

- Different α_{60} values depending on commodity type
  - A Tables – Crude Oils
  - B Tables – Refined Products
  - D Tables – Lubricants
  - C Tables – Individual & Special Applications

---

[1] Reported slope value is -0.00108 $(g/cm^3)^2/^\circ C$, *Hydrocarbon Processing*, April 1980, pp 229-231

What if we want to estimate volumetric shrinkage?

Method in Chapter 12.3 of API measurement manual

$$S = 4.86\times 10^{-8}\, C(100-C)^{0.819}\,(G_L - G_H)^{2.28} \quad \text{where} \quad C \equiv \frac{V_L}{V_H + V_L}\times 100$$

Example: Blend 95,000 bbl of 30.7°API (0.8724 specific gravity) crude oil with 5,000 bbl of 86.5°API (0.6491 specific gravity) natural gasoline

- By ideal mixing:

$$V_{mix} = V_H + V_L = 100{,}000 \text{ bbl}$$

$$\gamma_{mix} = \frac{\gamma_L V_L + \gamma_H V_H}{V_{mix}} = \frac{0.6491\times 5000 + 0.8724\times 95000}{100000} = 0.8612 \text{ and } G_{mix} = \frac{141.5}{\gamma_{mix}} - 131.5 = 32.8$$

- With shrinkage:

$$C = \frac{5000}{5000+95000}\times 100 = 5 \;\Rightarrow\; S = 4.86\times 10^{-8}\times 5\times(100-5)^{0.819}\,(86.5-30.7)^{2.28} = 0.0972$$

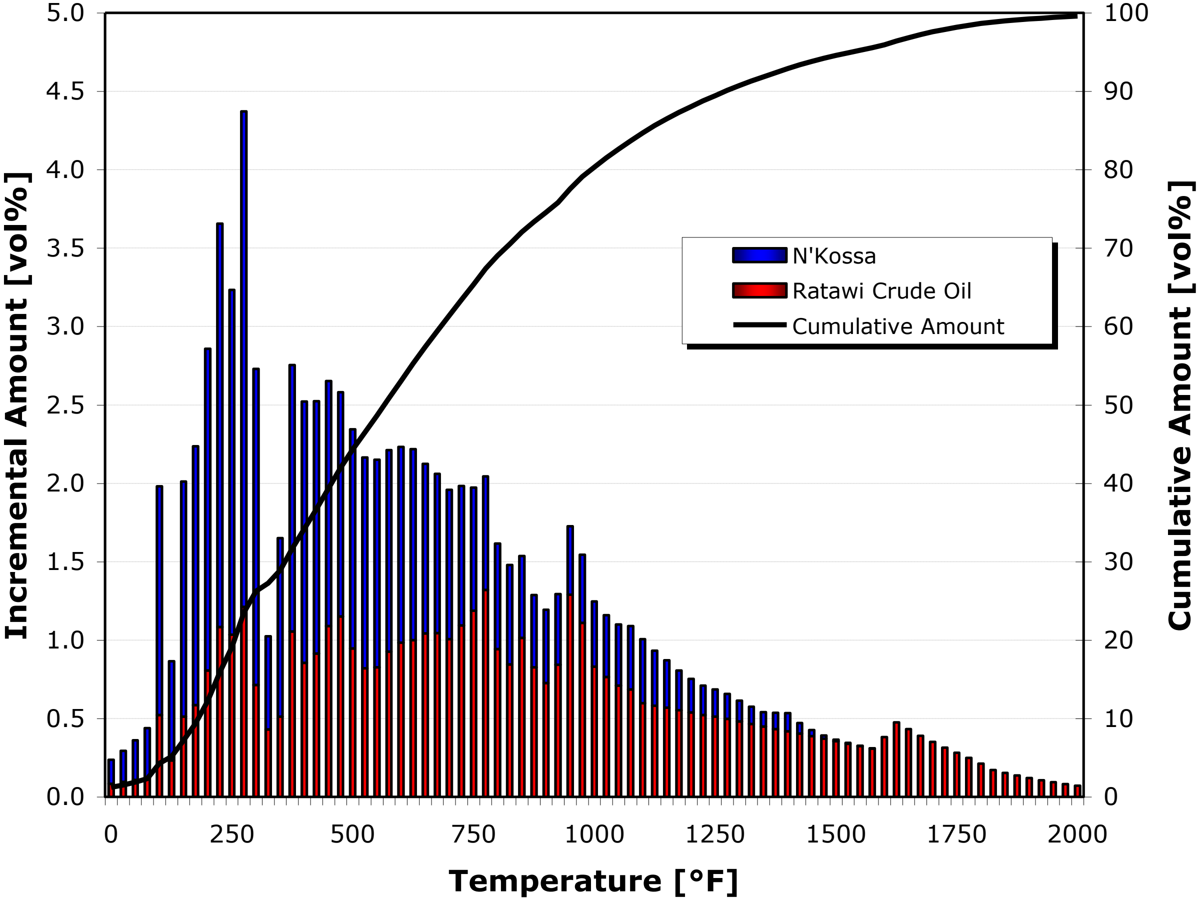
$$V_{mix} = (V_H + V_L)\left(\frac{100-S}{100}\right) = (100000)\left(\frac{100-0.0972}{100}\right) = 99{,}903 \text{ bbl}$$

$$\gamma_{mix} = \frac{\gamma_L V_L + \gamma_H V_H}{V_{mix}} = \frac{0.6491\times 5000 + 0.8724\times 95000}{99903} = 0.8621 \text{ and } G_{mix} = \frac{141.5}{\gamma_{mix}} - 131.5 = 32.6$$

How Do We Blend Yield Curves?

Amounts are added for the same TBP temperature ranges

- On a consistent volume, mass, or mole basis
- On an incremental or cumulative basis
- Temperatures "corrected" to 1 atm basis
- Distillation type corrected to TBP



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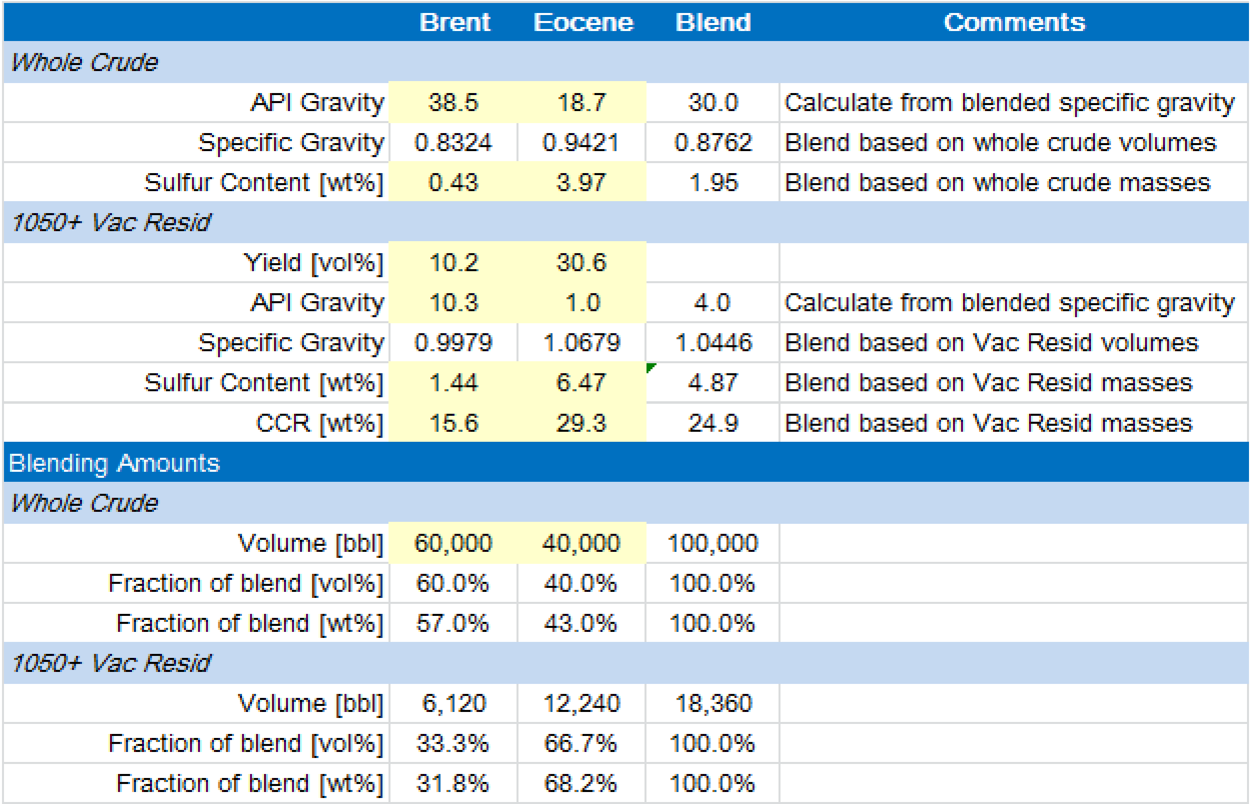
How Do We Blend Properties for Individual Fractions?

Blend based on properties and amounts for the ***fraction*** in each blend stock, ***not*** the ***overall amount*** of blend stock.



	Brent	Eocene	Blend	Comments
Whole Crude				
API Gravity	38.5	18.7	30.0	Calculate from blended specific gravity
Specific Gravity	0.8324	0.9421	0.8762	Blend based on whole crude volumes
Sulfur Content [wt%]	0.43	3.97	1.95	Blend based on whole crude masses
1050+ Vac Resid				
Yield [vol%]	10.2	30.6		
API Gravity	10.3	1.0	4.0	Calculate from blended specific gravity
Specific Gravity	0.9979	1.0679	1.0446	Blend based on Vac Resid volumes
Sulfur Content [wt%]	1.44	6.47	4.87	Blend based on Vac Resid masses
CCR [wt%]	15.6	29.3	24.9	Blend based on Vac Resid masses
Blending Amounts				
Whole Crude				
Volume [bbl]	60,000	40,000	100,000	
Fraction of blend [vol%]	60.0%	40.0%	100.0%	
Fraction of blend [wt%]	57.0%	43.0%	100.0%	
1050+ Vac Resid				
Volume [bbl]	6,120	12,240	18,360	
Fraction of blend [vol%]	33.3%	66.7%	100.0%	
Fraction of blend [wt%]	31.8%	68.2%	100.0%	

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How Do We Correct Boiling Point for Pressure?

Equation form of Maxwell-Bonnell charts (1955)

- P^{vap} units of mmHg, temperatures in units °R

$$\log_{10} P^{vap} = \begin{cases} \dfrac{3000.538X - 6.761560}{43X - 0.987672} & X > 0.002184346 \text{ for } P^{vap} < 1.7 \text{ mmHg} \\ \dfrac{2663.129X - 5.994296}{95.76X - 0.972546} & 0.001201343 \le X \le 0.002184346 \text{ for } 1817 \text{ mmHg} \ge P^{vap} \ge 1.7 \text{ mmHg} \\ \dfrac{2770.085X - 6.412631}{36X - 0.989679} & 0.001201343 > X \text{ for } 1817 \text{ mmHg} < P^{vap} \end{cases}$$

$$X = \frac{\dfrac{1}{T} - 0.0002867}{748.1\left(\dfrac{1}{T_B'} - 0.0002867\right)} \quad \& \quad T_B' = T_B - 2.5 f\left(K_W - 12\right)\log_{10}\left(\frac{P^{vap}}{760}\right)$$

$$f = \begin{cases} 1 & P^{vap} < 760 \text{ mmHg} \\ \text{Min}\left(1, \text{Max}\left(\dfrac{T_B - 659.67}{200}, 0\right)\right) & P^{vap} \ge 760 \text{ mmHg} \end{cases}$$

Pressure Correction Example

“Correct” a 437°F boiling point measured at 40 mmHg to the normal boiling point (at 760 mmHg).

Using the 2nd of 3 equations:

$$\log_{10}(40) = \frac{2663.129X - 5.994296}{95.76X - 0.972546} \Rightarrow X = \frac{0.972546\log_{10}(40) - 5.994296}{95.76\log_{10}(40) - 2663.129} = 0.001767618$$

With T=896.67°R determine T'_B=1094.98

$$0.001767618 = \frac{\frac{1}{437+459.67} - 0.0002867}{748.1\left(\frac{1}{T'_B} - 0.0002867\right)} \Rightarrow T'_B = 1094.98$$

If we neglect the Watson K factor correction (i.e., assume K_W = 12) then T_B = T'_B & the normal boiling point is 635°F

How Do We Interconvert D86 & TBP Temperatures?

Method from 1994 API Technical Data Book

- Consistent with the "API94" option in Aspen Plus

$$T_{\text{TBP},50\%} = 0.87180 \cdot T_{\text{D86},50\%}^{1.0258} \quad (T_{\text{TBP},50\%} \ \& \ T_{\text{D86},50\%} \text{ in °F})$$

$$\Delta T_{\text{TBP}} = A\left(\Delta T_{\text{D86}}\right)^{B} \quad (\Delta T_{\text{TBP}} \ \& \ \Delta T_{\text{D86}} \text{ in °F})$$

Vol%	A	B
100% to 90%*	0.11798	1.6606
90% to 70%	3.0419	0.75497
70% to 50%	2.5282	0.82002
50% to 30%	3.0305	0.80076
30% to 10%	4.9004	0.71644
10% to 0%*	7.4012	0.60244

*Reported 100% & 0% give better trends as 99% & 1%.

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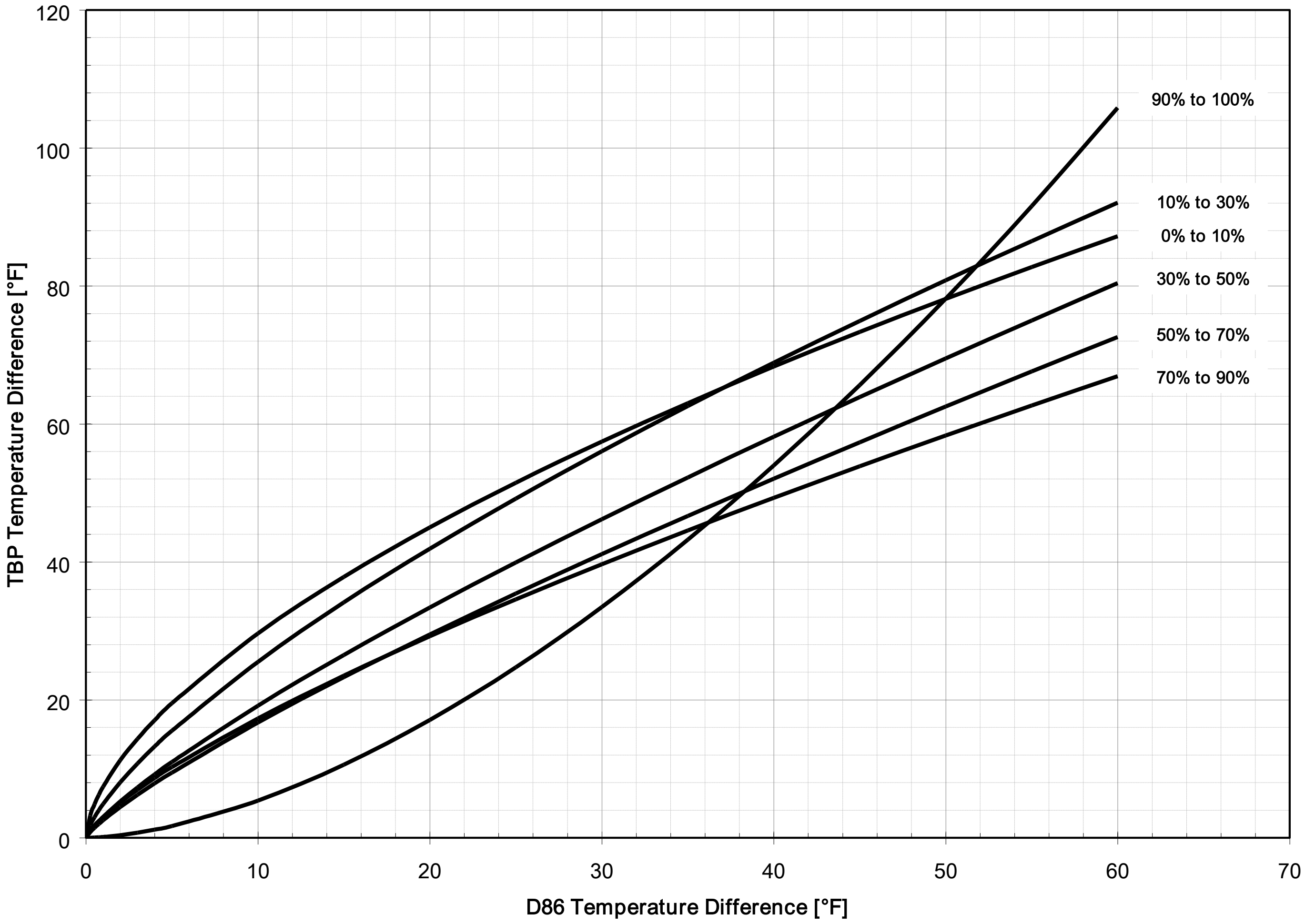
Interconvert D86 & TBP Temperatures



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How Do We Interconvert D86 & TBP Temperatures?

Method from 1987 API Technical Data Book

$$T_{\mathrm{TBP}} = a \cdot \left(T_{\mathrm{D86}}\right)^{b}$$

$$T_{\mathrm{D86}} = \left(\frac{T_{\mathrm{TBP}}}{a}\right)^{1/b} \qquad T_{\mathrm{TBP}} \ \& \ T_{\mathrm{D86}} \text{ in °R}$$

Vol%	a	b
0%*	0.9167	1.0019
10%	0.5277	1.0900
30%	0.7429	1.0425
50%	0.8920	1.0176
70%	0.8705	1.0226
90%	0.9490	1.0110
95%	0.8008	1.0355

Use with care – may give incorrect temperature vs. volume trends

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How Do We Interconvert D1160 & TBP Temperatures?

D1160 temperatures at 10 mm Hg are converted to TBP temperatures at 10 mm Hg — graphical method to interconvert

- D1160 temperatures at 50% & higher equal to the TBP temperatures
- 0% to 10%, 10% to 30%, & 30% to 50% D1160 temperature differences converted to TBP temperature differences

$$\Delta T_{TBP} = a\left(\Delta T_{D1160}\right) + b\left(\Delta T_{D1160}\right)^2 + c\left(\Delta T_{D1160}\right)^3 + d\left(\Delta T_{D1160}\right)^4$$

Vol% Distilled Range	a	B	c	d	Max ΔT
0% - 10%	2.23652561	-1.39334703E-2	3.6358409E-5	1.433117E-8	144°F
10%-30% 30%-50%	1.35673984	-5.4126509E-3	2.9883895E-5	-6.007274E-8	180°F

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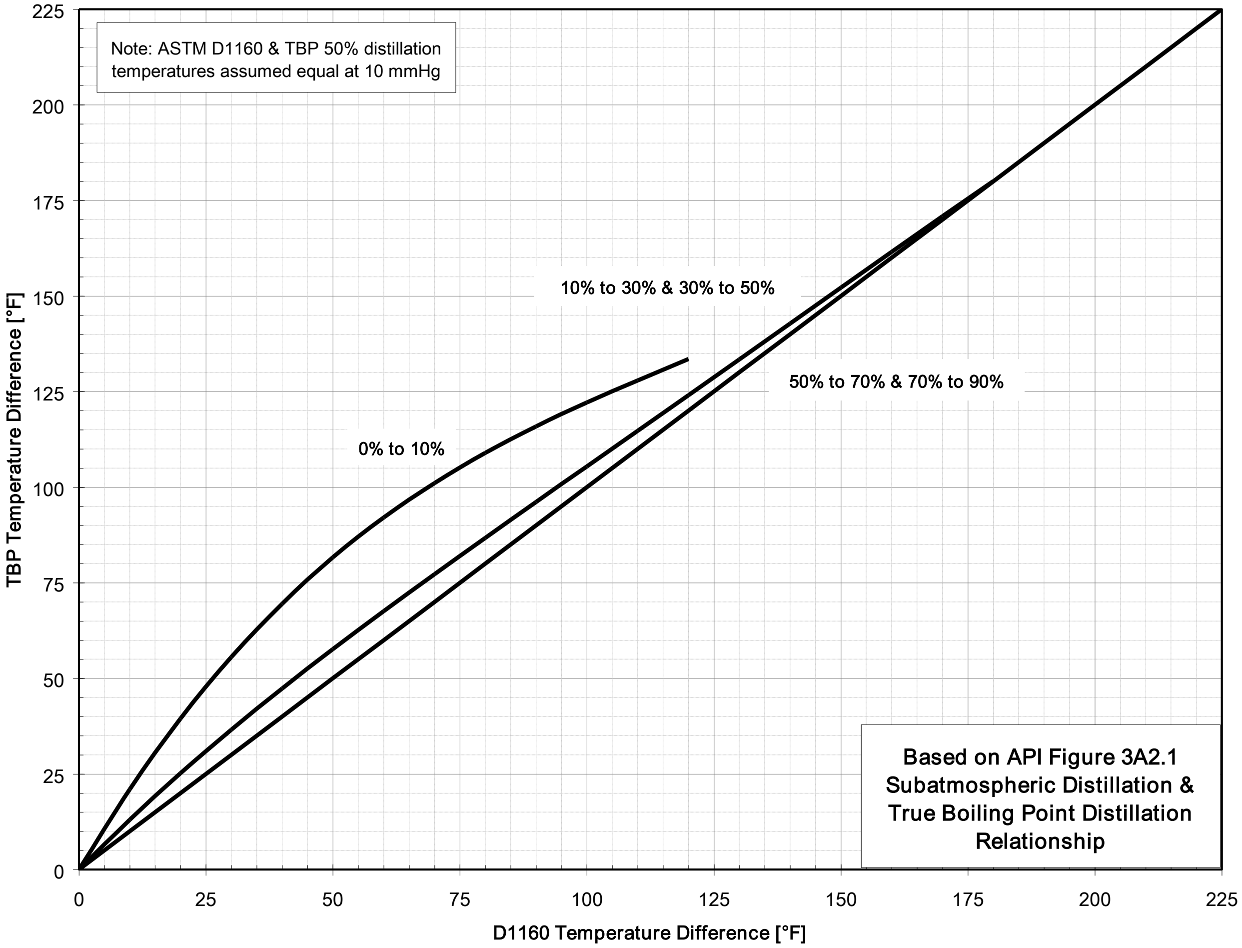
Interconvert D1160 & TBP Temperatures



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How Do We Interconvert D2887 & TBP Temperatures?

Method from 1994 API Technical Data Book

- D2887 essentially TBP on wt% basis, not vol%

$$T_{\text{TBP,50\%}} = T_{\text{D2887,50\%}}$$

$$\Delta T_{\text{TBP}} = A\left(\Delta T_{\text{D2887}}\right)^{B} \quad (\Delta T_{\text{TBP}} \ \& \ \Delta T_{\text{D2887}} \text{ in °F})$$

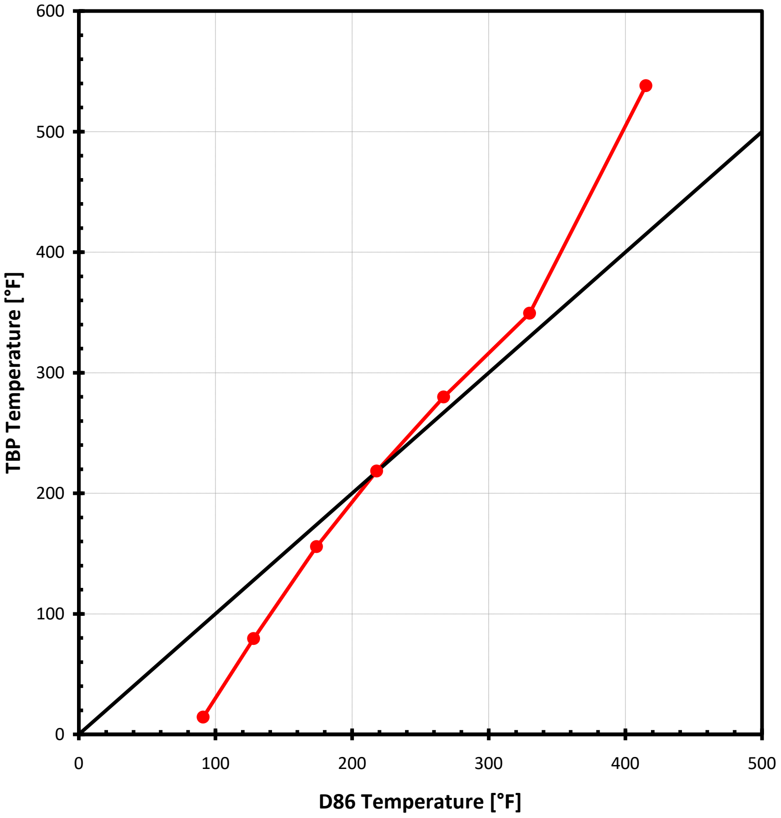
Vol%	A	B
100% to 95%	0.02172	1.9733
95% to 90%	0.97476	0.8723
90% to 70%	0.31531	1.2938
70% to 50%	0.19861	1.3975
50% to 30%	0.05342	1.6988
30% to 10%	0.011903	2.0253
10% to 0%*	0.15779	1.4296

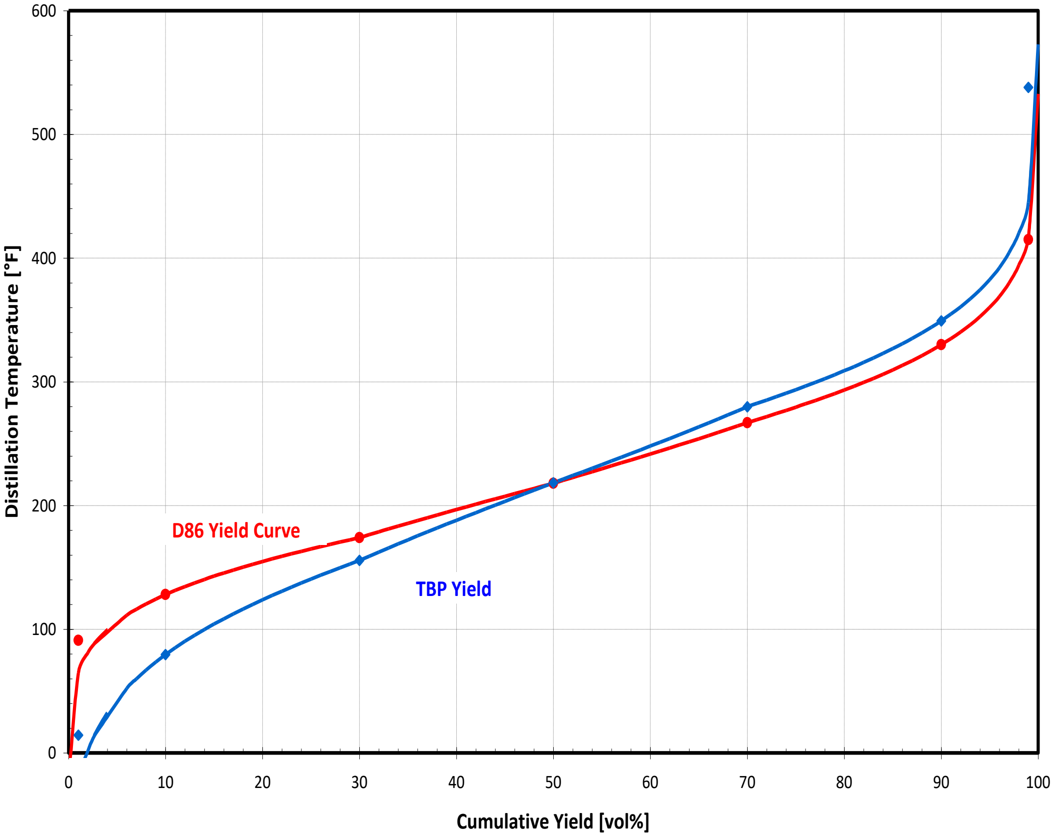
D86 Conversion Example

Vol%	D86	D86 ΔT	TBP ΔT	TBP
IBP	91			14.3
		37	65.2	
10	128			79.5
		46	76.1	
30	174			155.6
		44	62.7	
50	218			218.4
		49	61.5	
70	267			279.9
		63	69.4	
90	330			349.3
		85	188.7	
EP	415			538.0

Steps for this example

D-86 vs TBP Temperatures





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How Do We Correlate Yield to Boiling Point?

Needed for interpolation, extrapolation, and smoothing of data

Traditional methods

- Electronic version of plotting cumulative yield data vs. boiling point temperature on "probability paper"
  - Guarantees an "S" shaped cumulative yield curve
  - No specific 0% or 100% points

Distribution models

- Whitson method (1980)
  - Probability distribution function.
  - Can generate distribution from a limited amount of C6+ data

$$p(M)=\frac{1}{\beta\,\Gamma(\alpha)}\left(\frac{M-M_i}{\beta}\right)^{\alpha-1}$$

- Riazi method (1989)
  - Cumulative amount (Y)
  - 0% point, no 100% point
  - Essentially the same equation form as Dhulesia's equation (1984)

$$\frac{T-T_0}{T_0}=\left[\frac{A_T}{B_T}\ln\left(\frac{1}{1-Y}\right)\right]^{\frac{1}{B_T}} \Rightarrow Y=1-\exp\left[-\frac{B_T}{A_T}\left(\frac{T-T_0}{T_0}\right)^{B_T}\right]$$

How Do We Use the Probability Form?

Distillation yield curves typically have an “S” shape

Traditional to linearize on “probability” graph paper

- Axis transformed using functions related to Gaussian distribution function

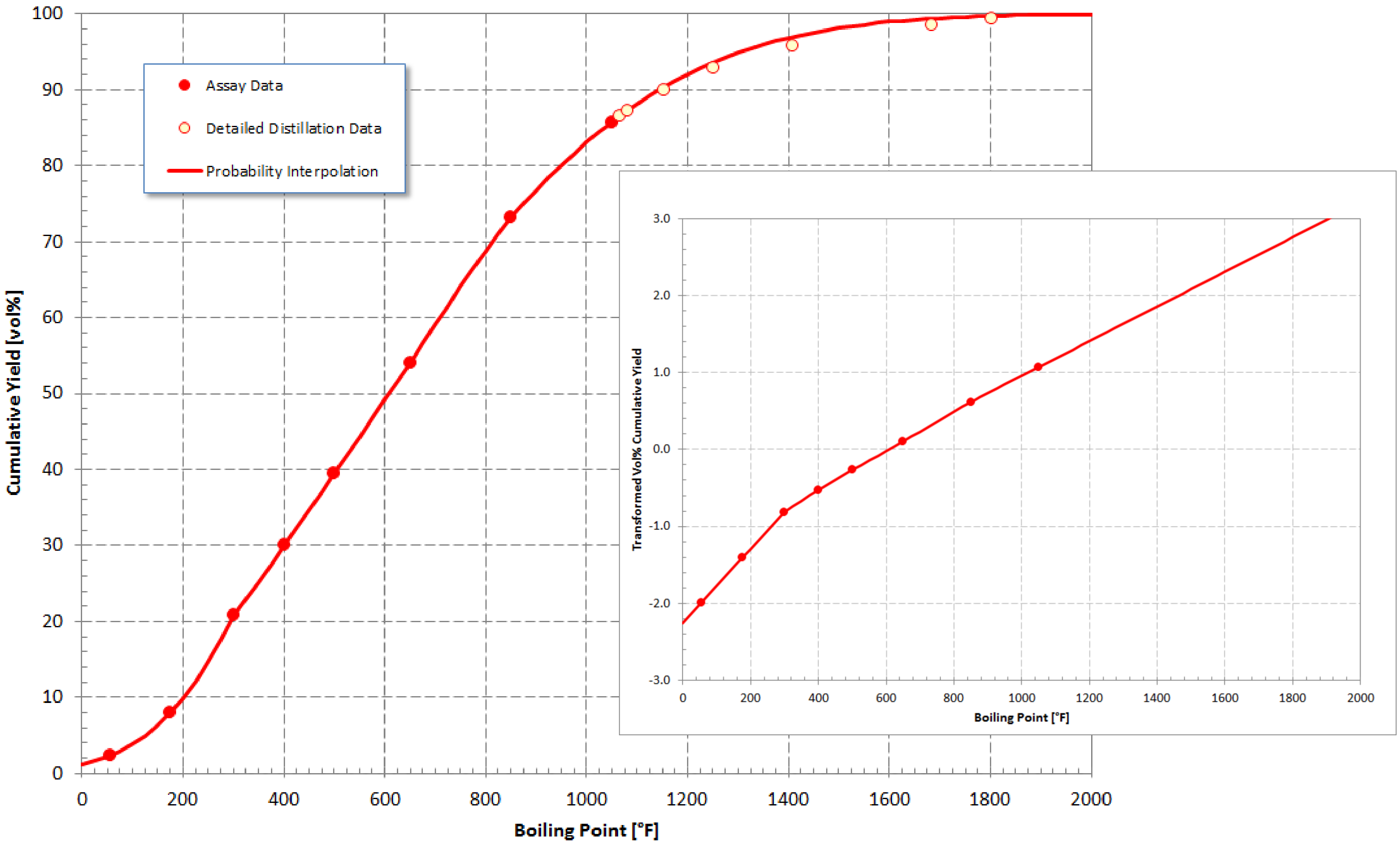
Functions available in Excel

- Transformed Yield: =NORMSINV(Pct_Yield/100)
- From interpolated value: =NORMSDIST(Value) * 100

Transformed 0% & 100% values undefined

- Typical to set IBP & EP to 1% & 99%

“Linearized” Distillation Yield Curves



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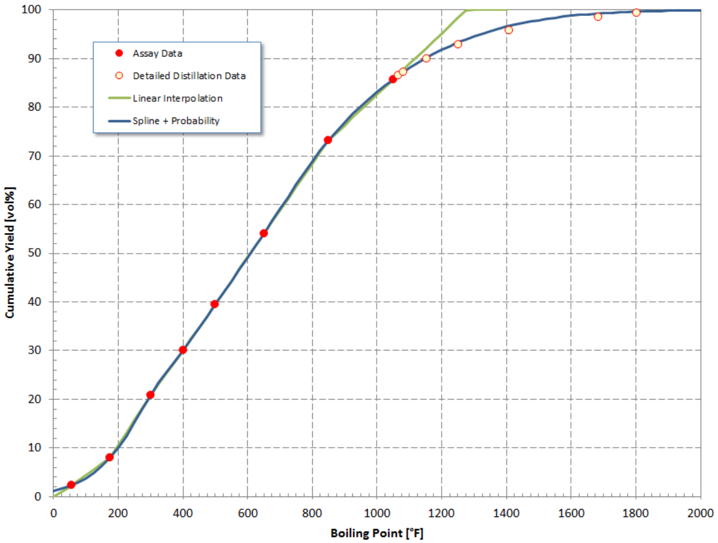
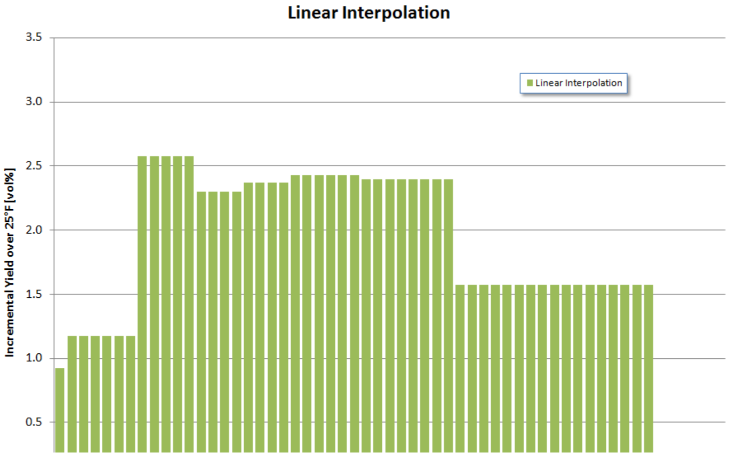
Incremental vs. Cumulative Yield

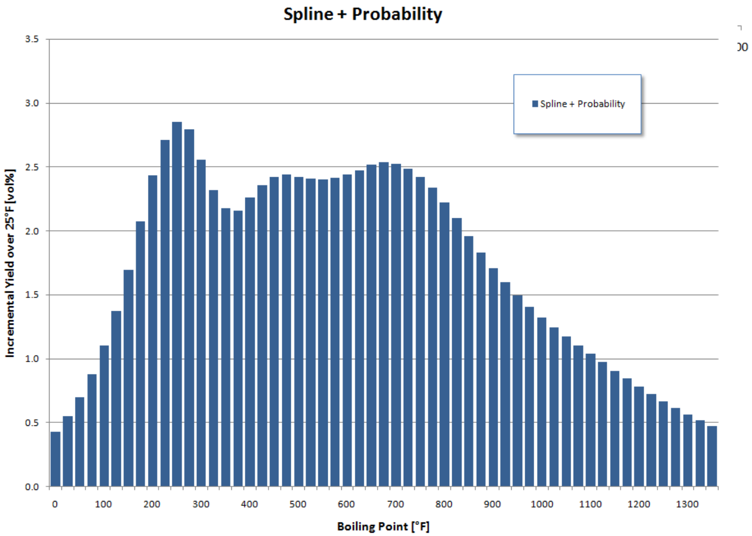
Incremental yield can be calculated as the difference in the cumulative yields at the final & initial boiling points

$$\Delta Y\left(T_i,T_f\right)=Y\left(T_f\right)-Y\left(T_i\right)$$

- Values impacted by method chosen to interpolate/extrapolate







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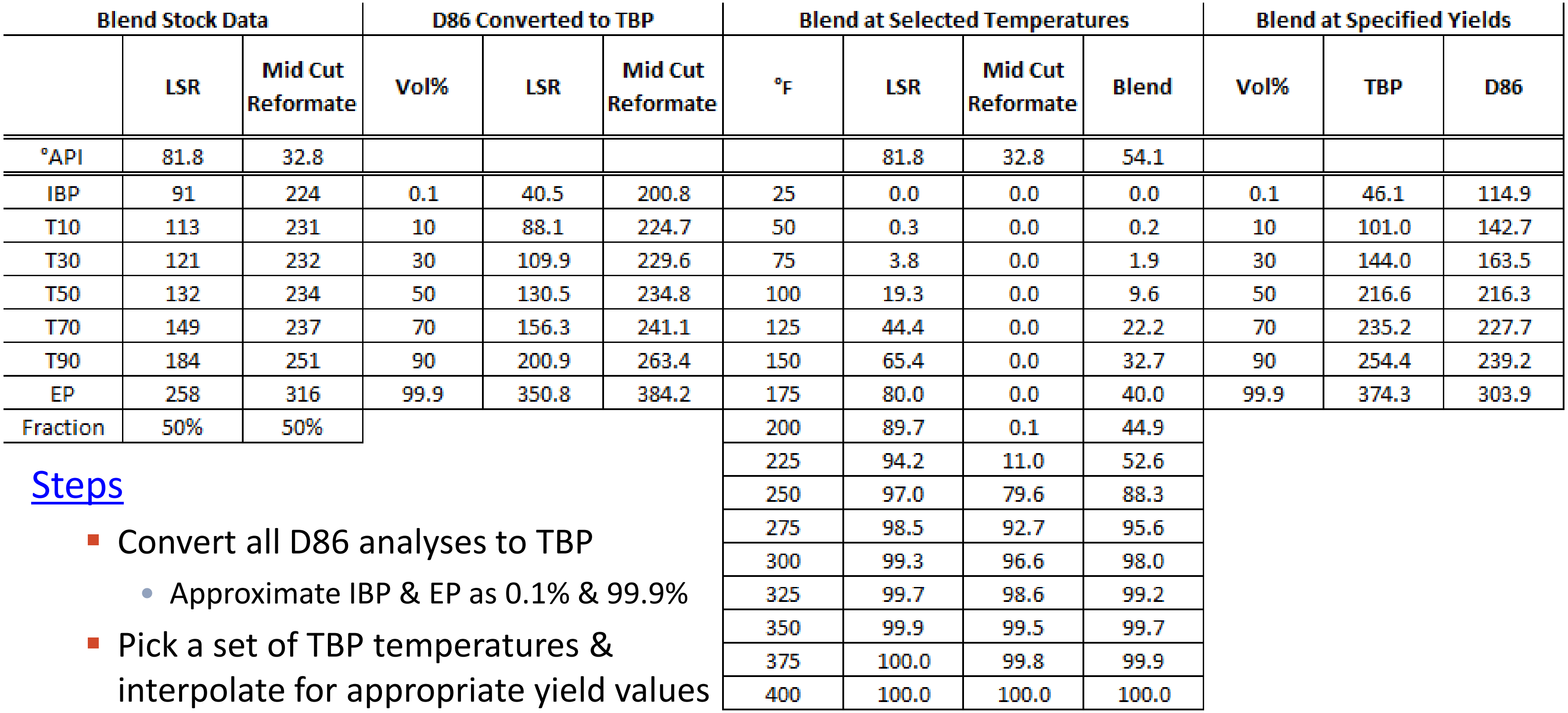
How Do We Blend Distillation Curves?

Blend the distillation curves for all blend stocks & extract the temperatures from the resulting curve

Steps

- Convert all of the starting distillation analyses to TBP basis (@ 1 atm)
- Pick a set of TBP temperatures for which the blend calculations will proceed. Extract the yield values for at these selected temperature values for all blend stocks.
  - Use whatever temperatures seem reasonable to cover the span of all input values
- Calculate a yield curve for the blend at the temperatures chosen in the previous step
- Extract the temperature values for the specified yield values
- Convert to original distillation basis (if required)

Distillation Curve Blend Example



Blend Stock Data			D86 Converted to TBP			Blend at Selected Temperatures				Blend at Specified Yields		
	LSR	Mid Cut Reformate	Vol%	LSR	Mid Cut Reformate	°F	LSR	Mid Cut Reformate	Blend	Vol%	TBP	D86
°API	81.8	32.8					81.8	32.8	54.1			
IBP	91	224	0.1	40.5	200.8	25	0.0	0.0	0.0	0.1	46.1	114.9
T10	113	231	10	88.1	224.7	50	0.3	0.0	0.2	10	101.0	142.7
T30	121	232	30	109.9	229.6	75	3.8	0.0	1.9	30	144.0	163.5
T50	132	234	50	130.5	234.8	100	19.3	0.0	9.6	50	216.6	216.3
T70	149	237	70	156.3	241.1	125	44.4	0.0	22.2	70	235.2	227.7
T90	184	251	90	200.9	263.4	150	65.4	0.0	32.7	90	254.4	239.2
EP	258	316	99.9	350.8	384.2	175	80.0	0.0	40.0	99.9	374.3	303.9
Fraction	50%	50%				200	89.7	0.1	44.9			
						225	94.2	11.0	52.6			
						250	97.0	79.6	88.3			
						275	98.5	92.7	95.6			
						300	99.3	96.6	98.0			
						325	99.7	98.6	99.2			
						350	99.9	99.5	99.7			
						375	100.0	99.8	99.9			
						400	100.0	100.0	100.0			

Steps

- Convert all D86 analyses to TBP
  - Approximate IBP & EP as 0.1% & 99.9%
- Pick a set of TBP temperatures & interpolate for appropriate yield values
- Volumetrically blend at each temperature for combined TBP curve
- Interpolate for appropriate TBP values at the standard volumetric yields
- Convert to D86 analysis

How Do We Estimate Light Ends from Yield Curve?

Determine the incremental amount from the difference in cumulative yields between adjacent pure component boiling points

Steps

- Choose light-ends components
  - Typically methane, ethane, propane, iso & normal butane, iso & normal pentane
- Determine boiling point ranges associated with pure component boiling points
  - Sometimes extend range to 0.5°C above the pure component boiling point
- Extrapolate distillation yield curve to find cumulative yields at the boiling point ranges. Find differences to determine incremental amounts.

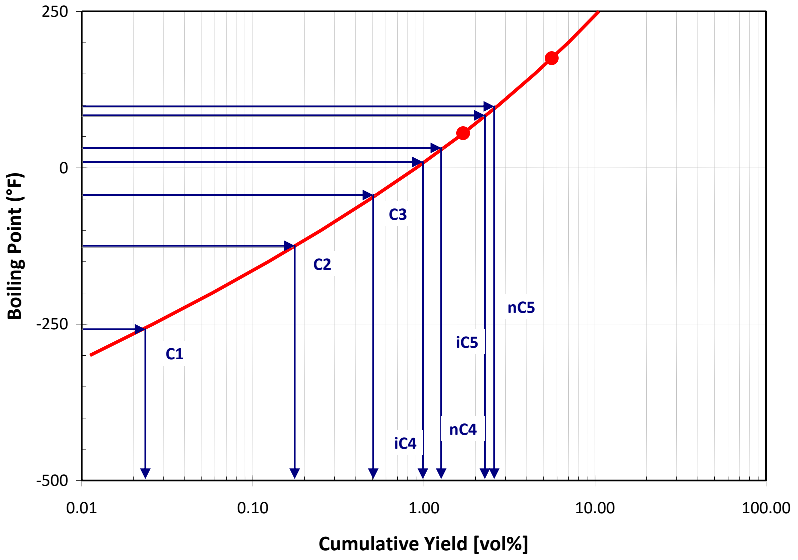
Light Ends Example

	TBP [°F]		Yield [vol%]	
	Initial	Final	Cumulative @ Initial	Cumulative @ Final
Whole Crude				
Light Naphtha	55	175	1.7	5.6
Medium Naphtha	175	300	5.6	15.3
Heavy Naphtha	300	400	15.3	21
Kero	400	500	21	29.2
Atm Gas Oil	500	650	29.2	40.4
Light VGO	650	850	40.4	57.3
Heavy VGO	850	1050	57.3	71.5
Vacuum Resid	1050	End	71.5	100

	TBP [°F]			Yield [vol%]		
	Pure Component	Initial	Final	Cumulative @ Initial	Cumulative @ Final	Increment
Methane	-258.73	N/A	-258.73	0.0	0.02	0.02
Ethane	-127.49	-258.73	-127.49	0.02	0.17	0.15
Propane	-43.75	-127.49	-43.75	0.17	0.53	0.36
i-Butane	10.78	-43.75	10.78	0.53	1.03	0.50
n-Butane	31.08	10.78	31.08	1.03	1.30	0.27
i-Pentane	82.12	31.08	82.12	1.30	2.27	0.97
n-Pentane	96.92	82.12	96.92	2.27	2.65	0.38

Steps

- Choose light-ends components
- Determine boiling point ranges associated with pure component boiling points. Use as the Final Boiling Point for range.
- Extrapolate distillation yield curve to find cumulative yields at all boiling point values.
- Calculate differences to determine incremental amounts.



How Do We Estimate Other Properties of Fractions?

Properties inferred from measured trends

- Relative density / specific gravity / API gravity
- Sulfur content
- Carbon residue

Properties from correlations

- Molecular weight / molar mass

$$M = 20.486 T_B^{1.26007} \gamma_o^{4.98308} \exp\left(0.0001165 T_B - 7.78712 \gamma_o + 0.0011582 T_B \gamma_o\right)$$

- Critical properties & accentric factor
- Heat of combustion (Btu/lb, liquid state @ 60°F)

$$\hat{H}_{\mathrm{LHV}} = 16792 + 54.5G - 0.217G^2 - 0.0019G^3$$
$$\hat{H}_{\mathrm{HHV}} = 17672 + 66.6G - 0.316G^2 - 0.0014G^3$$

What Happens When We Change Cut Points?

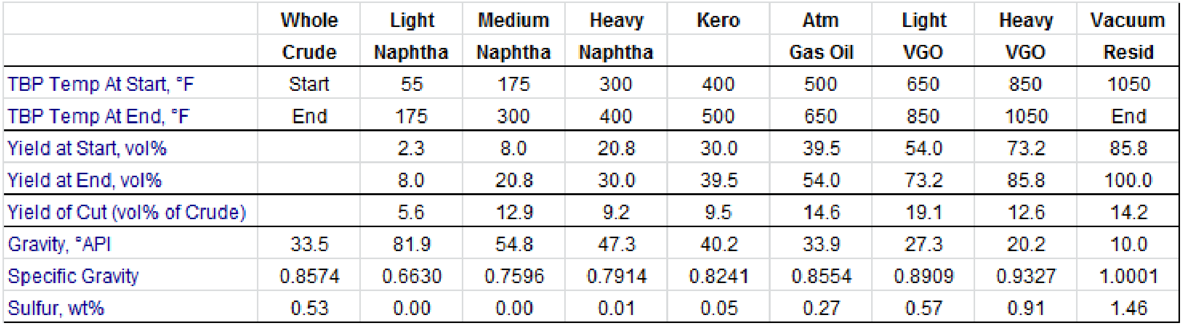
In general

- The amount can be calculated as the difference in cumulative yields between the new initial & final boiling points
    - Interpolate within the yield vs. temperature curve using the probability form
- The properties can be determined by interpolating the curve for the property vs. the mid-increment yield
    - Linear interpolation usually sufficient

Special cases

- Slightly smaller than a given cut in the assay – find properties of the "excluded" fraction & subtract contribution from the given cut
- Slightly larger than a given cut in the assay – find properties of the "included" fraction & add contribution to the given cut
- Combination of two or more given cuts in the assay – find properties by adding all contributions

Revised Cut Points – Example #1



	Whole Crude	Light Naphtha	Medium Naphtha	Heavy Naphtha	Kero	Atm Gas Oil	Light VGO	Heavy VGO	Vacuum Resid
TBP Temp At Start, °F	Start	55	175	300	400	500	650	850	1050
TBP Temp At End, °F	End	175	300	400	500	650	850	1050	End
Yield at Start, vol%		2.3	8.0	20.8	30.0	39.5	54.0	73.2	85.8
Yield at End, vol%		8.0	20.8	30.0	39.5	54.0	73.2	85.8	100.0
Yield of Cut (vol% of Crude)		5.6	12.9	9.2	9.5	14.6	19.1	12.6	14.2
Gravity, °API	33.5	81.9	54.8	47.3	40.2	33.9	27.3	20.2	10.0
Specific Gravity	0.8574	0.6630	0.7596	0.7914	0.8241	0.8554	0.8909	0.9327	1.0001
Sulfur, wt%	0.53	0.00	0.00	0.01	0.05	0.27	0.57	0.91	1.46

What is the yield of the total gas oil (500 – 1050°F)? What are the properties?

- Add contributions for the Atm Gas Oil, Light VGO, & Heavy VGO

$$\Delta V_{GO} = Y\left(1050^\circ F\right) - Y\left(500^\circ F\right) = 85.8 - 39.5 = 46.3 \text{ vol\%}$$

$$\gamma_{GO} = \frac{\sum (\Delta V)_i \gamma_i}{V_{GO}} = \frac{(14.6)(0.8554)+(19.1)(0.8909)+(12.6)(0.9327)}{46.3} = 0.8911$$

$$S_{GO} = \frac{\sum (\Delta V)_i \gamma_i S_i}{\sum (\Delta V)_i \gamma_i} = \frac{(14.6)(0.8554)(0.27)+(19.1)(0.8909)(0.57)+(12.6)(0.9327)(0.91)}{(14.6)(0.8554)+(19.1)(0.8909)+(12.6)(0.9327)} = 0.58 \text{ wt\%}$$

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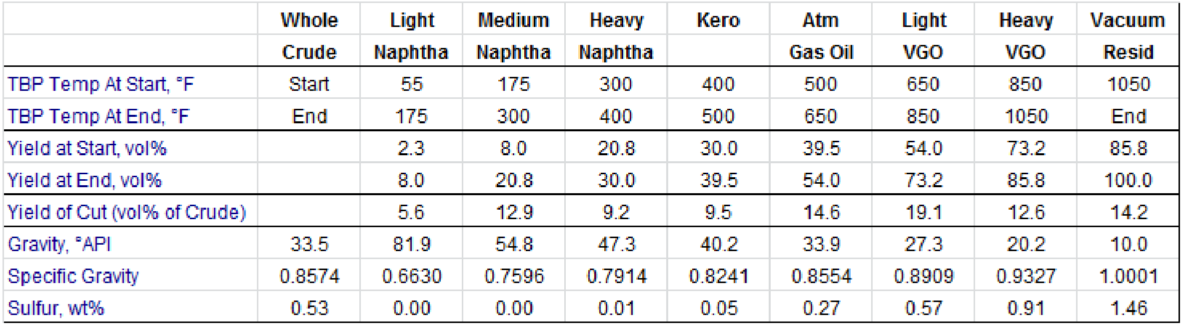
Revised Cut Points – Example #2



	Whole Crude	Light Naphtha	Medium Naphtha	Heavy Naphtha	Kero	Atm Gas Oil	Light VGO	Heavy VGO	Vacuum Resid
TBP Temp At Start, °F	Start	55	175	300	400	500	650	850	1050
TBP Temp At End, °F	End	175	300	400	500	650	850	1050	End
Yield at Start, vol%		2.3	8.0	20.8	30.0	39.5	54.0	73.2	85.8
Yield at End, vol%		8.0	20.8	30.0	39.5	54.0	73.2	85.8	100.0
Yield of Cut (vol% of Crude)		5.6	12.9	9.2	9.5	14.6	19.1	12.6	14.2
Gravity, °API	33.5	81.9	54.8	47.3	40.2	33.9	27.3	20.2	10.0
Specific Gravity	0.8574	0.6630	0.7596	0.7914	0.8241	0.8554	0.8909	0.9327	1.0001
Sulfur, wt%	0.53	0.00	0.00	0.01	0.05	0.27	0.57	0.91	1.46

What is the yield of the HVGO if the cut range is 850 – 1000°F? What are the properties?

- Determine amount & estimate properties of 1000 – 1050°F cut.
- Cumulative yield @ 1000°F from interpolation of yield vs. temperature

$$Y(1000^\circ F) = 83.1 \text{ vol\%} \quad \Rightarrow \quad Y_{mid} = \frac{83.1 + 85.8}{2} = 84.4$$

$$\Delta V = 85.8 - 83.1 = 2.7 \text{ vol\%}$$

- Properties from linear interpolation of mid-increment yield vs. property

$$G(84.4 \text{ vol\%}) = 16.5 \quad \Rightarrow \quad \gamma = 0.9564$$

$$S(84.4 \text{ vol\%}) = 1.12 \text{ wt\%}$$

- Remove contributions from the Heavy VGO in the assay

$$\Delta V_{GO} = Y(1000^\circ F) - Y(500^\circ F) = 83.1 - 73.2 = 9.9 \text{ vol\%}$$

$$\gamma_{GO} = \frac{(12.6)(0.9327) - (2.7)(0.9564)}{9.9} = 0.9262$$

$$S_{GO} = \frac{(12.6)(0.9327)(0.91) - (2.7)(0.9564)(1.12)}{(9.9)(0.9262)} = 0.86 \text{ wt\%}$$

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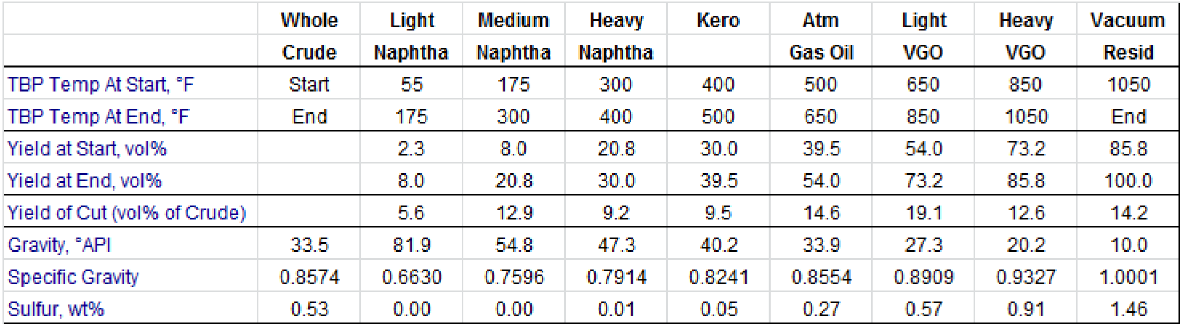
Revised Cut Points – Example #3



	Whole Crude	Light Naphtha	Medium Naphtha	Heavy Naphtha	Kero	Atm Gas Oil	Light VGO	Heavy VGO	Vacuum Resid
TBP Temp At Start, °F	Start	55	175	300	400	500	650	850	1050
TBP Temp At End, °F	End	175	300	400	500	650	850	1050	End
Yield at Start, vol%		2.3	8.0	20.8	30.0	39.5	54.0	73.2	85.8
Yield at End, vol%		8.0	20.8	30.0	39.5	54.0	73.2	85.8	100.0
Yield of Cut (vol% of Crude)		5.6	12.9	9.2	9.5	14.6	19.1	12.6	14.2
Gravity, °API	33.5	81.9	54.8	47.3	40.2	33.9	27.3	20.2	10.0
Specific Gravity	0.8574	0.6630	0.7596	0.7914	0.8241	0.8554	0.8909	0.9327	1.0001
Sulfur, wt%	0.53	0.00	0.00	0.01	0.05	0.27	0.57	0.91	1.46

What is the yield of the Vac Resid if the cut point is 1000°F+? What are the properties?

- Determine amount & estimate properties of 1000 – 1050°F cut.
- Cumulative yield @ 1000°F from interpolation of yield vs. temperature

$$Y\left(1000°F\right)=83.1\text{ vol\%} \quad \Rightarrow \quad Y_{mid}=\frac{83.1+85.8}{2}=84.4$$

$$\Delta V=85.8-83.1=2.7\text{ vol\%}$$

- Properties from linear interpolation of mid-increment yield vs. property

$$G\left(84.4\text{ vol\%}\right)=16.5 \quad \Rightarrow \quad \gamma=0.9564$$

$$S\left(84.4\text{ vol\%}\right)=1.12\text{ wt\%}$$

- Add contributions to the Vac Resid in the assay

$$\Delta V_{GO}=100-Y\left(1000°F\right)=100-83.1=16.9\text{ vol\%}$$

$$\gamma_{GO}=\frac{(14.2)(1.0001)+(2.7)(0.9564)}{16.9}=0.9931$$

$$S_{GO}=\frac{(14.2)(1.0001)(1.46)+(2.7)(0.9564)(1.12)}{(16.9)(0.9931)}=1.41\text{ wt\%}$$

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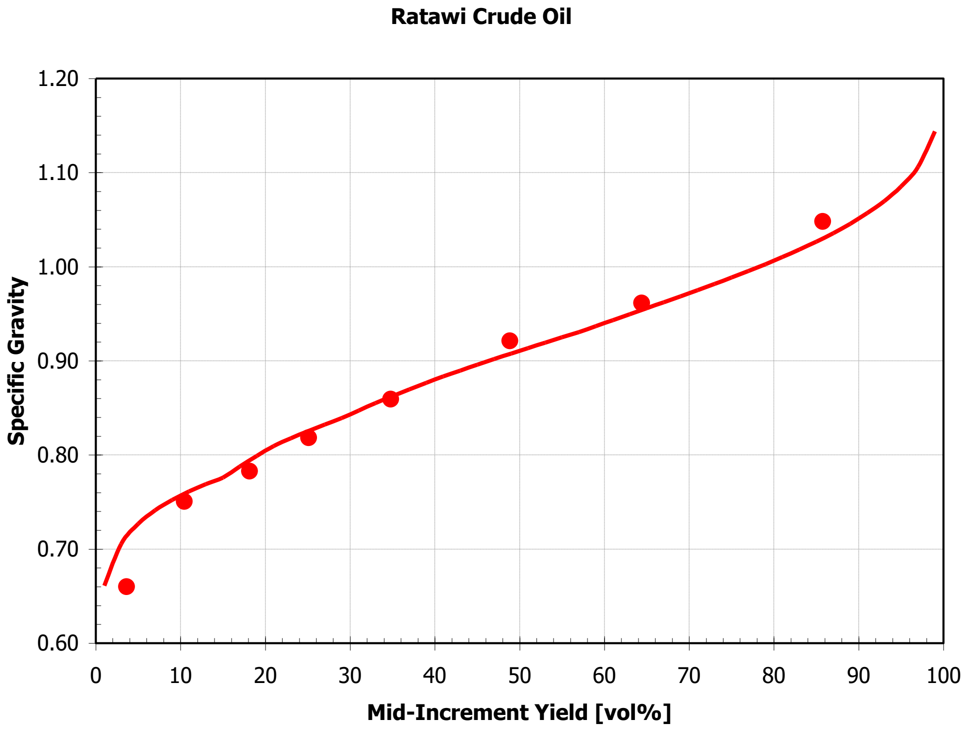
Can We Estimate Gravity Curve When None Given?

Assume that all fractions have the same Watson K factor

$$K_w = \frac{\gamma_o}{\sum v_i \left(\sqrt[3]{T_{Bi}} \right)} \quad \text{from} \quad \gamma_o = \sum v_i \gamma_{oi} = \sum v_i \left(K_{wi} \sqrt[3]{T_{Bi}} \right)$$

Example – Estimate Ratawi Watson K factor & gravity curve based on overall gravity & distillation analysis

- Curve is estimate, points are from the assay



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How Do We Blend Watson K Factor?

Best method

- Blend specific gravity
- Determine new average boiling point from blended yield curve

Approximate method

- Blend individual Watson K factors by weight

$$K_{mix} = \sum w_i K_i = \frac{\sum v_i \gamma_{oi} K_i}{\sum v_i \gamma_{oi}}$$

  - Implies average boiling point from volumetric blend of cube root of boiling point

What is the Average Boiling Point for a Mixture?

5 types are defined in the API Technical Data Book

- Volume average boiling point $\left(T_b\right)_v = \sum_{i=1}^{n} v_i T_{b,i}$
- Mass average boiling point $\left(T_b\right)_w = \sum_{i=1}^{n} w_i T_{b,i}$
- Molar average boiling point $\left(T_b\right)_M = \sum_{i=1}^{n} x_i T_{b,i}$
- Cubic average boiling point $\left(T_b\right)_{cubic} = \left(\sum_{i=1}^{n} v_i \sqrt[3]{T_{b,i}}\right)^3$
- Mean average boiling point $\left(T_b\right)_{mean} = \frac{\left(T_b\right)_M + \left(T_b\right)_{cubic}}{2}$

Watson K-factor is to use the Mean Average Boiling Point (MeABP)

Estimate Average Boiling Points from Distillation Curve

Procedure 2B1.1 of the API *Technical Data Book* using D86 distillation values

$$(\text{VABP}) = \frac{T_{10} + T_{30} + T_{50} + T_{70} + T_{90}}{5}$$

$$(\text{SL}) = \frac{T_{90} - T_{10}}{90 - 10}$$

$$(\text{WABP}) = (\text{VABP}) + \Delta_1$$

$$(\text{MABP}) = (\text{VABP}) - \Delta_2$$

$$(\text{CABP}) = (\text{VABP}) - \Delta_3$$

$$(\text{MeABP}) = (\text{VABP}) - \Delta_4$$

$$\ln(\Delta_1) = -3.062123 - 0.01829\left[(\text{VABP}) - 32\right]^{0.6667} + 4.45818(\text{SL})^{0.25}$$

$$\ln(\Delta_2) = -0.563793 - 0.007981\left[(\text{VABP}) - 32\right]^{0.6667} + 3.04729(\text{SL})^{0.333}$$

$$\ln(\Delta_3) = -0.23589 - 0.06906\left[(\text{VABP}) - 32\right]^{0.45} + 1.8858(\text{SL})^{0.45}$$

$$\ln(\Delta_4) = -0.94402 - 0.00865\left[(\text{VABP}) - 32\right]^{0.6667} + 2.99791(\text{SL})^{0.333}$$

How Do We Blend Heating Values?

Heating Value

- Molar, mass, or liquid-volume average (depending on units)

$$\tilde{H}_{mix} = \sum x_i \tilde{H}_i \quad \text{or} \quad \hat{H}_{mix} = \sum w_i \hat{H}_i$$

- Lower/net heating value (LHV) — water in gas state

$$\text{Fuel} + \text{O}_2 \rightarrow \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{g}) + \text{N}_2(\text{g}) + \text{SO}_2(\text{g})$$

- Higher/gross heating value (HHV) — water in liquid state

$$\text{Fuel} + \text{O}_2 \rightarrow \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\ell) + \text{N}_2(\text{g}) + \text{SO}_2(\text{g})$$

$$\tilde{H}_{\text{HHV}} = \tilde{H}_{\text{LHV}} + n_{\text{H}_2\text{O}} \cdot \Delta\tilde{H}_{\text{H}_2\text{O}}^{vap}\left(T_{ref}\right)$$

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Vapor Pressure Calculations

Bubble Point – TVP (True Vapor Pressure)

- At 1 atm, could use ideal gas & liquid assumptions – molar blending

$$\sum y_i = \sum x_i K_i = 1 \quad \Rightarrow \quad \sum x_i \left(\frac{P_i^{vap}(T)}{P} \right) = 1$$

- Vapor pressure approximation using accentric factor

$$\log_{10}\left(\frac{P_i^{vap}}{P_{ci}} \right) = \frac{7}{3}(1+\omega_i)\left(1 - \frac{T_{ci}}{T} \right)$$

- Maxwell-Bonnell relationship for petroleum fractions
- EOS (equation of state) calculations more rigorous
  - Soave-Redlich-Kwong or Peng-Robinson

How Do We Blend RVPs?

RVP is nearly equal to the True Vapor Pressure (TVP) at 100°F

For ideal gas & liquid mixtures, TVP blends linearly with molar fraction

$$y_i \phi_i P = x_i \gamma_i P_i^{vap} \exp\left(\int_{P_i^{vap}}^{P} \frac{\overline{v}_i}{RT} dP \right) \Rightarrow \quad y_i P = x_i P_i^{vap}$$

$$\Rightarrow \quad (\text{TVP})_{mix} = \sum x_i P_i^{vap}$$

Approximate volumetric linear blending with "RVP Blending Indices"

$$(\text{RVP})_{mix}^{1.25} = \sum v_i (\text{RVP})_i^{1.25} \quad \Rightarrow \quad (\text{RVP})_{mix} = \left[\sum v_i (\text{RVP})_i^{1.25} \right]^{1/1.25}$$

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RVP & TVP – API Technical Data Book Methods

Intent is to estimate true vapor pressures (TVPs) from a measured RVP

Can also estimate RVP from any measured vapor pressure value

- TVP could be measured at any temperature – could use boiling point
- Slope is of the ASTM D86 distillation curve @ T10

Figure 5B1.1 – True Vapor Pressure of Gasolines and Finished Petroleum Products
(1994)

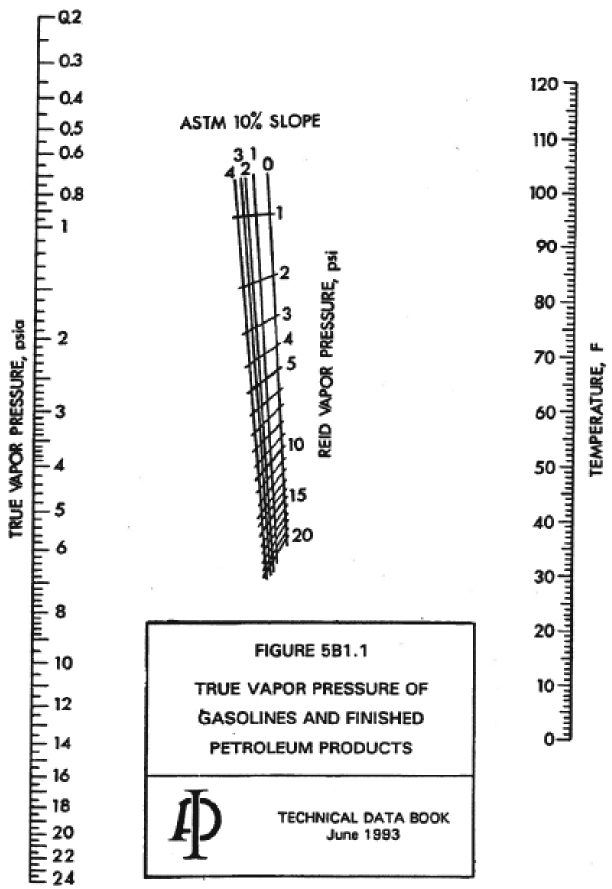
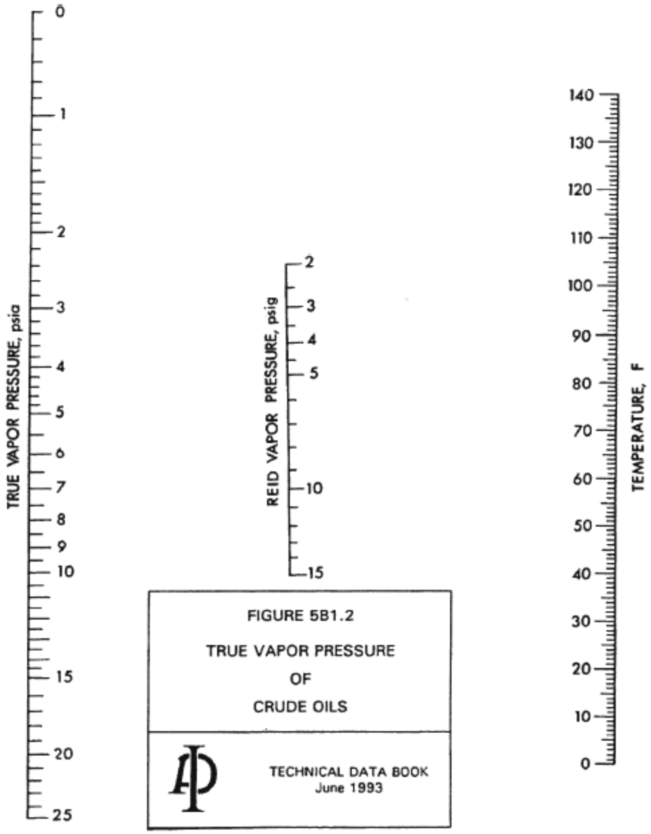


Figure 5B1.2 – True Vapor Pressure of Crude Oils
(1994)



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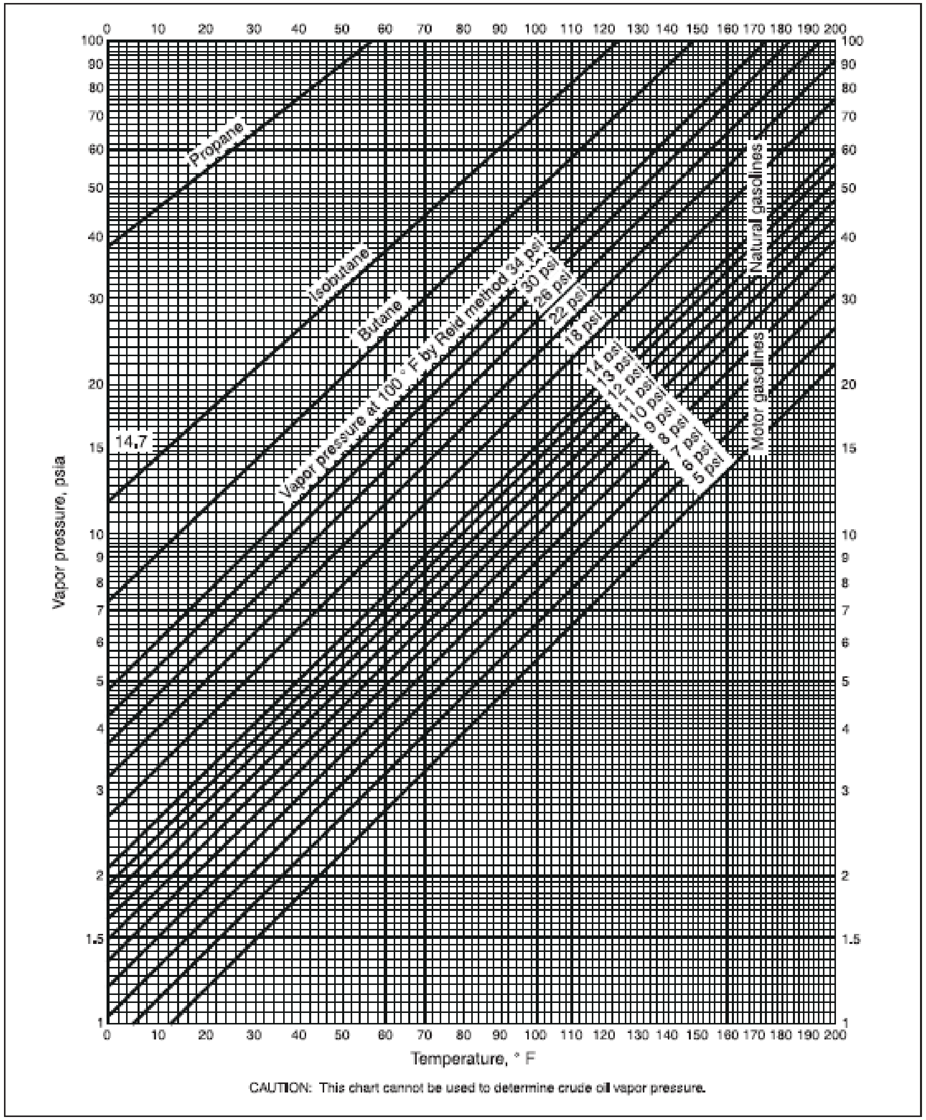
Other Correlations

GPSA Fig. 6-4 makes use of Kremser relationship (1930) for TVP @ 100°F:

$$TVP = 1.07\ (RVP) + 0.6$$

FIG. 6-4

True Vapor Pressures vs. Temperatures for Typical LPG, Motor, and Natural Gasolines



CAUTION: This chart cannot be used to determine crude oil vapor pressure.

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Other correlations

Santa Barbara County APCD Rule 325, Attachment B, equation 25:

$$TVP = (RVP)\exp(C_o\,(IRTEMP - ITEMP)) + C_F$$

where:
C_o RVP dependent coefficient
ITEMP $1/(559.69\ {}^oR)$
IRTEMP $1/(T_s + 559.69\ {}^oR)$
T_s ${}^oF$ temperature stored fluid

Based on API Figure 5B1.2

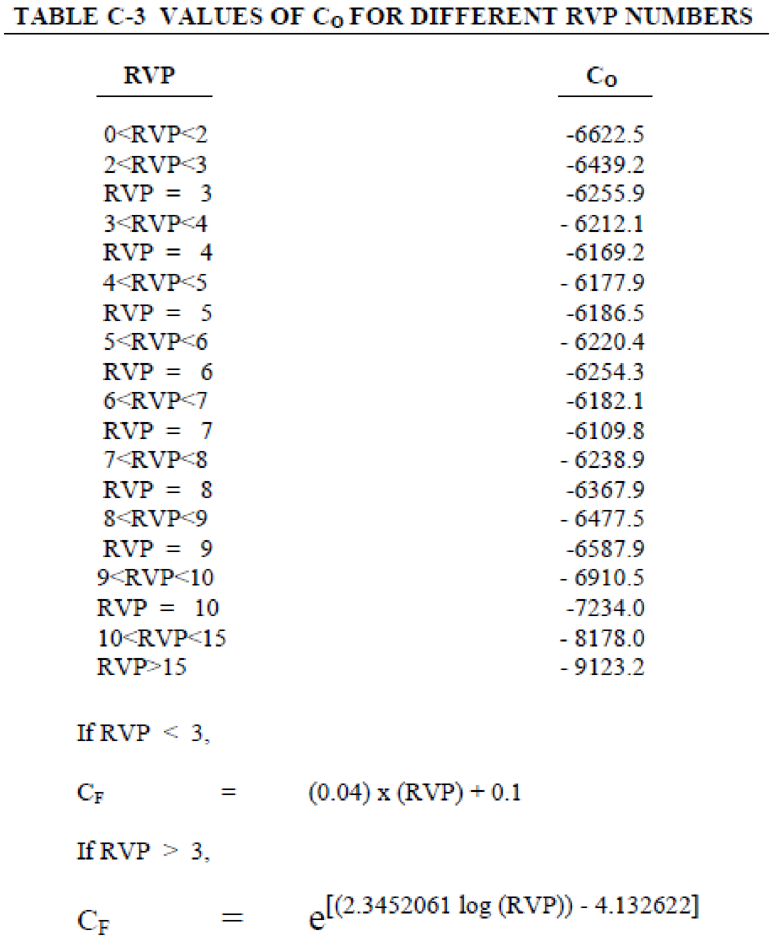

TABLE C-3 VALUES OF C_O FOR DIFFERENT RVP NUMBERS

RVP	C_O
0<RVP<2	-6622.5
2<RVP<3	-6439.2
RVP = 3	-6255.9
3<RVP<4	- 6212.1
RVP = 4	-6169.2
4<RVP<5	- 6177.9
RVP = 5	-6186.5
5<RVP<6	- 6220.4
RVP = 6	-6254.3
6<RVP<7	-6182.1
RVP = 7	-6109.8
7<RVP<8	- 6238.9
RVP = 8	-6367.9
8<RVP<9	- 6477.5
RVP = 9	-6587.9
9<RVP<10	- 6910.5
RVP = 10	-7234.0
10<RVP<15	- 8178.0
RVP>15	- 9123.2

If RVP < 3,

$C_F = (0.04) \times (RVP) + 0.1$

If RVP > 3,

$C_F = e^{[(2.3452061 \log (RVP)) - 4.132622]}$

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How Do We Blend Octane Numbers?

Octane numbers generally blend non-linearly

- Interactions between components in mixture

Approximate linear blending with “Octane Blending Indices”

- Indices are fairly closely guarded

In this class we’ll generally assume linear blending with volume

$$(RON)_{mix} = \sum v_i (RON)_i$$

$$(MON)_{mix} = \sum v_i (MON)_i$$

Non-Linear Octane Blending Formula

Developed by Ethyl Corporation using a set of 75 & 135 blends

$$R = \bar{R} + a_1\left[\overline{RJ} - \bar{R}\cdot\bar{J}\right] + a_2\left[\overline{\left(O^2\right)} - \bar{O}^2\right] + a_3\left[\overline{\left(A^2\right)} - \bar{A}^2\right]$$

$$M = \bar{M} + b_1\left[\overline{MJ} - \bar{M}\cdot\bar{J}\right] + b_2\left[\overline{\left(O^2\right)} - \bar{O}^2\right] + b_3\left[\frac{\overline{\left(A^2\right)} - \bar{A}^2}{100}\right]^2$$

$$\text{"Road" Octane} = \frac{R+M}{2}$$

$$\text{Sensitivity} = J \equiv R - M$$

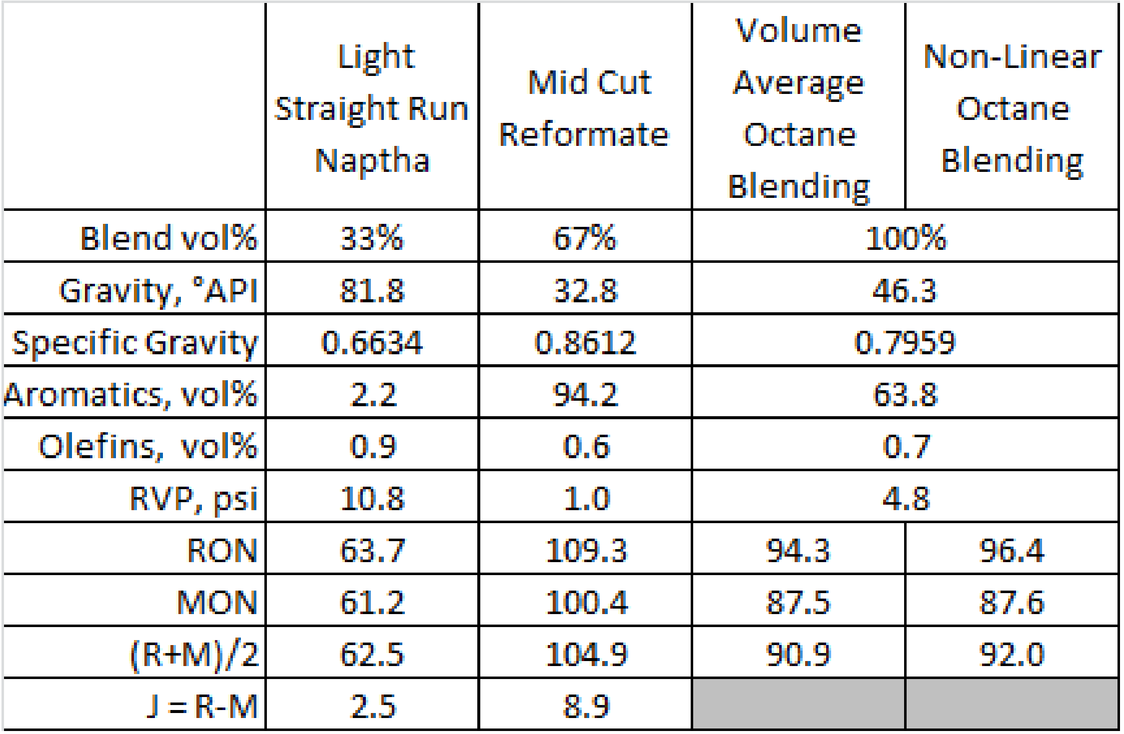
$$\text{Volume Average} = \bar{X} \equiv \frac{\sum V_i \cdot X_i}{\sum V_i}$$

	75 blends	**135 blends**
a_1	0.03224	0.03324
a_2	0.00101	0.00085
a_3	0	0
b_1	0.04450	0.04285
b_2	0.00081	0.00066
b_3	-0.00645	-0.00632

Petroleum Refinery Process Economics, 2nd ed. ,
by Robert E. Maples, PennWell Corp., 2000

Gasoline Blending Sample Problem

What are the API gravity, RVP, & average octane number for a 33/67 blend of Light Straight Run Gasoline & Mid-Cut Reformate?



	Light Straight Run Naptha	Mid Cut Reformate	Volume Average Octane Blending	Non-Linear Octane Blending
Blend vol%	33%	67%	100%	
Gravity, °API	81.8	32.8	46.3	
Specific Gravity	0.6634	0.8612	0.7959	
Aromatics, vol%	2.2	94.2	63.8	
Olefins, vol%	0.9	0.6	0.7	
RVP, psi	10.8	1.0	4.8	
RON	63.7	109.3	94.3	96.4
MON	61.2	100.4	87.5	87.6
(R+M)/2	62.5	104.9	90.9	92.0
J = R-M	2.5	8.9		

Steps for this example

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What is Driveability Index (DI)?

Oriented towards the auto industry

Need enough volatility to completely vaporize fuel in the cylinder

- Lowering RVP makes the fuel harder to vaporize

Empirical relationship between gasoline volatility & engine performance (driveability & emissions)

$$DI = 1.5\,T_{10} + 3\,T_{50} + T_{90} + (2.4^{o}\mathrm{F})(\mathrm{EtOH\ vol\%})$$

The lower the DI, the better the performance

- Alkylates raise T_{50}
- Ethanol raises RVP & depresses T_{50}, but not the DI

How Can We Estimate Flash Point?

Related to volatility of mixture.

- Assume ideal gas since tests done at 1 atm.

Method of Lenoir

$$\sum_{i=1}^{N} x_i M_i \gamma_i P_i^{vap} = 1.3$$

Method of Gmehling & Rasmussen

- Related to lower flammability limit

$$\sum_{i=1}^{N} \frac{x_i \gamma_i P_i^{vap}}{L_i} = 1 \quad \text{with} \quad L_i = L_i\left(25°C\right) - 0.182\left(\frac{T-25}{\Delta H_{c,i}}\right)$$

How Can We Estimate Flash Point?

API Procedure 2B7.1 for closed cup test (using ASTM D 86 T_{10})

- 1987 Version (units of °R)

$$\frac{1}{T_F} = -0.014568 + \frac{2.84947}{T_{10}} + 0.001903\ln\left(T_{10}\right)$$

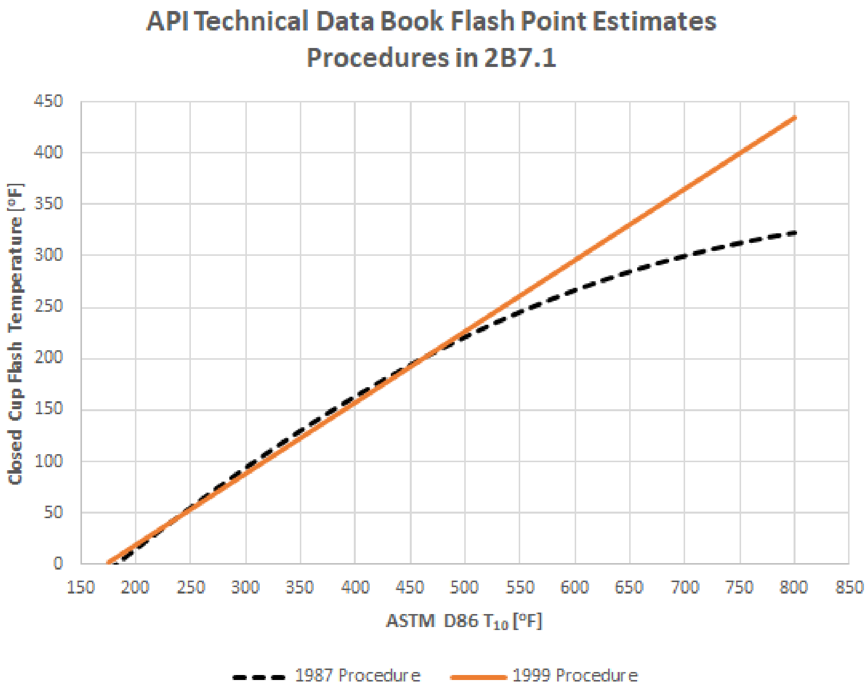
- 1997 Version (units of °F)
  - Open Cup

$$T_F = 0.68\,T_{10} - 109.6$$

  - Closed Cup

$$T_F = 0.69\,T_{10} - 118.2$$

- 2016 API Data Book has revised Procedure 2C1.1 using IBP & T_5


API Technical Data Book Flash Point Estimates Procedures in 2B7.1

How Do We Estimate & Blend Cetane Index?

Cetane index is an estimate of the cetane number based on composition. It does not take into account effects of additives to improve cetane number.

Estimation method outlined by ASTM D 976

$$\text{Index} = -420.34 + 0.016\,G^2 + 0.192\,G\log(T_{50}) + 65.01[\log(T_{50})]^2 - 0.0001809\,T_{50}^{\;2}$$

where T_{50} is 50% point as determined by D 86 distillation [°F] & G is the API gravity

- Four Variable methods outlined in ASTM D 4737
  - Different correlations for 15 ppmw & 500 ppmw diesels

Cetane index can be linearly blended by volume (as an approximation)

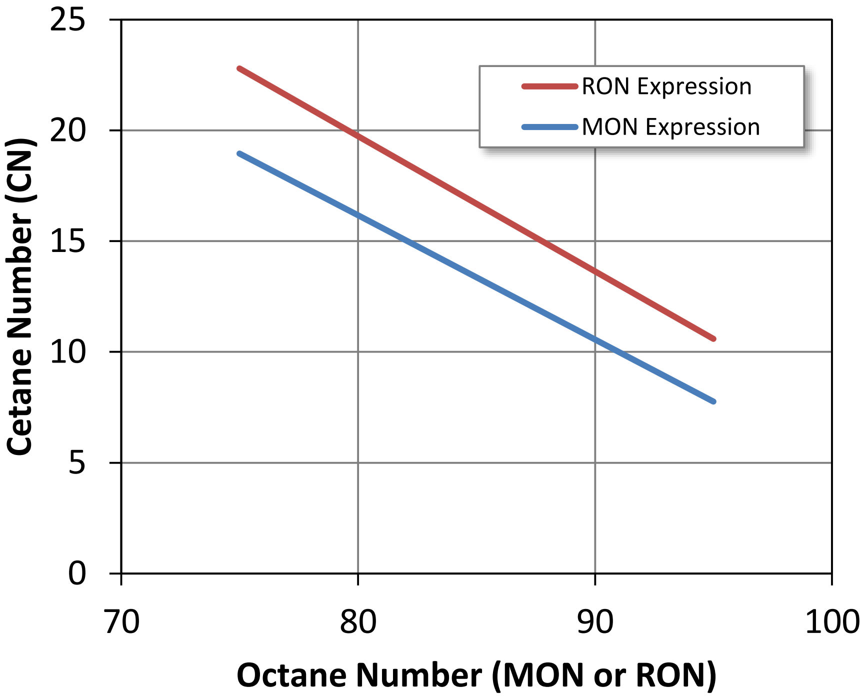
How Are Octane & Cetane Numbers Related?

In general compounds with high octane numbers have low cetane numbers

Correlation developed from gasoline samples

$$CN = 60.96 - 0.56(MON)$$

$$CN = 68.54 - 0.61(RON)$$



Bowden, Johnston, & Russell, "Octane-Cetane Relationship",
Final Report AFLRL No. 33, March 1974,
Prepared by U.S. Army Fuels & Lubricants Research Lab & Southwest Research Institute

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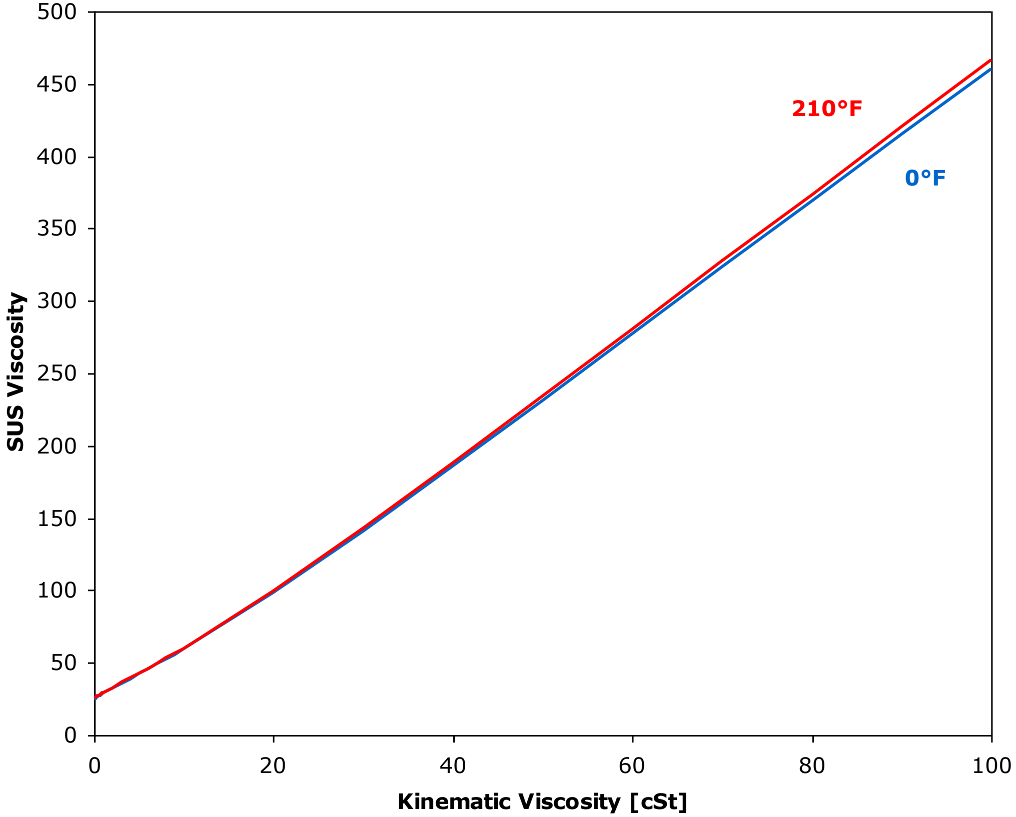
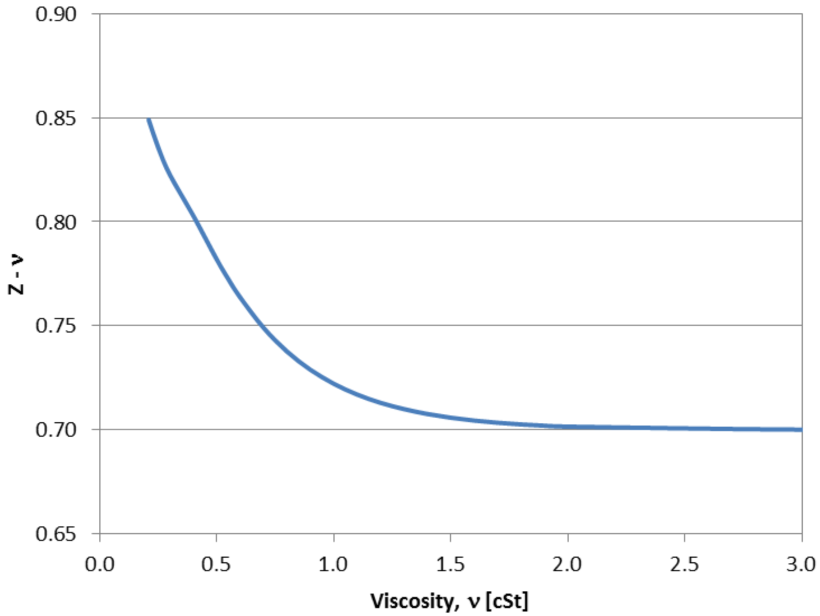
How Do We Convert SUS viscosity?

$$\nu_{SUS} = \left[1.0 + 0.000061(T-100)\right]\left[4.6324\nu + \frac{1.0+0.03264\nu}{\left(3930.2+262.7\nu+23.97\nu^2+\nu^3\right)\times10^{-5}}\right]$$



How do we adjust viscosity for temperature?

ASTM D341 for viscosities above 0.21 cSt



$$\log\left(\log\left(Z\right)\right) = A + B\cdot\log\left(T\right)$$

$$Z = \nu + 0.7 + C - D + E - F + G - H$$

$$C = \exp\left(-1.14883 - 2.65868\nu\right)$$

$$D = \exp\left(-0.0038138 - 12.5645\nu\right)$$

$$E = \exp\left(5.46491 - 37.6289\nu\right)$$

$$F = \exp\left(13.0458 - 74.6851\nu\right)$$

$$G = \exp\left(37.4619 - 192.643\nu\right)$$

$$H = \exp\left(80.4945 - 400.468\nu\right)$$

$$\nu \approx \left(Z-0.7\right) - \exp\left[-0.7487 - 3.295\left(Z-0.7\right) + 0.6119\left(Z-0.7\right)^2 - 0.3193\left(Z-0.7\right)^3\right]$$

For viscosities greater than 2.0 cSt the equation is essentially:

$$\log\left(\log\left(\nu+0.7\right)\right) = A + B\cdot\log\left(T\right)$$

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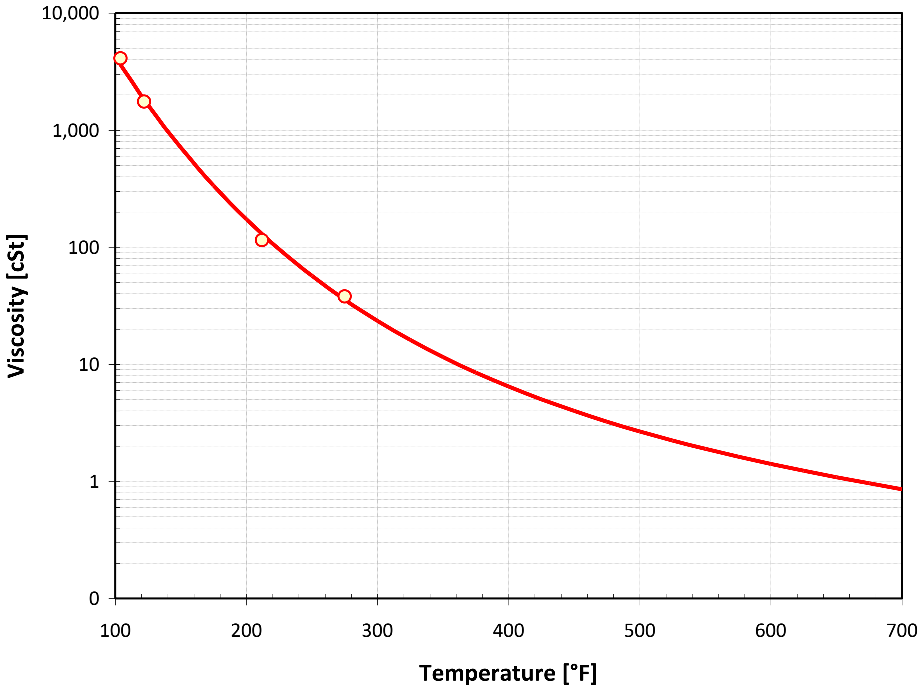
Viscosity vs. Temperature Example

°F	cSt	log(log(Z))	log(°R)	Est log(log(Z))	Est cSt	Relative Deviation
104	4,102	0.5579	563.67	0.5514	3,629	-12%
122	1,750	0.5110	581.67	0.5137	1,836	5%
212	115	0.3146	671.67	0.3253	130	13%
275	37.9	0.2005	734.67	0.1934	35.7	-6%

By linear regression	
A:	1.732
B:	-0.002094
r^2:	0.997



Steps

- Calculate the *Z* & temperature terms from the given data
    - Convert temperatures to absolute basis
- Determine *A* & *B* parameters from data
    - This case uses linear regression & all 4 points
- Use *A* & *B* parameters to find *Z* at other temperatures
- Convert *Z* to cSt
    - Approximate formula used here

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How Do We Blend Viscosities?

Viscosity blending has complicated composition effects

Simple viscosity blending equations are more appropriate for gas-phase viscosity – ***should not be used*** for blending liquid-phase petroleum fraction values

- Arrhenius

$$\ln\left(\mu_{mix}\right) = \sum v_i \ln\left(\mu_i\right)$$

- Bingham

$$\frac{1}{\mu_{mix}} = \sum \frac{v_i}{\mu_i}$$

- Kendall & Monroe

$$\mu_{mix} = \left[\sum x_i \ln\left(\mu_i^{1/3}\right)\right]^3$$

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How Do We Blend Viscosities?

Desire to blend viscosity with either volume or mass amounts

Linear blending with “Viscosity Blending Indices” of kinematic viscosity

$$\log\left(\log\left(\nu_{mix}+\nu_c\right)\right)=\sum v_i \log\left(\log\left(\nu_i+\nu_c\right)\right) \quad \text{where } \nu_c=0.7$$

May see an index based on log-log terms with extra coefficients and/or natural-log terms. Give identical results.

For heavy fractions often mass blending is suggested with ν_c of 0.8 to 1.0

- Refutas equation – mass blending

$$(\text{VBN})_{blend}=\sum w_i (\text{VBN})_i \quad \text{where } (\text{VBN})_i \equiv 14.534\cdot\ln\left(\ln\left(\nu_i+0.8\right)\right)+10.975$$

Other types of blending indices

- Chevron Method 2

$$\frac{\ln\left(\nu_{mix}\right)}{\ln\left(1000\,\nu_{mix}\right)}=\sum v_i \frac{\ln\left(\nu_i\right)}{\ln\left(1000\,\nu_i\right)}\equiv \mathcal{W} \quad \Rightarrow \quad \ln\left(\nu_{mix}\right)=\ln\left(1000\right)\cdot\frac{\mathcal{W}}{1-\mathcal{W}}$$

ASTM D 7152 Viscosity Blending

Procedure C when using viscosity values all at the same temperature

- "ASTM Blending Method" – volume blending
- "Modified ASTM Blending Method" – mass blending

Based on log-log (MacCoull-Walther-Wright) transformation viscosity

$$Z_i = \nu_i + 0.7 + \exp\left(-1.47 - 1.84\nu_i - 0.51\nu_i^2\right)$$

$$W_i = \log\left(\log\left(Z_i\right)\right)$$

$$W_B = \sum v_i W_i$$

$$Z_B = 10^{10^{W_B}} - 0.7$$

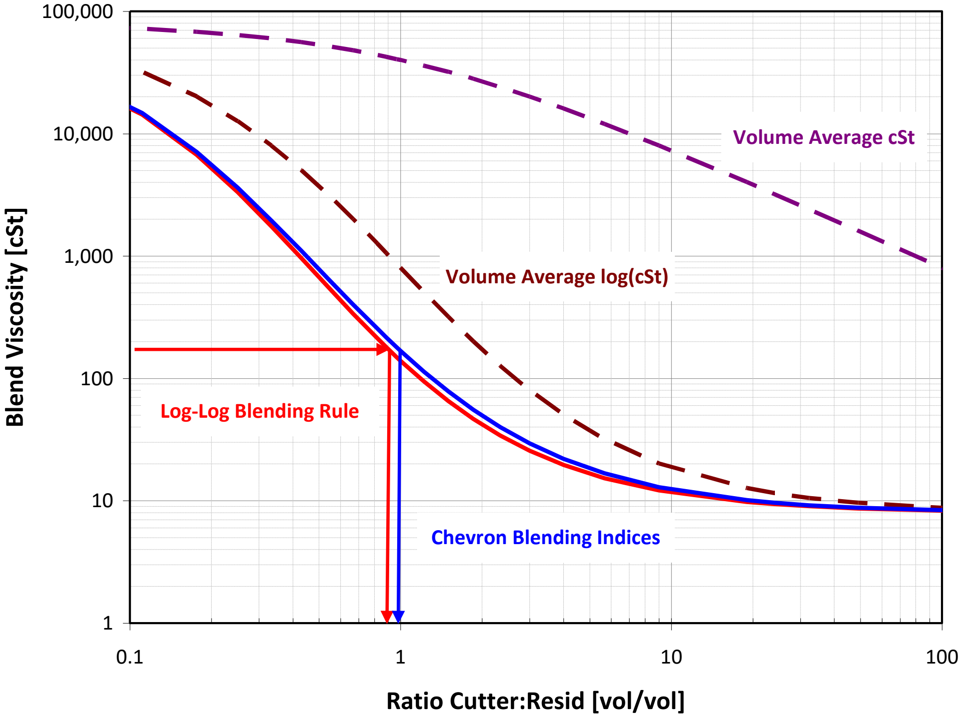
$$\nu_B = Z_B - \exp\left[-0.7487 - 3.295 Z_B + 0.6119 Z_B^2 - 0.3193 Z_B^3\right]$$

- Developed for volume blending & kinematic viscosity but could be used for mass blending
  - For base stock blends, no significant difference between volumetric & mass blending
  - For fuel blends (chemically converted blend stocks), mass blending more accurate
- Exponential correction term insignificant above 2 cSt
- Extends the use of log-log terms from down to 0.2 cSt.

Viscosity Blending Example

Determine the amount of cutter stock needed to blend with 5,000 bpd 80,000 cSt vacuum resid to make a fuel oil with 180 cSt @ 122°F. The cutter stock has 8.0 cSt viscosity.

	Vacuum Resid	Cutter Stock	Total Blend
Volume	5,000		
Viscosity	80,000	8.0	180
ASTM Blending Method			
log(log(ν + 0.7))	0.69047	-0.02709	0.35352
Required Volumes	5,000	4,426	9,426
Volume Fraction	53%	47%	
Volume Ratio		0.89	1.89
Chevron Method 2			
ln(ν)/ln(1000 ν)	0.62040	0.23138	0.42914
Required Volumes	5,000	4,835	9,835
Volume Fraction	51%	49%	
Volume Ratio		0.97	1.97



ASTM Blending Method & Chevron Method 2 essentially the same results

Solid & Near-Solid Formation: Pour Point, Cloud Point, & Freezing Point

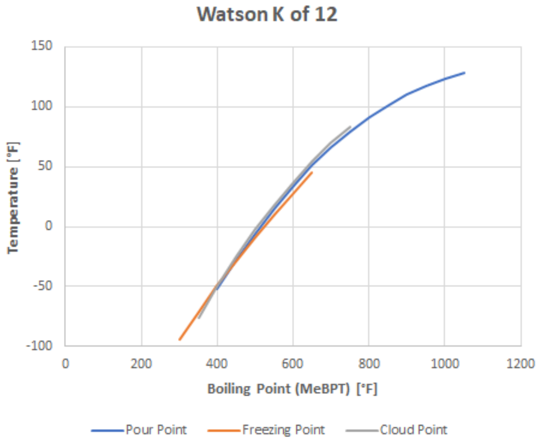
Estimates based on physical properties

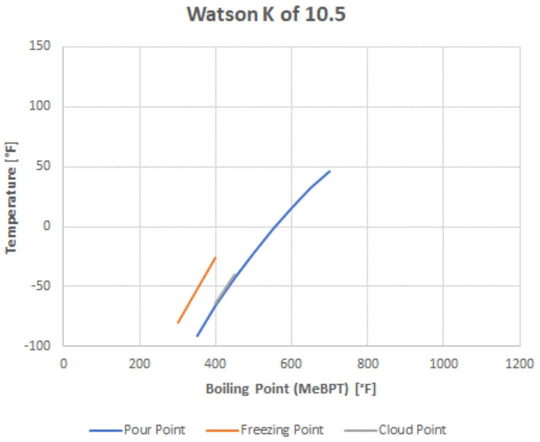
- API Technical Data Book, Procedures 2C5.1, 2C2, & 2C6.1
- Good to about ±7°F

$$T_{FPT,°R} = -2390.42 + 1826\gamma_o + 122.49K_W - 0.135(\text{MeABP})$$

$$T_{pour,°R} = 3.85 \cdot 10^{-8} (\text{MeABP})^{5.49} \, 10^{-\left(0.712(\text{MeABP})^{0.315} + 0.133\gamma_o\right)} + 1.4$$

$$\log_{10}\left(T_{CPT,°R}\right) = -7.41 + 5.49\log_{10}(\text{MeABP}) - 0.712(\text{MeABP})^{0.315} - 0.133\gamma_o$$


Watson K of 12


Watson K of 10.5

Updated: July 1, 2019

How are the Carbon Residues Related?

Carbon residue – coking tendency

- ASTM D 524 — Ramsbottom (RCR)
- ASTM D 189 — Conradson (CCR)
- ASTM D 4530 – Microcarbon (MCRT)

<u>CCR & MCRT essentially the same</u>

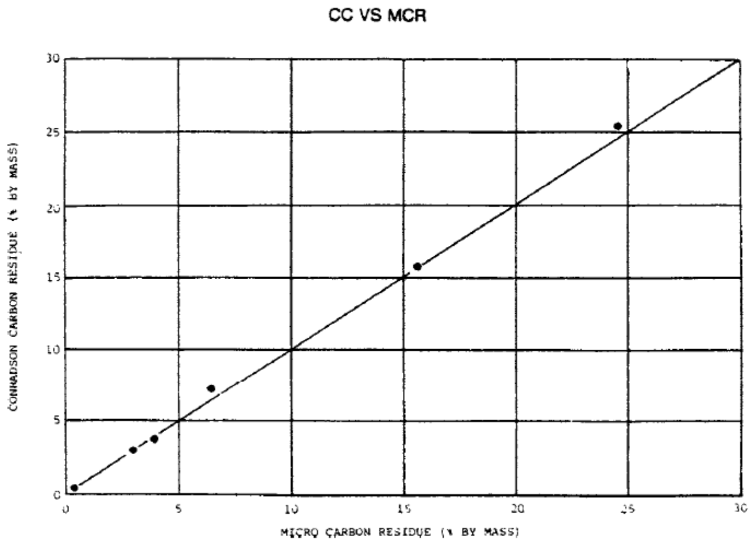


FIG. X1.2 Correlation of Conradson and Micro Carbon Residue Tests

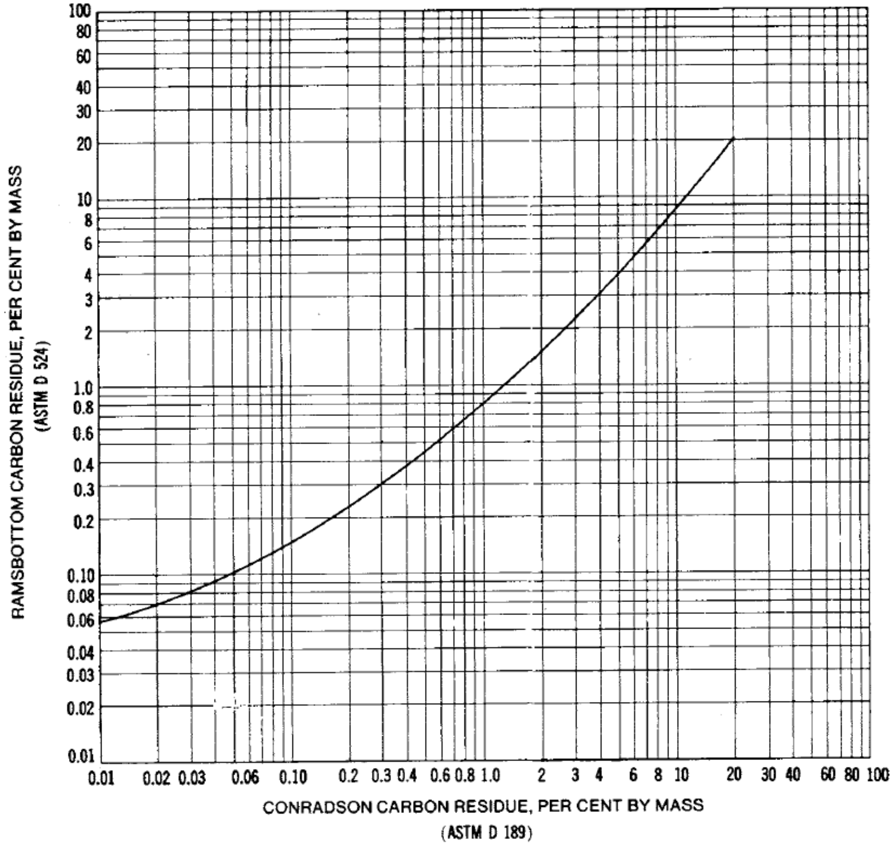
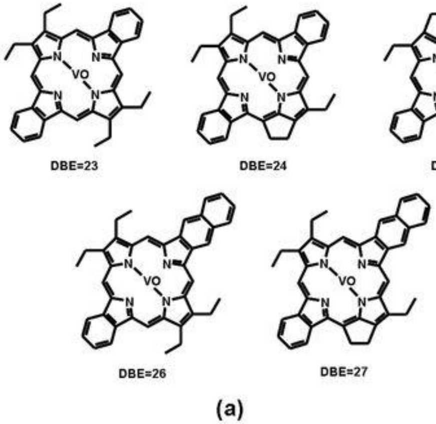
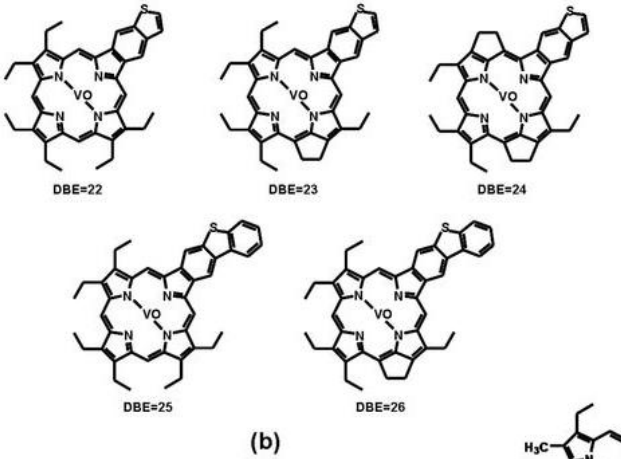


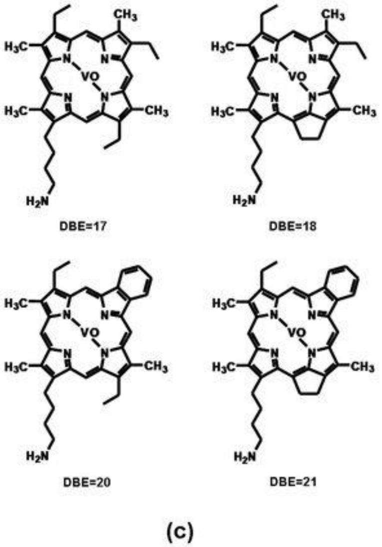
FIG. X1.1 Correlation Data

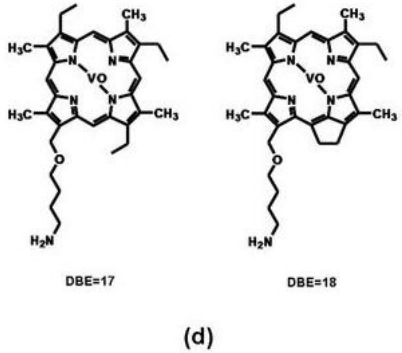
$$RCR = \exp\left[-0.236 + 0.883\ln\left(CCR\right) + 0.0657\ln^2\left(CCR\right)\right]$$

New vanadium compounds identified in heavy Venezuelan crude oil









"New Vanadium Compounds in Venezuela Heavy Crude Oil Detected by Positive-ion Electrospray Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry"
Xu Zhao, Quan Shi, Murray R. Gray & Chunming Xu
Scientific Reports 4, Article number: 5373 (2014)
https://www.nature.com/articles/srep05373/figures/4