Lecture 2

Practical Transport Fuels – Composition, Properties, Manufacture, Specifications

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(Ch.2. Fuel/Engine Interactions, Richards P. 2014. Automotive Fuels Reference Book, Third Edition, SAE International, Warrendale PA)

Current IC Engines

- Spark Ignition (SI) fuel/air are mixed and compressed, heat release via expanding flame.
 - Uses gasoline.
 - Light duty.
- Compression Ignition (CI) air is compressed, heat release via autoignition of fuel as it mixes with air.
 - Uses diesel fuel.
 - Mostly heavy duty.
- CI engines more efficient but more expensive

Current Fuels for IC Engines

- Gasoline and diesel complex mixtures of hydrocarbons
- Primary fuel property is the autoignition quality –
- Gasolines are resistant to autoignition to avoid knock (measured by octane numbers, RON and MON) – used in SI engines
- Diesel fuels are prone to autoignition (measured by Cetane Number) – used in diesel engines
- Diesels are also less volatile, heavier. (Jet fuel is like a lighter diesel)

Jet fuel accounts for around 12% of transport energy and is like a light diesel

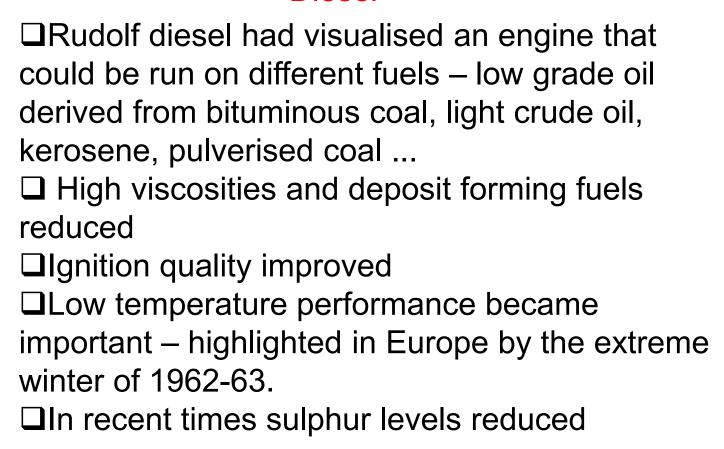
Fuels Have Developed along with Engines

Gasoline

☐ Start of the 20 th Century, only fuels available were lighter
fractions from distillation of crude oils and shale oils
☐ As engine designers sought improved efficiency, knock
became a limiting factor
☐ Initially fuel quality was improved by adding aromatics
produced by distillation of coal tar
□Lead additives discovered in 1921. Great resistance initially
because of concerns about toxicity!
□1929 Octane scale and Octane Numbers
☐ Continuous improvements in refinery processes and anti-
knock quality
□Emissions concerns and fuels to enable after-treatment
technologies from the 1970s onwards – removal of lead,
reduction in sulphur

Fuels Have Developed along with Engines

Diesel

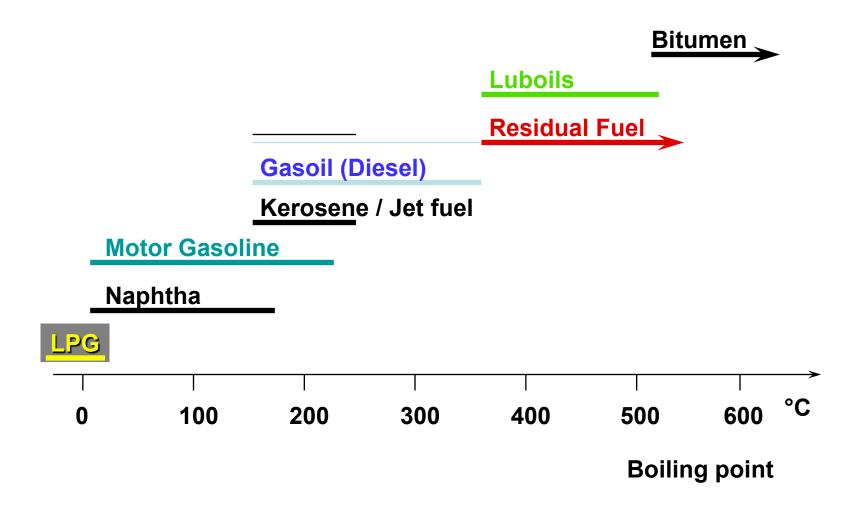


Fuel manufacture in outline

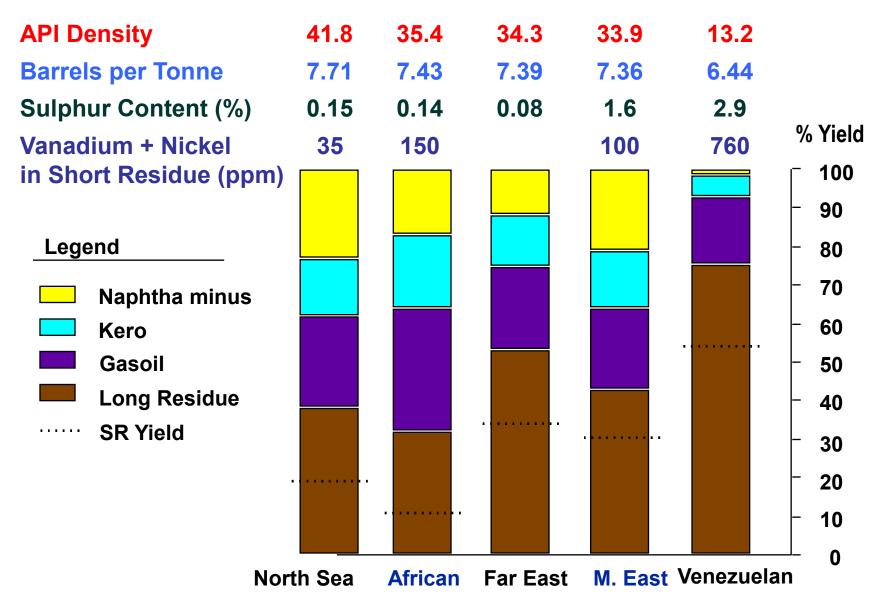


- Most transport fuels made in refineries starting with crude oil
- Initially, petroleum is separated into different boiling ranges (Distillation) – 40%-60% is residue with B.P. > 380° C
- Many different processes cracking, change of composition, redistribution of C/H ratios, removal of contaminants ..
- Fuels are blended from different components + other sources e.g. ethanol, MTBE...
- Refineries also supply feedstocks to the chemical industry

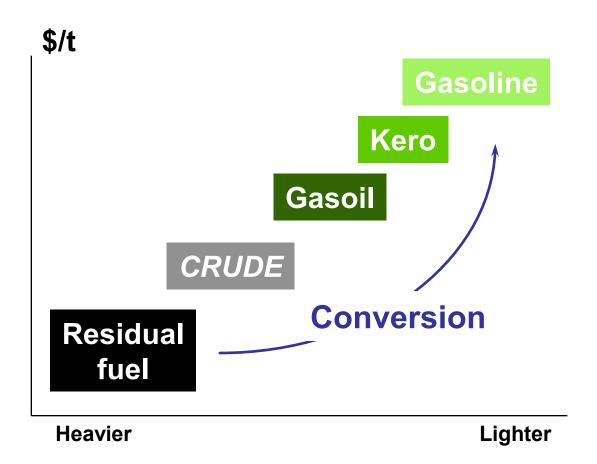
Boiling Ranges



Some differences between Crudes

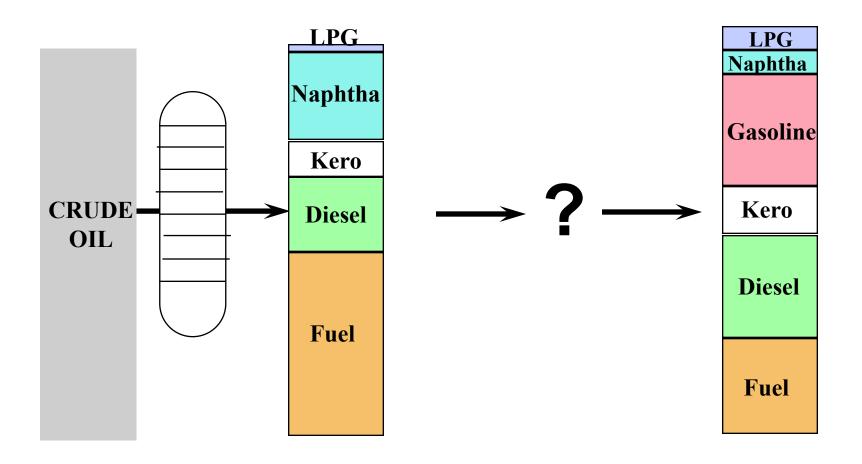


The Price Balance



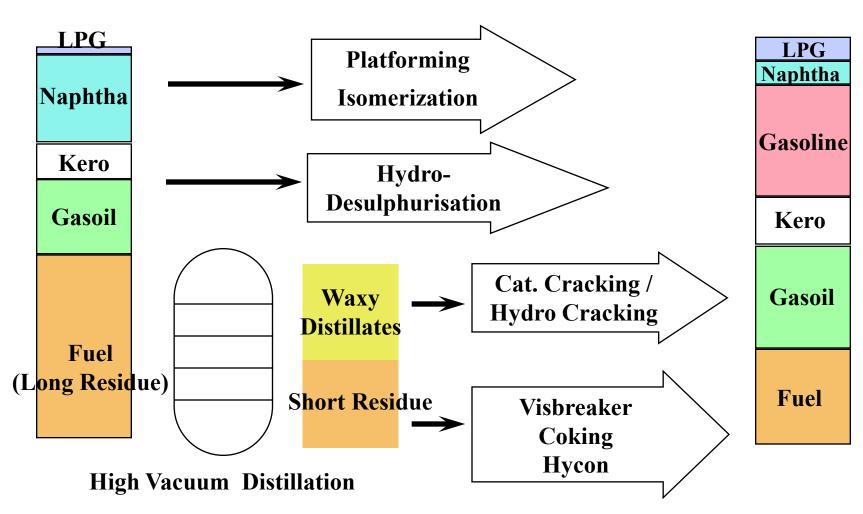
CONVERSION = HIGHER MARGINS

From CRUDE QUALITY.....to MARKET DEMAND

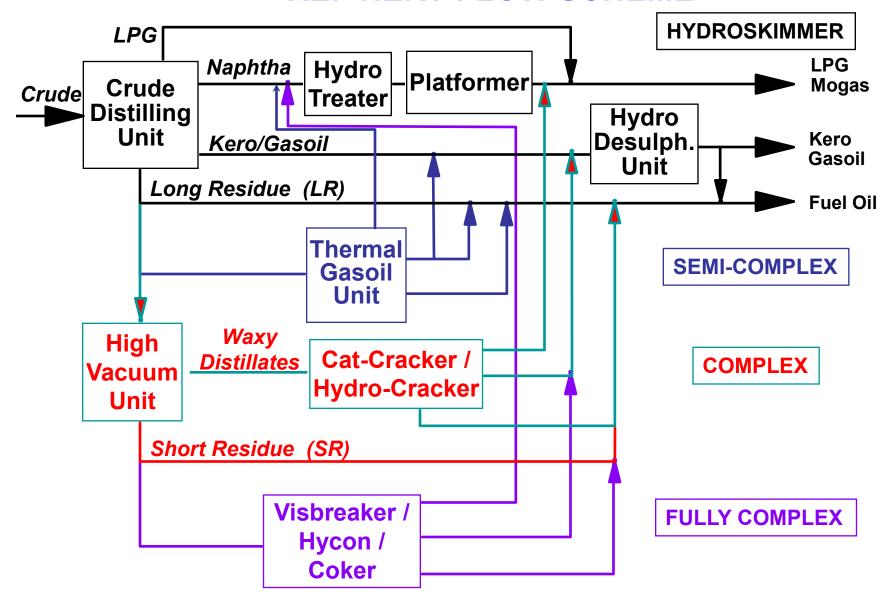


From CRUDE QUALITY.....to MARKET DEMAND

FULLY-COMPLEX REFINERY



REFINERY FLOW SCHEME



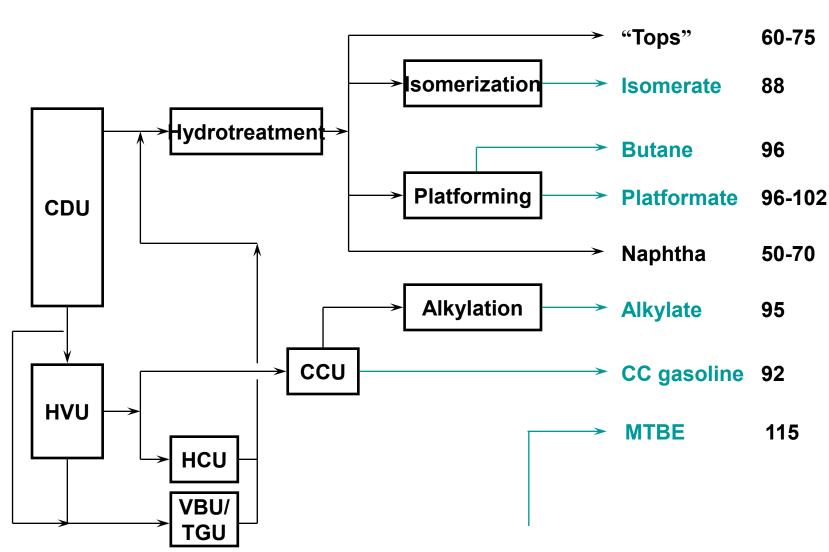
TYPICAL YIELD STRUCTURE

Yield (%moc)	Simple Dist.	Hydro Skimm.	Semi Compl.	I	_	Fully Co	-
			•	,		(CCU/ VBU)	(HCU\ VBU)
LPG	1.5	1.6	2.2	4.5	2.1	5.0	2.3
Naphtha	23.2	5.7	6.4	6.7	5.9	7.2	6.3
Gasoline	0.0	16.2	18.8	26.2	19.3	28.8	20.4
Kero/Jet	11.0	11.1	11.1	11.1	16.7	11.1	16.7
Diesel	24.8	25.0	31.4	24.6	33.9	27.5	40.0
Fuel oil	37.5	37.8	25.7	21.3	14.9	13.7	6.0
Fuel & Loss	2.0	2.6	3.6	5.6	7.2	6.7	8.3

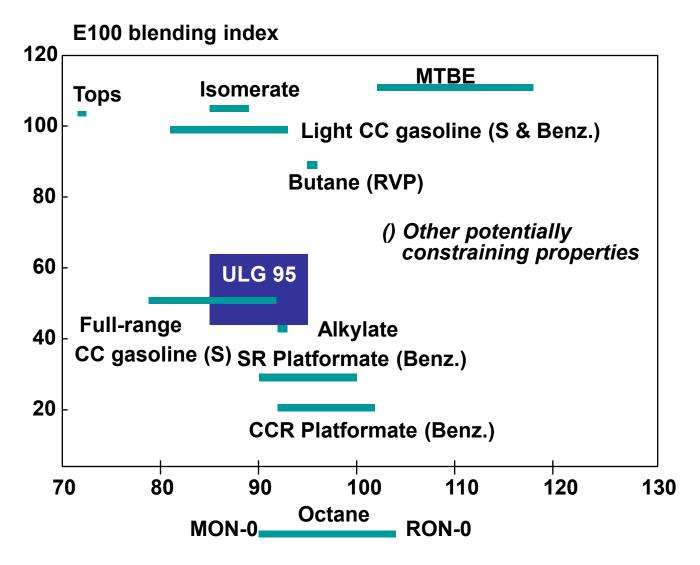
CRUDE TYPE: BRENT

Gasoline blending components

Typical RON



GASOLINE BLENDING...



...is a SOPHISTICATED PROCESS

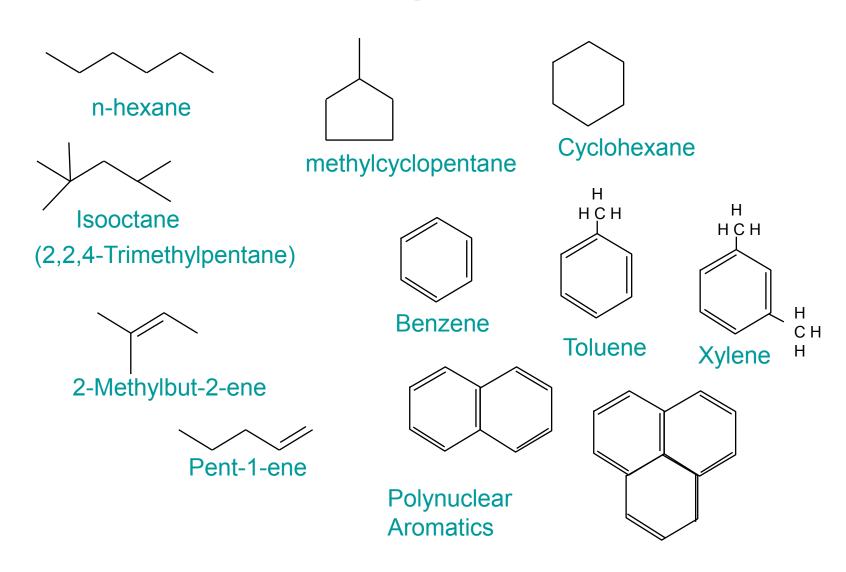
Fuel Properties in outline

What does gasoline & diesel consist of?

A complex mixture of hydrocarbons

- Paraffins (alkanes)
- Olefins (alkenes)
- Naphthenes (cycloalkanes)
- Aromatics
 - Monoaromatics
 - Polynuclear aromatics (PNA, PAH, Di/Tri+ aromatics)
- Oxygenates (ethers, alcohols, FAME)
- Sulphur Compounds
- Additives (performance, VSRP etc.)

Paraffins, Olefins, Naphthenes & Aromatics



Effects of Gasoline Composition

Sulphur – Adverse effect on catalysts in both SI and diesel engines and on-board diagnostic (OBD) sensors.

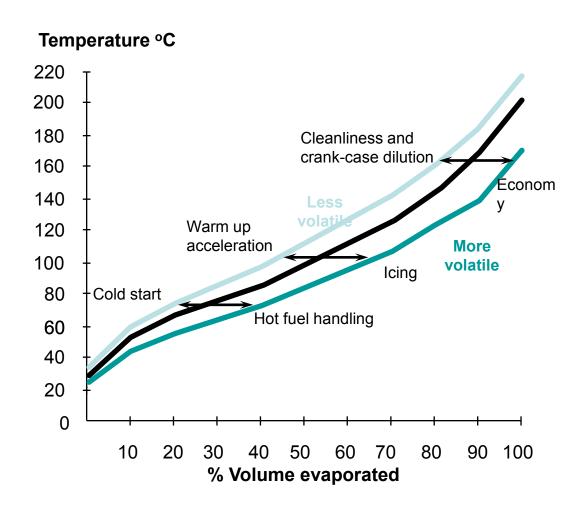
Aromatics — High anti-knock quality in SI engines. Some effect on benzene formation in the exhaust, combustion chamber deposit formation in SI engines. NOx and particulates in diesel engines (diesel aromatics are heavier), CO2 level **Olefins** — High anti-knock quality in SI engines. May lead to gum formation and inlet system deposits, chemically reactive, hence ozone and diene forming potential.

Oxygenates - High anti-knock quality. Lower energy content. Reduction in CO, lower driveability, higher evaporative emissions, degradation of plastics and elastomers

Iron, manganese, silicon, phosphorous – Bad for catalysts and other sensors (e.g. Oxygen sensors)

Gasoline Volatility - 1

Performance factors and gasoline volatility

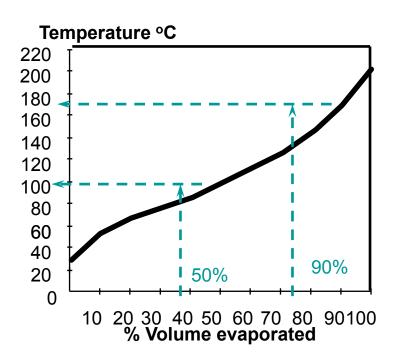


Two ways to express volatility

T numbers

 $T50\%E = 100^{\circ} C$

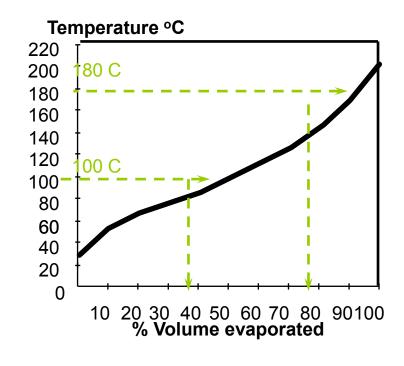
 $T90\%E = 170^{\circ} C$



E numbers

E100 = 50%

E180 = 93%



Vapour Pressure - Gasoline

Gasoline Volatility - Warm-up and Cold Driveability

- Driveability describes the smoothness of response to the throttle whilst the engine warms up (easily perceived by drivers), influenced by:
 - Ambient temperature
 - Mid-range volatility
 - Fuel and inlet system design
- Driveability problems are caused by:
 - Incomplete fuel vaporisation pools of liquid fuel in manifold, fuel hang-up in valve deposits for EFI engines which rely on hot inlet valves to vaporise fuel
 - Inability of the liquid to keep up with air flow during acceleration.
 - Maldistribution of this liquid between cylinders for carb/SPI engines.
- The result is:
 - Stalling, hesitation, stumble and even backfire during acceleration
 - Surging during cruise
 - E100 or T50% correlates best with cold driveability

Knock Damage to Piston

Knock is abnormal combustion resulting in very high pressure rise rate

Damage starts at edge of piston furthest from sparkplug, i.e. in the "endgas) causes erosion and pitting of piston



High heat transfer to the piston can cause local melting and burning leading to catastrophic engine failure

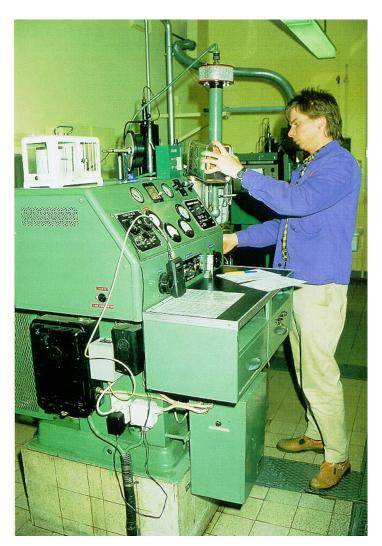
Anti-knock quality of the fuel is specified by Octane Numbers

Gasoline Octane

Measured with a Cooperative Fuels Research (CFR) engine

Knock limits efficiency and performance in SI engines.

Octane quality is the most important property of gasoline – refining and retailing are driven by Octane



Gasoline Octane Number

- Engine knock intensity of the sample compared with knock intensity of a reference fuel
- Based on a scale with n-heptane = 0; isooctane = 100. Linear blending between these ('Primary Reference fuels')
- Octane numbers above 100 compared with leaded isooctane reference fuel.
- Toluene/isooctane/heptane blends used as secondary checks.

Gasoline Octane Number

- Two octane methods:
 - Research Octane Number (RON) (ASTM D2699)
 - Motor Octane Number (MON) (ASTM D2700)
 - MON has higher engine speed and inlet temperature to simulate more severe operating conditions
- RON higher than MON (RON-MON = sensitivity) usually by 10 ON (95/85; 98/88)
- Refinery streams used to blend octane have widely varying sensitivity - one ON usually constraining

The MON test is faster (900rpm) than the RON test (600rpm) and has heated inlet air:

— The temperature, at a given pressure, is higher in the MON test than in the RON test

Gasoline Quality Effects on Emissions

To reduce hydrocarbons:-

- Reduce RVP (affects evaporative emissions esp. non-cat cars)
- Reduce aromatics content
- Add oxygenates (for non-catalyst cars)
- Increase mid-range to back-end volatility
- Reduce sulfur (catalyst cars)

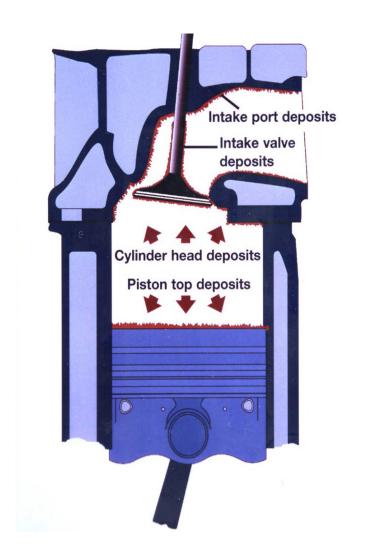
To reduce NOx emissions:-

- Reduce aromatics for non-catalyst cars, but increase aromatics for catalyst cars (the NOx/aromatics effect)
- Reduce sulfur (catalyst cars only)
- Reduce mid-range to back-end volatility
 - fuel effects are relatively small

SI Engine deposits

Fuel derived deposits form at several places in engine and usually degrade its performance

- Carburettor
- Injector (esp for direct injection)
- Inlet port, inlet valves
- Spark plug
- Combustion chamber head and piston top





Diesel Fuel Properties and Their effects

- Cetane Number CN Increasing CN makes cold start easier, reduce noise, reduce CO and HC
- Density Reduced density will reduce particulates and power but increase fuel consumption
- Sulphur Increased sulphur increases particulates, adversely affects after-treatment systems
- Aromatics Higher aromatics lead to higher NOx and higher particulates
- Cold Flow Properties Wax crystals can form as paraffins freeze
- Foaming Slows filling and risks overflow
- Deposits Injector deposits reduce power
- Lubricity High pressure pumps can be ruined without sufficient lubricity

Fuel Specifications

- Fuel quality is defined by selected properties and composition
- Criteria for measuring these are standardised and harmonised
- Specifications require that a given fuel property must fall within a certain range
- To ensure that engines operate smoothly and cleanly with no harm
- Are agreed by oil and auto industries and are legally binding
- Extremely important affect how fuels are manufactured

Fuel Specifications

- To help understand why certain properties are specified, see World Wide Fuels Charter http://www.acea.be/uploads/publications/Worldwide_ Fuel_Charter_5ed_2013.pdf
- Very complex issue different in different areas

http://transportpolicy.net/index.php?title=Global_Comp arison: Fuels

http://europa.eu.int/comm/environment/air/legis.htm

Examples of some specifications

	Europe	Saudi	China		Europe	Saudi	China
	EN 228	Arabia	Nationwide		EN 590	Arabia	Nationwide
	Gasoline		Gasoline		Diesel		Diesel
RON, min	95	95/91	90/93/97	Cetane Number, min	51	45 CI	49/46/45
MON, min	85			Sulphur, max	10 ppm	500	350
Sulphur, max	10 ppm	1000 ppm	150	Polyaromatics, wt% max	11		11
Benzene, vol% max	1	3	1	Density @ 15° C, kg/m3	800-845	810-870	790-840
Aromatics, vol% max	35		40	Viscosity @ 40° C, cSt	1.2-4.5	1.9-4.1	7-Feb
Olefins, vol% max	18	25	30	T50° C,max			300
Oxygen, wt% max	2.7	2.7	2.7	T85° C,max	350	350	
Density @ 15° C, kg/m3	720-775			T95° C,max	360		365
RVP @ 37.8° C kPa, summer	45-60	65.5	72 max	Flash Point [°] C, min	55	55	55
RVP @ 37.8° C kPa, winter	70-100		88 max	CFPP° C, max	5 to -44	-4	2 to -44
E70, vol%	20-50	20-48		Water, vol %	0.02 max		trace
E70, vol%, min	75			Lubricity @ 60° C, micron	460 max		460 max
E100, vol%, min	46	46-71					
Full Boiling Point, ° C	210	225	205				
Oxidation Stability, minutes, min	360		480				

There are different specs in Beijing and Shanghai

PROPERTIES UNITS ISO ASTM JIS Other – GASOLINE – TEST METHODS

Research Octane Number - EN 5164 D 2699 K 2280

Motor Octane Number - EN 5163 D 2700 K 2280-96

Oxidation stability minutes 7536 D 525 K 2287

Sulphur content mg/kg 20846 D 2622 K 2541

20884 D 5453

Lead content mg/l D 3237 K 2255 EN 237

Potassium (K) content mg/l NF M 07065

EN 14538

Metal content mg/l ICP (1)

Phosphorus content mg/l D 3231

Manganese content mg/l D 3831

Silicon content mg/kg ICP-AES (Reference in-house methods

with detection limit = 1 mg/kg

Oxygen content % m/m D 4815 K 2536 EN 13132

Olefins content (2) % v/v 3837 D 1319 K 2536

Aromatics content (2) % v/v 3837 D 1319 K 2536 EN 14517

Benzene content % v/v D 5580 K 2536 EN 238

D 3606 EN 14517

Vapour Pressure kPa D 5191 K 2258 EN 13016/1 DVPE

Distillation: T10/T50/T90, E70/E100/E180, End Point, residue 3405 D 86 K 2254

Vapour/liquid ratio (V/L) °C D 5188

Sediment mg/l D 5452

Unwashed gums mg/100 ml 6246 D 381 K 2261 May be replaced with CCD test

Washed gums mg/100 ml 6246 D 381 K 2261

Density kg/m3 3675 D 4052 K 2249

12185

Copper corrosion merit 2160 D 130 K 2513

Appearance D 4176 Visual inspection

Carburettor cleanliness merit CEC F-03-T

Fuel injector cleanliness, Method 1 % flow loss D 5598

Fuel injector cleanliness, Method 2 % flow loss D 6421

Particulate contamination, code rating 4406

size distribution no of particles/ml 4407 & 11500

Intake-valve sticking pass/fail CEC F-16-T

Intake valve cleanliness I merit CEC F-04-A

Intake valve cleanliness II avg. mg/valve

PROPERTIES UNITS ISO ASTM JIS Other DIESEL FUEL – TEST METHODS

Cetane Number - 5165 D 613 K 2280

Cetane Index - 4264 D 4737 K 2280

Density @ 15°C kg/m3 3675 D 4052 K 2249

12185

Viscosity @ 40°C mm2/s 3104 D 445 K 2283

Sulphur content mg/kg 20846 D 5453 K 2541

20884 D 2622

Total aromatics content % m/m D 5186 EN 12916

PAH content (di+, tri+) % m/m D 2425 EN 12916

T90, T95, FBP °C 3405 D 86 K 2254

Flash point °C 2719 D 93 K 2265

Carbon residue % m/m 10370 D 4530 K 2270

Cold Filter Plugging Point (CFPP) °C D 6371 K 2288 EN 116, IP 309

Low Temperature Flow Test (LTFT) °C D 4539

Cloud Point (CP) °C 3015 D 2500 K 2269

Water content mg/kg 12937 D 6304 K 2275

Oxidation stability, Method 1 g/m3 12205 D 2274

Oxidation stability, Method 2 induction time (1)

Foam volume ml NF M 07-075

Foam vanishing time sec. NF M 07-075

Biological growth - NF M 07 070

FAME content % v/v EN 14078

Ethanol/Methanol content % v/v D 4815 (modified)

Total acid number mg KOH/g 6618 D 664

Ferrous corrosion - D 665 (2)

Copper corrosion merit 2160 D 130 K 2513

Appearance D 4176 Visual inspection

Ash content % m/m 6245 D 482 (3) K 2272

Particulate contamination, total mg/kg D 5452 DIN 51419

EN 12662 (4)

Particulate contamination, size distribution code rating 4406

no of

particles/ml 4407, 11500

Injector cleanliness % air flow loss CEC (PF-023) TBA

Lubricity (HFRR wear scar diameter @ 60°C) micron 12156-1.3 D 6079 CEC F-06-A

Metal content ICP (5)

Fuels and engines

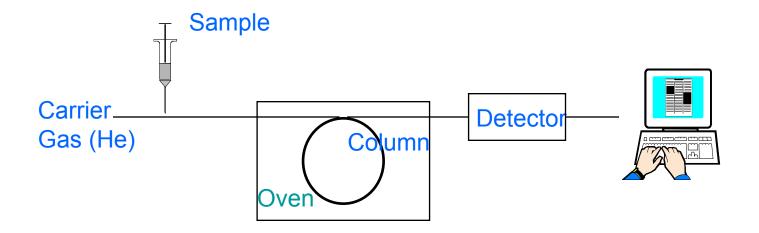
- Engine and fuels are a chicken and egg situation: advances in one must use the existing technology of the other.
- But the highest performance and efficiency must come from optimisation of the engine and fuel together.

Gasoline HC Composition - Specifications

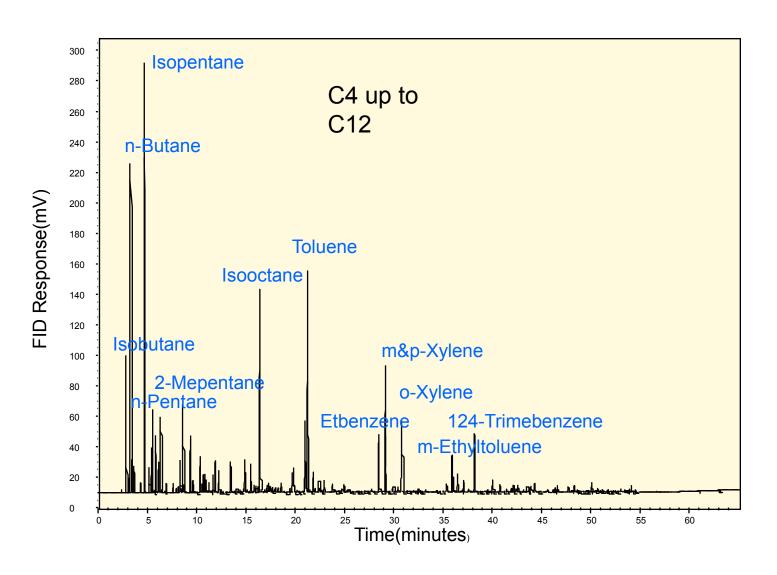
- Currently: Benzene, Total Aromatics and Olefins
- GC or IR method used for benzene (e.g. ASTM D3606)
- Fluorescence Indicator Adsorption ('FIA', ASTM D1319) is current method for aromatics/olefins:
 - based on column chromatography
 - for aromatics & olefins
 - Method precision poor (especially for olefins) but can be improved (advice available)

Measuring Gasoline HC Composition

Gas Chromatography can be used for obtaining detailed compositional analysis of a gasoline



Detailed GC of a typical Gasoline



Propene	0.01	2,4-Dimethylpentane	0.58	2-Methylheptane	0.27	l,2-Dimethyl-3-ethylbenzene	0.06
Propane	0.06	2,3,3-Trimethylbut-l-ene	0.09	4-Methylheptane	0.15	n-Undecane	0.05
Isobutane	1.87	2,2,3-Trimethylbutane	0.03	3-Methylheptane	0.37	1,2,4,5-Tetramethylbenzene	0.15
Isobutene + But-1-ene	0.55	Benzene + l-Methylcyclopentene		2,2,5-Trimethylhexane	0.34	1,2,3,5-Tetramethylbenzene	0.21
n-Butane	5.41	3-Methylhex-l-ene	0.04	c1,3-Ethylmethylcyclopentane	0.05	5-Methylindan	0.13
tBut-2-ene	0.93	Cyclohexane	0.15	1,c2,c3-Trimethylcyclopentane	0.14	1-Ethyl-2-n-propylbenzene	0.16
2,2-Dimethylpropane	0.02	2-Methyl-thex-3-ene	0.09	n-Octane	0.28	1,3-Di-isopropylbenzene	0.09
cis But-2-ene	0.25	Unknown Peak	0.03	trans-Oct-2-ene	0.06	Naphthalene	0.28
3-Methylbut-l-ene	0.26	4-Methyl-cis/trans-hex-2-ene	0.13	2,4,4-Trimethylhexane	0.07	Dimethylindan isomer	0.12
Isopentane	11.43	2-Methylhexane + 2,3-dimeC5	1.24	2,3,5-Trimethylhexane	0.03	n-Dodecane	0.05
Pent-l-ene	0.74	Cyclohexene	0.07	n-Propylcyclopentane	0.04	C12 Aromatic	0.08
2-Methylbut-l-ene	1.39	3-Methylhexane	0.74	1,1,4-Trimethylcyclohexane	0.08	C12 Aromatic	0.02
n-Pentane	2.02	3,4-Dimethyl-cis-pent-2-ene	0.04	Ethylbenzene	3.04	Unknown Peak	0.04
2-Methyl-1,3-butadiene	0.09	cis-l,3-Dimethylcyclopentane	0.22	m-Xylene	6.93	Unknown Peak	0.02
trans-Pent-2-ene	1.70	trans-1,3-Dimethylcyclopentane	0.19	p-Xylene	2.58	Unknown Peak	0.05
3,3-Dimethylbut-l-ene	0.02	trans-1,2-Dimethylcyclopentane	0.26	4-Methyloctane	0.08	Unknown Peak	0.06
cis-Pent-2-ene	0.93	Isooctane	4.34	2-Methyloctane	0.13	2-Methylnaphthalene	0.04
2-Methylbut-2-ene	2.30	Hept-l-ene	0.14	3-Methyloctane	0.13	Unknown Peak	0.12
trans-1,3-Pentadiene	0.08	3-Methyl-cis-hex-3-ene	0.02	o-Xylene	4.04	Unknown Peak	0.04
cis-1,3-Pentadiene	0.03	C7 Olefin	0.12	n-Nonane	0.11	Unknown Peak	0.02
2,2-Dimethylbutane	0.21	trans-Hept-3-ene	0.30	Isopropylbenzene	0.16	Unknown Peak	0.03
Cyclopentene	0.30	n-Heptane	0.26	n-Propylbenzene	0.47		
4-Methylpent-l-ene	0.08	cHept-3-ene	0.16	m-Ethyltoluene	1.65		
3-Methylpent-l-ene	0.13	2-Methylhex-2-ene	0.17	p-Ethyltoluene	0.70	Paraffins	9.2
Cyclopentane	0.16	3-Methyl-ttrans-hex-3-ene	0.13	1,3,5-Trimethylbenzene	0.82	Isoparffins	30.1
2,3-Dimethylbutane	0.77	trans-Hept-2-ene	0.16	o-Ethyltoluene	0.70	Olefins	16.8
2,3-Dimethylbut-l-ene	0.13	3-Ethylpent-2-ene	0.06	2-Methylnonane	0.07	Dienes	0.2
4-Methyl-cpent-2-ene	0.08	3-Methyl-cis-hex-2-ene	0.10	1,2,4-Trimethylbenzene	2.69	Naphthenes	2.7
2-Methylpentane	2.07	cis-Hept-2-ene	0.14	n-Decane	0.10	Aromatics	40.6
4-Methyl-tpent-2-ene	0.23	2,3-Dimethylpent-2-ene	0.14	1,2,3-Trimethylbenzene	0.61	Unknowns	0.6
3-Methylpentane	1.31	Methylcyclohexane	0.37	Indan	0.26		
2-Methylpent-1-ene	0.37	Ethylcyclopentane	0.12	C11 Alkane	0.08	Total peaks <5%	64.5
Hex-l-ene	0.24	2,5-Dimethylhexane	0.49	1,3-Diethylbenzene	0.07	RON	98.2
n-Hexane	0.82	2.4-Dimethylhexane	0.57	m-n-Propyltoluene	0.27	MON	86.2
cis + trans-Hex-3-ene	0.62	1,t2,c4-Trimethylcyclopentane	0.07	p-n-Propyltoluene + 1,4-Dietbz	0.16		00.2
trans-Hex-2-ene	0.55	2,3.4-Trimethylpentane	1.30	n-Butylbenzene	0.22	T.L. 7.1	
2-Methylpent-2-ene	0.71	Unknown Peak	0.14	o-n-Propyltoluene	0.04	Table 7.1	
3-Methyl-cis-pent-2-ene	0.42		11.70	4-Methyldecane	0.19	Composition (weight	%) by
cis-Hex-2-ene	0.30	2-Methyl-trans-hept-3-ene	0.05	2-Methyldecane	0.16	gc of a super unlea	ded
3-Methyl-trans-pent-2-ene	0.53	2,3-Dimethylhexane	0.48	1,4-Dimethyl-?-ethylbenzene	0.27	.	ucu
Methylcyclopentane	0.89	2,5-Dimethylhex-2-ene	0.11	1,2-Dimethyl-4-ethylbenzene	0.39	gasoline.	
	0.07	-,- 2v <u>-</u> •v		-,2 2	/		

Gasoline Specification Summary

		Europe	EU DIRE	CTIVE	US	Cal.	Japan
Fuel prop	Units	EN 228	2000	2005	RFG	Phase 2/3	
RVP, summer	(kPa) max	70/80	60 (70**)	60	50/56	48.3	72
E100	(%v) min	46/71	46	46		=50	
E150	(%v) min	75	75	75	#	=90	
Olefins	(%v) max		18*	18	#	6	
Arom	(%v) max		42	35		25	-
Benzene	(%v) max	1.0	1.0	1.0	1.0	1.0/0.8	1.0
Oxygen	(%m) max	2.5/3.7	2.7	2.7	2.0-2.7	1.8-2,2	7%MTBE
Sulphur	(mg/kg) max	500	150	50 (10)*	# 30	40/20	100
Lead	(g/l) max	0.013	0.005	0.005			0

NOTES:

EU ban on sales of leaded gasoline from 2000

^{*} Except for unleaded regular with RON/MON less than 91/81 when limit is 21%v

^{* 10} pm S fuel to be available from Jan 2005, all gasoline to be at 10 ppm by Jan 2009

^{**} April - September: may be relaxed to 70kPa May - August for "arctic" climate countries

[#] No higher than 1990 average, US RFG must meet targets for VOCs and Toxics. 30 ppm from 2004-6

Gasoline Octane - NIR

- Near infra red (NIR) increasingly used for measuring octane in refineries (for QMI)
- NIR still only a secondary method calibration of instrument necessary against CFR measurements
- Calibration depends on gasoline composition most analysers need calibrating for local conditions
- A quick, convenient way of measuring octane