3-9-2012

Changes in Gasoline Chemistry

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Gasoline

Matt Dixon

Jim Halderman

Introductions

- Matt Dixon-
- Former technician and Chrysler Trainer, Assistant Professor of Automotive Technology

- Jim Halderman-
- Former flat-rate technician, business owner and professor of Automotive Technology; author

Topics to be discussed

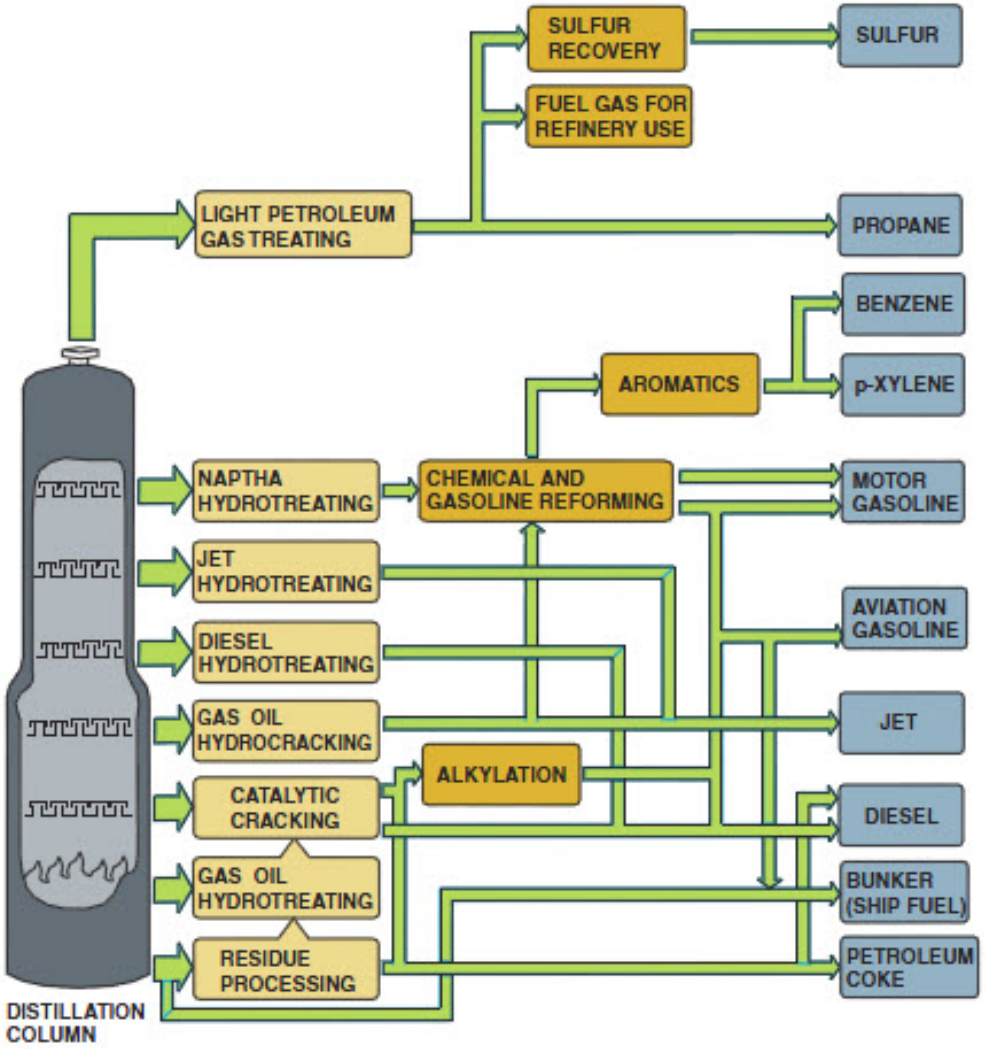
- What is gasoline?
- Octane ratings and what they mean
- Oxygenated, Reformulated Gasoline
- Reid vapor pressure/seasonal changes
- Alcohol content (E10; E15; E85)
- Testing gasoline for contamination
- Recommendations/Suggestions
- Gasoline taxes

What is Gasoline?

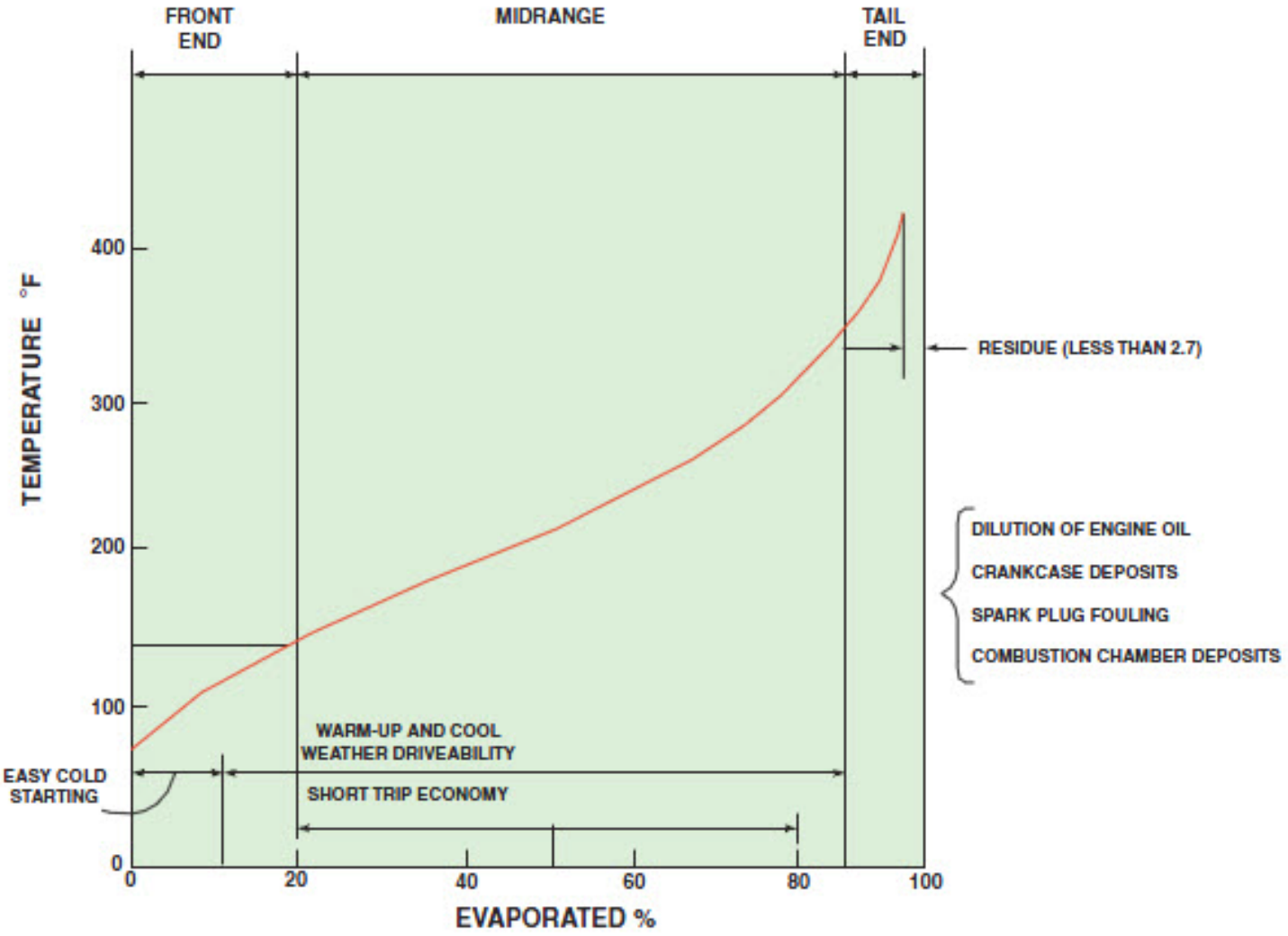
Gasoline has is a hydrocarbon fuel made from hydrocarbons with 1 to 15 carbon atoms.

- Methane = one carbon
- Ethane = two carbons
- Propane = three
- Butane = four
- Pentane = five
- Hexane = six
- Heptane = seven
- Octane = eight
- Nonane= nine
- Decane= ten

Distillation

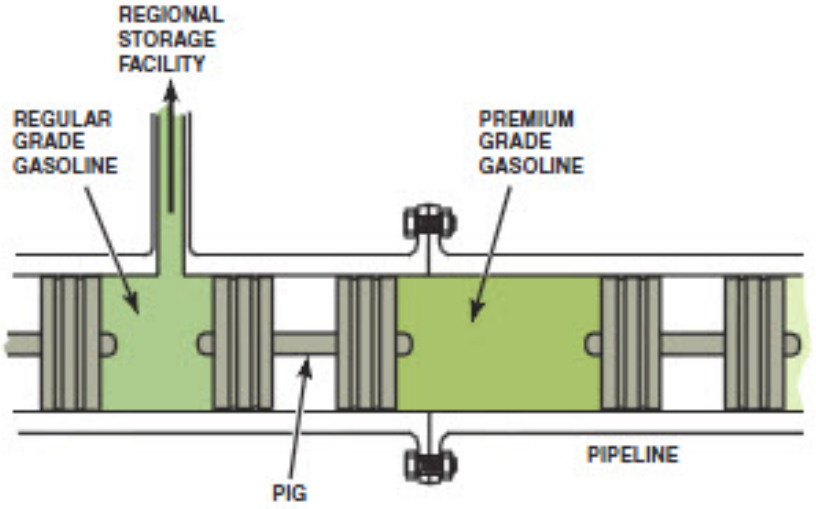


Distillation curve



Transportation of gasoline

- All gasoline that meets grade is called fungible.
- This means that regardless of what company refines the gasoline, it can be mixed without a problem because it is all the same.



Energy Content of gasoline

- BTU content varies with seasonal RVP blends and amount of alcohol
- 108,000 to 117,000 BTU's (generally higher during summer months)
- For comparison, Ethanol has approx. 76,000 BTU

ASTM

Formally known as:
American Society for Testing and Materials

Gasoline is blended in accordance with ASTM specifications

Current Specification: ASTM D4814-11b

Worldwide Fuel Charter

Document containing preferred/suggested gasoline specifications published by Alliance of Automobile Manufacturers

Top Tier Gasoline is gasoline that has engine cleaning chemicals to help reduce engine deposits

What is Gasoline?

Alkanes

Alkenes

Alkynes

Arenes (Aromatics)

Alcohol

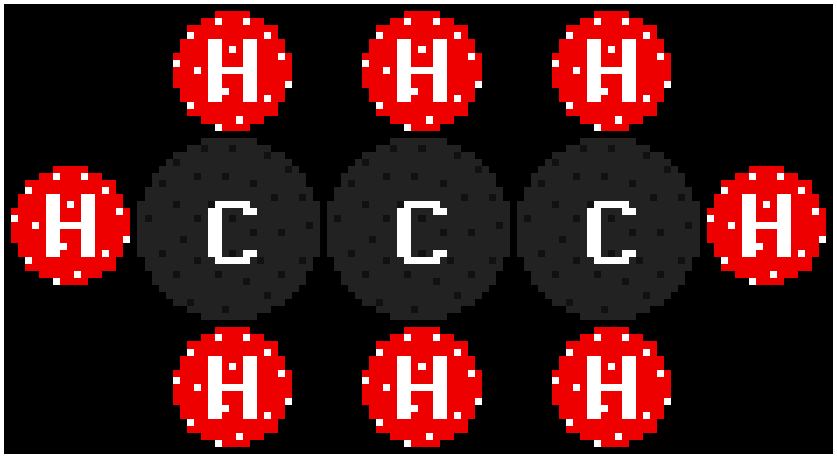
Additives

N-Parrafins

Also known as **Alkanes**, single bonds, straight chained hydrocarbons

About 15% of gasoline by volume

These are butane, pentane, hexane etc.



Example of (butane) reaction:

$2C_4H_{10} + 13O_2 \rightarrow 8CO_2 + 10H_2O$

ISO-parrafins

The refinery “cracks” larger carbon chains using heat and or a catalyst

About 30% of gasoline by volume

Higher octane values

Examples: 3 methyhexane; 2,2- dimethylpentane; 2,2,3 trimethylbutane

Cycloparaffins

- Up to 12% of volume
- Very high in octane value
- Examples include cyclopentane, cyclohexane, methylcyclopentane

Olefins and Diolefins

Up to 8% of gasoline volume

High energy content (**Alkenes**)

Concerns with contributions to O_3
(Ozone/Smog)

Concerns with engine deposits: gums/lacquers

Aromatic Hydrocarbons (Arenes)

25-35% of gasoline

Ring molecular structure of alternating single and double bonds: Toluene, Benzene etc.

Good energy content

Generally high octane rating value

Some such as Benzene are limited (to 1% of volume) because Benzene is a carcinogen

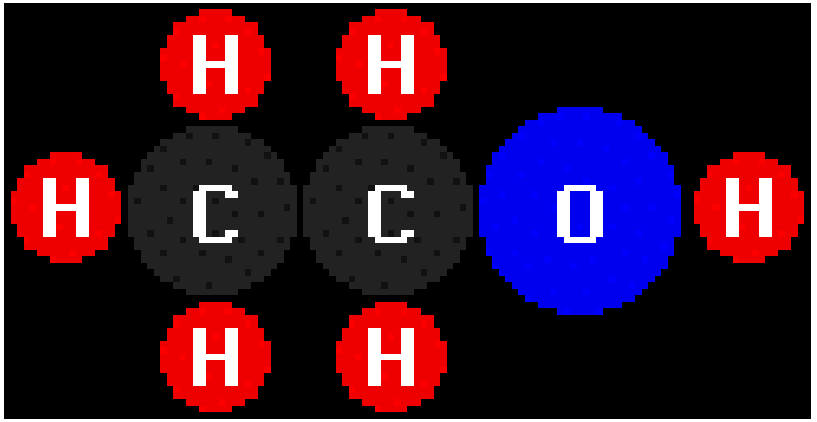
Alcohol: Ethanol

The current oxygenate of choice, gasoline reaches 3.1% oxygen by weight with a 6.2% ethanol volume

Boosts octane rating (ethanol is 108 octane)

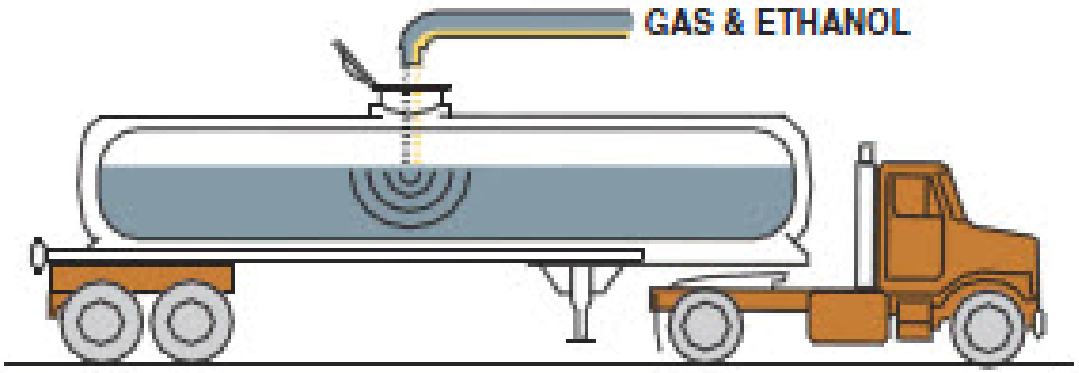
Lowers energy content

Impact on RVP

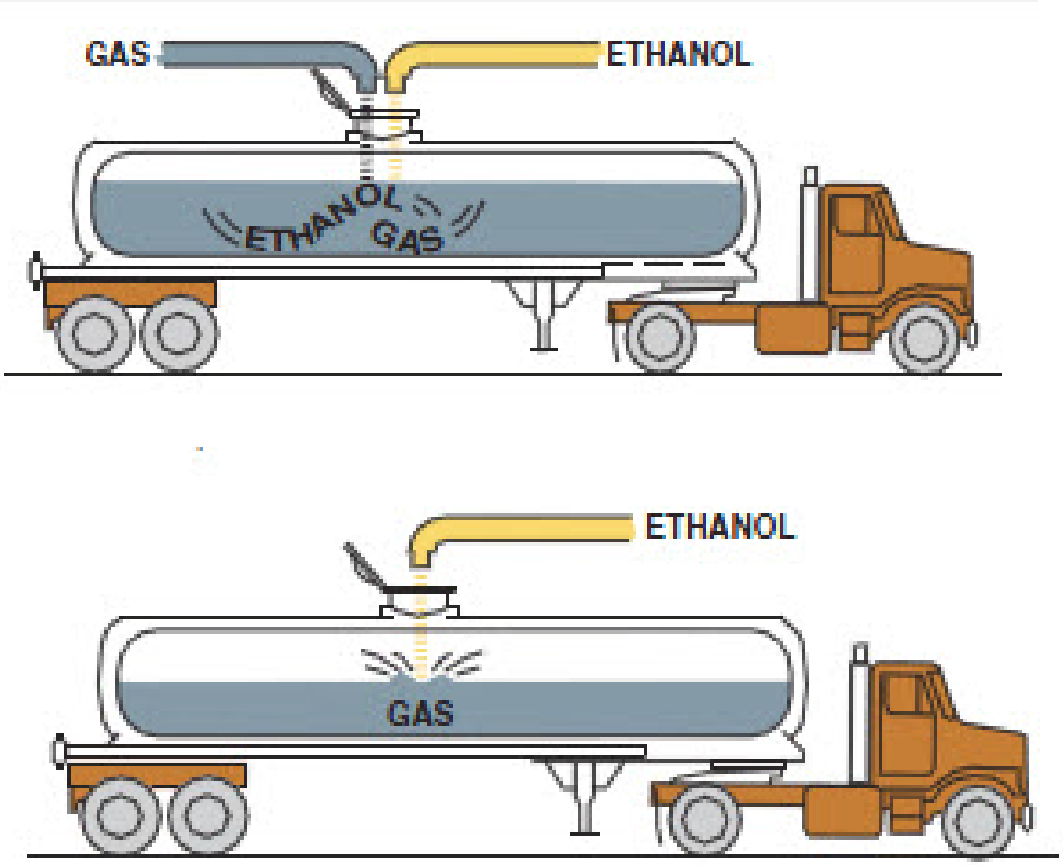


Gasoline/Alcohol Blending

- Done at the distributor level
- Usually locally
- Designed to meet local conditions and climatic



Gasoline/Alcohol Blending



EPA: final rule on E15

As of 8-24-11:

- EPA final rule allows E15 and requires pump labeling

Picture of E15 label from EPA website

Additives

Since 1995 EPA has required **ALL gasolines** sold to have **detergents** blended in

Other additives:

- Anti-Icing
- Anti Oxidants
- Anti wear
- Metal Deactivators
- Corrosion inhibitors
- Oil soluble dye: identify grade etc.

Octane Ratings

- Octane rating is the measured ratio between isooctane (octane rating of 100) and heptane which has an octane rating of zero.

Pump Octane Number

- The rating on the pumps is the average of two ratings: Motor (MON) and Research (RON)
- R+M/2
- Regular = 87
- Midgrade (plus) = 89
- Premium = 91+

Two Octane Methods

Research Method (RON)–

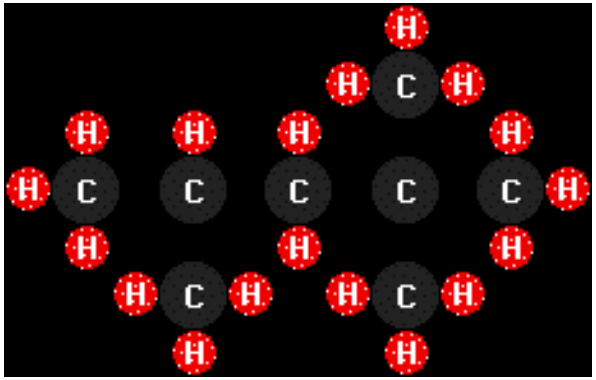
Uses no spark advance

Results in higher number of the two

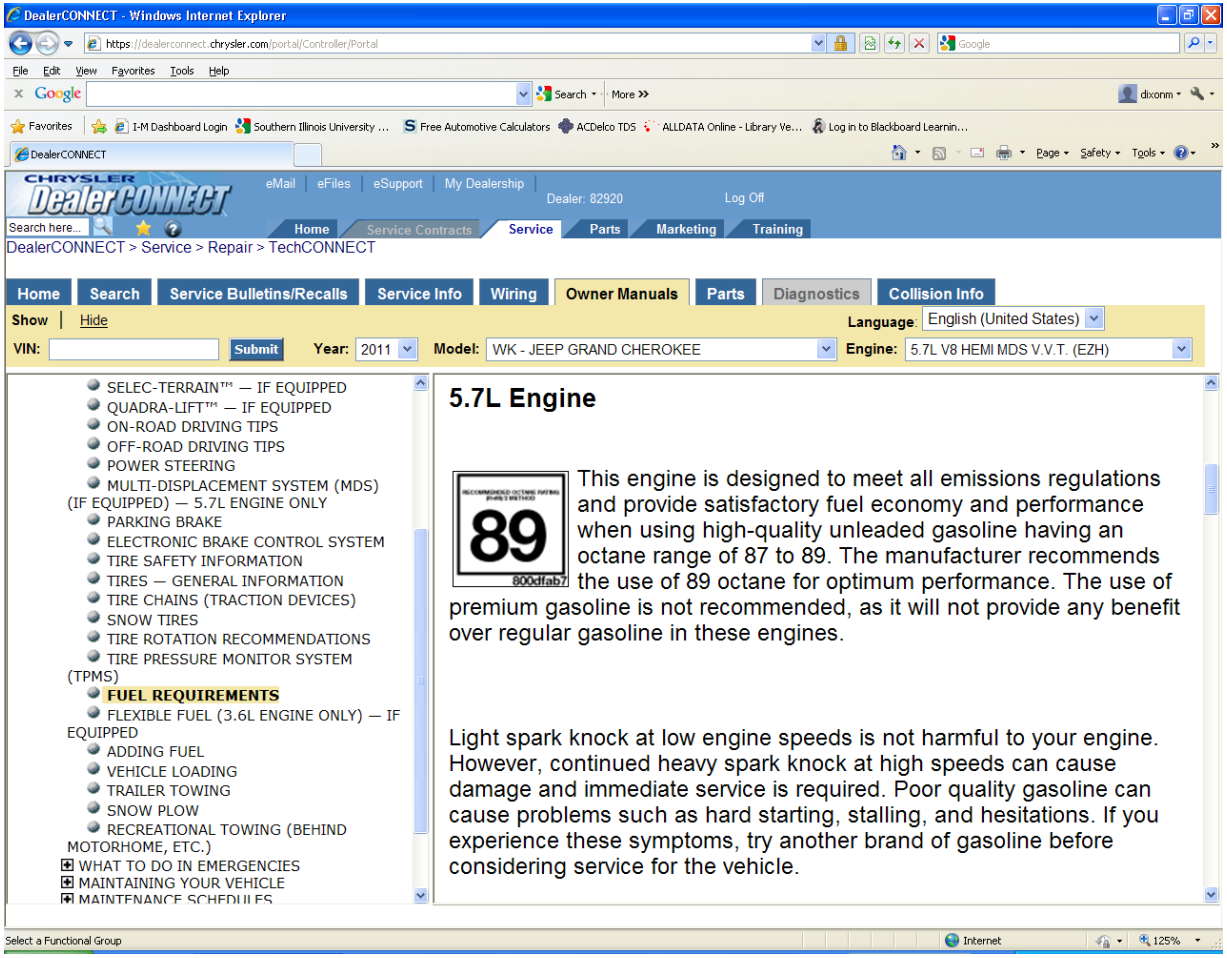
Motor Method (MON)-

Uses spark advance

Results in a lower rating number



Midgrade Recommended



Refer to Service Info or Owner’s Manual

Station in N.M. @ 5,000 ft.

Air less dense: less pressure and heat: lowers engine octane needs

Methods to improve Octane

- Add alcohol or alcohol ethers: TAME ETBE MTBE
- Increased proportion of aromatics
- Metallic additives: lead (banned since 1996) and MMT

Product containing MMT

MMT $(CH_3C_5H_4)Mn(CO)_3$.

Methylcyclopentadienyl manganese tricarbonyl, banned by EPA: 1978-1995

MMT warning from Jeep owners manual

MMT In Gasoline

MMT is a manganese-containing metallic additive that is blended into some gasoline to increase octane. Gasoline blended with MMT provides no performance advantage beyond gasoline of the same octane number without MMT. Gasoline blended with MMT reduces spark plug life and reduces emissions system performance in some vehicles. The manufacturer recommends that gasoline without MMT be used in your vehicle. The MMT content of gasoline may not be indicated on the gasoline pump, therefore, you should ask your gasoline retailer whether the gasoline contains MMT. It is even more important to look for gasoline without MMT in Canada, because MMT can be used at levels higher than those allowed in the United States. MMT is prohibited in Federal and California reformulated gasoline.

MMT leaves rust-like Appearance

Spark plug after running fuel containing MMT

Tetraethyl lead (TEL)

$(CH_3CH_2)_4$ Pb

Anti-knock agent of the past

Coats Catalysts and oxygen sensor surfaces rendering them ineffective and hence the ban

Clean Air Act of 1990 prohibited sale of gasoline containing lead after 12-31-1995 for on road use.

After Lead…

Refiners in the 1980's needed away to boost octane

1. Increased aromatics % (some toxic)
2. Increased butane content (led to high vapor)
3. Used **alcohol ethers** such as MTBE, ETBE and TAME

When oxygenated and reformulated fuel requirements came along in the 90's MTBE was the most popular **oxygenate**

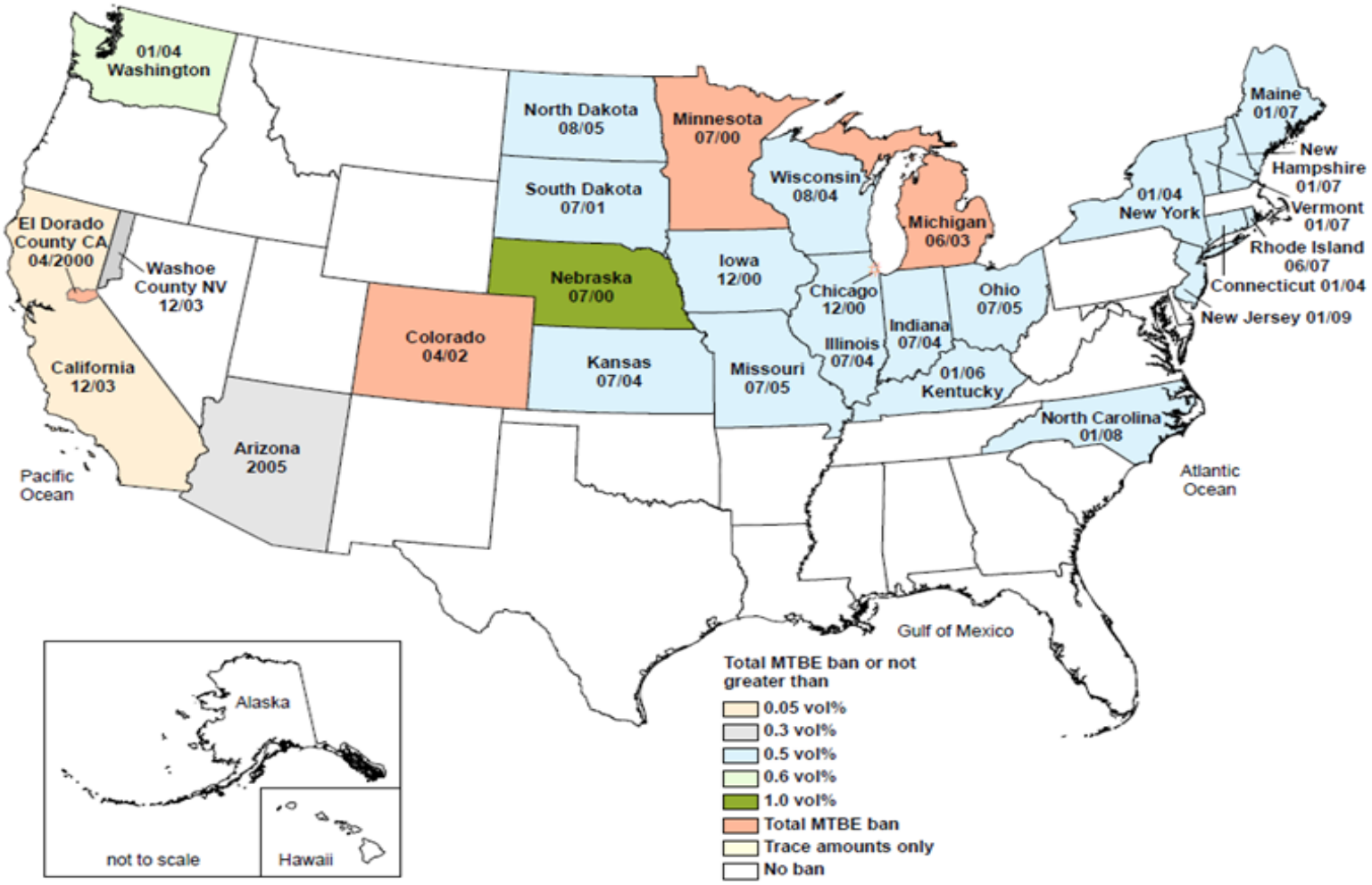
MTBE (methyl tertiary butyl ether)

MTBE, an alcohol ether, was the octane enhancer of choice since the early 80's and later the most widely used oxygenate of 1990s Reformulated Gasoline

(Ethers smell bad as did gasoline in this era)

Because of groundwater contamination issues, 25 states **banned or severely limited MTBE** between 1999-2009

MTBE Ban


01/04
Washington
El Dorado
County CA
04/2000
Washoe
County NV
12/03
California
12/03
Arizona
2005
Colorado
04/02
Nebraska
07/00
Kansas
07/04
North Dakota
08/05
South Dakota
07/01
Minnesota
07/00
Iowa
12/00
Missouri
07/05
Wisconsin
08/04
Illinois
07/04
Chicago
12/00
Michigan
06/03
Indiana
07/04
Ohio
07/05
01/06
Kentucky
01/04
New York
Maine
01/07
New
Hampshire
01/07
Vermont
01/07
Rhode Island
06/07
Connecticut 01/04
New Jersey 01/09
North Carolina
01/08
Pacific
Ocean
Atlantic
Ocean
Gulf of Mexico
Alaska
not to scale
Hawaii
Total MTBE ban or not
greater than
0.05 vol%
0.3 vol%
0.5 vol%
0.6 vol%
1.0 vol%
Total MTBE ban
Trace amounts only
No ban

ETBE

Ethyl Tertiary Butyl Ether: another oxygenate and octane enhancer

More expensive than MTBE

If gasoline is blended with ETBE at 20% volume the oxygen weight is about 3.2%

Still currently used in small quantities in some areas

TAME

Tert- amyl methyl ether

Oxygenate and octane booster for gasoline

Needed about 20% blend by volume to exceed 3.1% oxygenate by weight

Still currently used in small quantities in some areas

Oxygenated Gasoline: Winter months

1992 – present, today mostly in southwest

Required in CO non attainment zones.

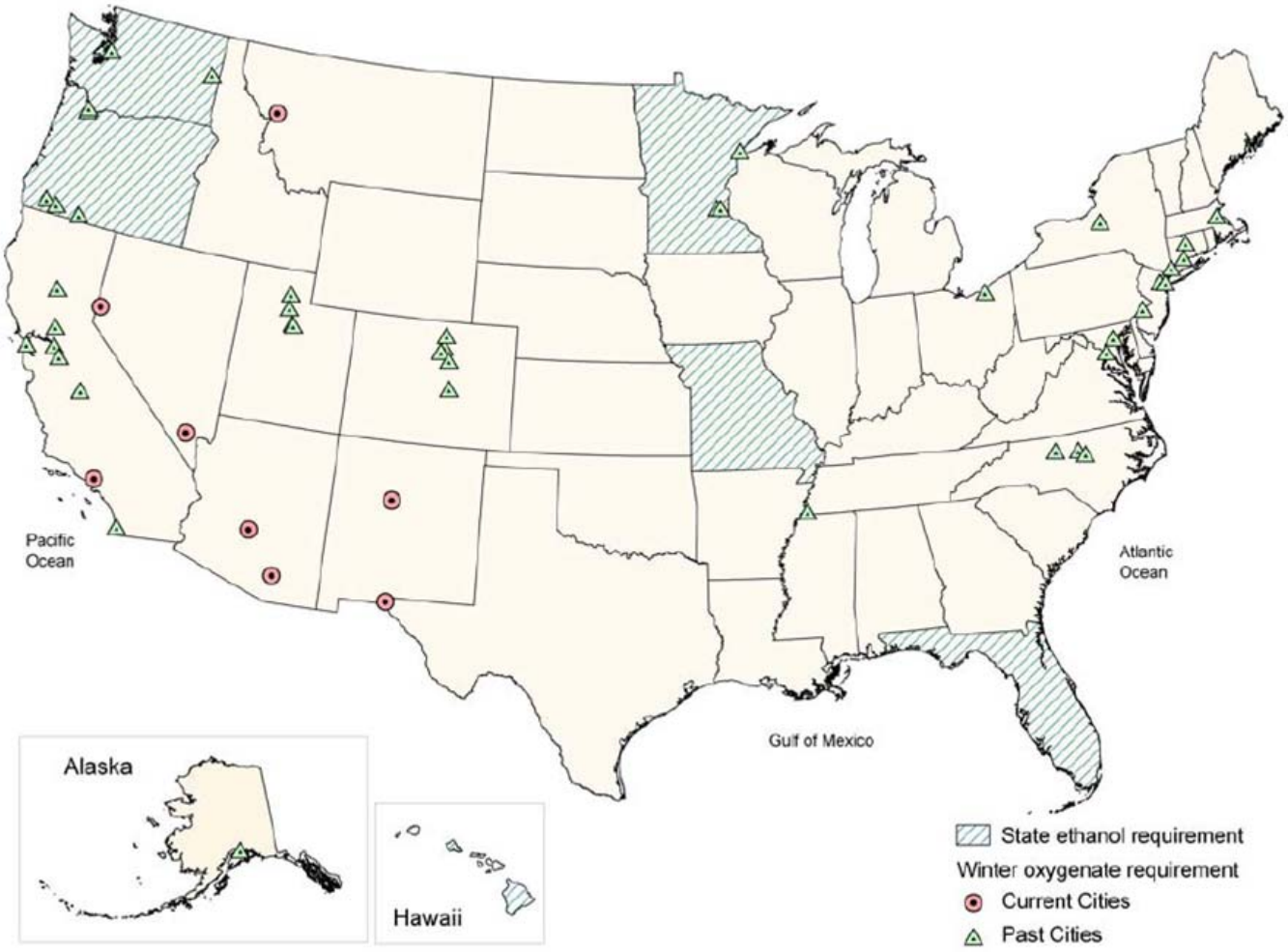
2 levels: Base is **2.7% oxygen by weight**

Continued offenders: 3.1% by weight

Ethanol: The current oxygenate of choice

(mostly) in the past: MTBE, ETBE and TAME

Oxygenated Fuel Program: Past/Present



Reformulated Gasoline (RFG)

1995-present for “Ozone non-attainment zones”

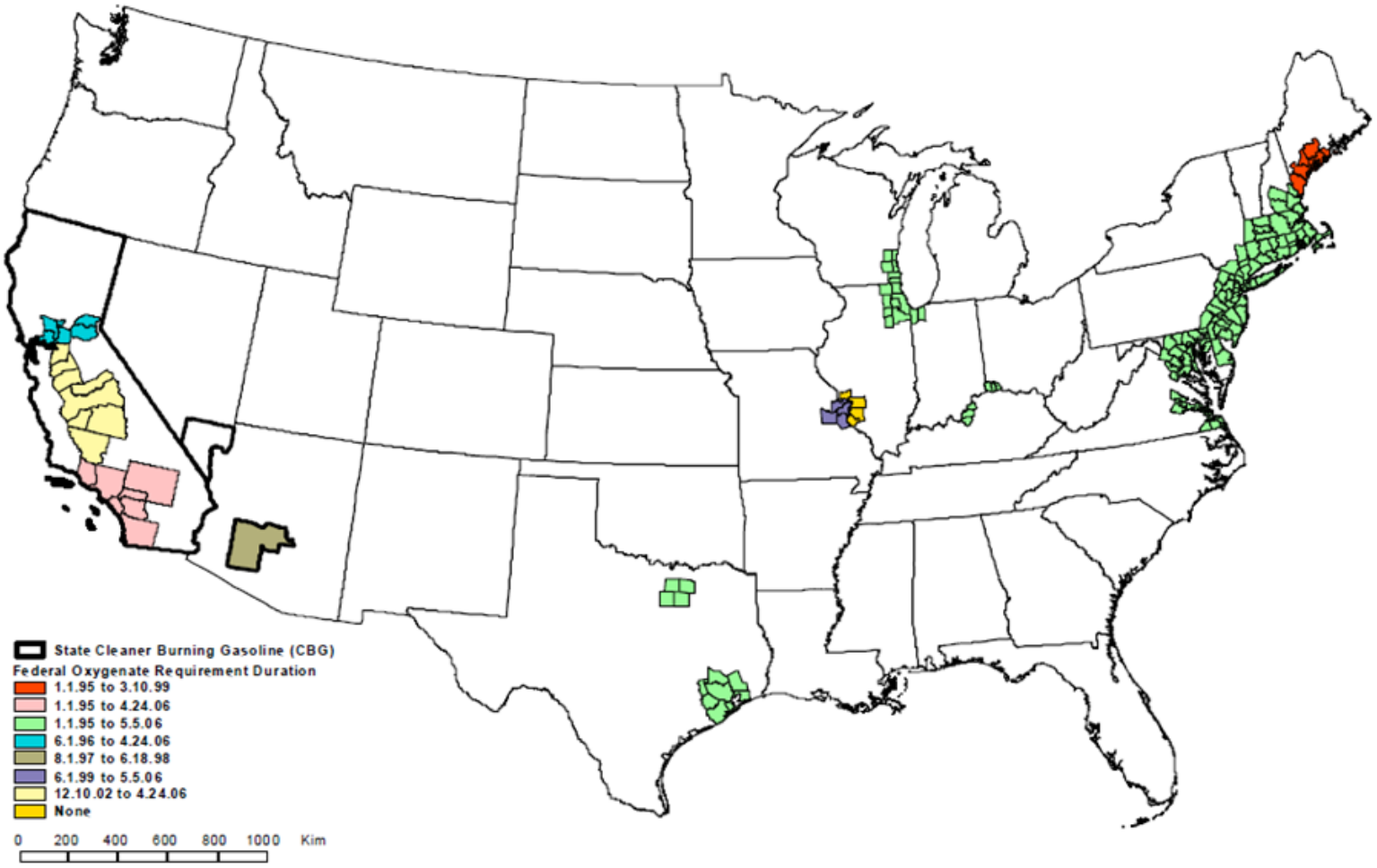
Lower RVP numbers, lower benzene % , limits on other volatile organic compounds and on sulfur PPM and no MMT

Originally required 2.0% oxygen by weight

Had Phase 1, Phase 2 (more stringent)

Also simple model, complex model

Federal/State RFG areas



2005 Energy Policy Act

Federal legislation did away with requirements that RFG had to contain oxygen

Largely in response to states banning MTBE

NH and RI also banned other ethers such as ETBE and TAME and DIPE (di-isopropyl ether)

Recent Legislative Changes

Mobile Sources Air Toxics Rule:

All USA gasoline has a capped limit on **benzene** at .62% (went into effect 2011)

Limited hydrocarbons such as 1,3-butadiene, formaldehyde, acetaldehyde, acrolein, and naphthalene

State Renewable Standards

At least 8 states require a minimum amount of "renewable fuel source" AKA **ethanol** blended with gasoline.

A minimum percentage is required but there may be loopholes

Governors may act to temporarily override requirements or some laws have price triggers that can reduce the requirement based on terminal price or if in state production drops below minimum levels

Volatility

Measure of how easily liquid gasoline vaporizes

Most common method for technician is to measure RVP (Reid Vapor Pressure)

This is the pressure in PSI formed above the liquid sample when heated to 100°F

Changes with seasons

Too numerically low: cold start issues

Too numerically high: excess purge, concern with EVAP leaks and possible vapor lock

EPA RVP requirements by county

- Alaska, Hawaii, and U.S. territories are exempted from federal volatility regulations.

State	County/ Parish	City	Month & RVP PSI Max						
			May	June	July	August	Sept 1–15		
ID	All counties			9.0			9.0	9.0	9.0	9.0
IL	Madison	E. St. Louis		9.0			7.2[D]	7.2	7.2	7.2
IL	Monroe			9.0			7.2[D]	7.2	7.2	7.2
IL	St. Clair			9.0			7.2[D]	7.2	7.2	7.2
IL	All other conventional gasoline counties			9.0			9.0	9.0	9.0	9.0
IL	(See EPA RFG list)[B]									
IN	Clark			7.8[A]			7.8	7.8	7.8	7.8
IN	Floyd			7.8[A]			7.8	7.8	7.8	7.8
IN	All other conventional gasoline counties			9.0			9.0	9.0	9.0	9.0

RVP Testing

Drivability index

This measures the distillation temperature at points when 10%, 50% and 90% of gasoline evaporates

$DI = (1.5 \times T_{10}) + (3.0 \times T_{50}) + T_{90} + (2.4°F \times V\% \text{ eth})$

Distillation classes AA, A, B, C, D, E

Testing for contamination

- Water
- Alcohol
- Diesel Fuel

Tool for drawing a sample

Checking for water contamination

Weight per gallon:
Gasoline 6 lbs.; water about 8 lbs

Gasoline

Water: heavier will sink to bottom

Diesel about 7.25 lbs E85: about 6.5 lbs.

Both heavier than gasoline: sink to bottom

Diesel

E-85

Checking for Alcohol

Checking for Alcohol: E85

Filled to 50 ml with E85

Added 50 ml of water

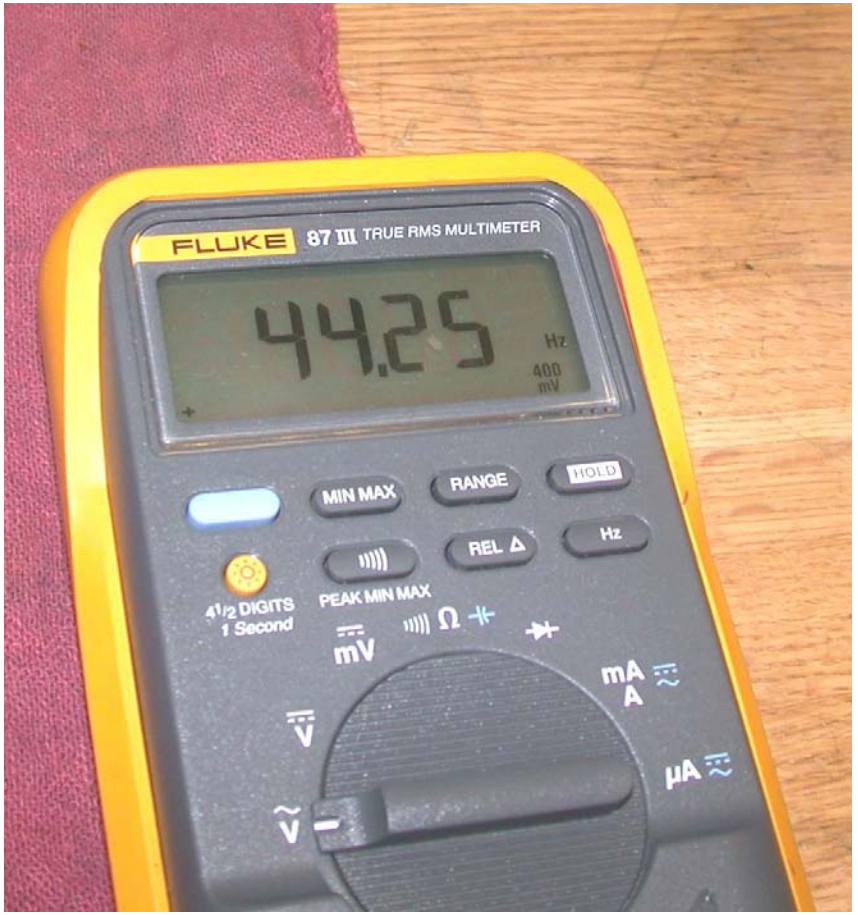
Mark is at about 85 mL
which indicates about
70% alcohol

Gasoline vs. Alcohols

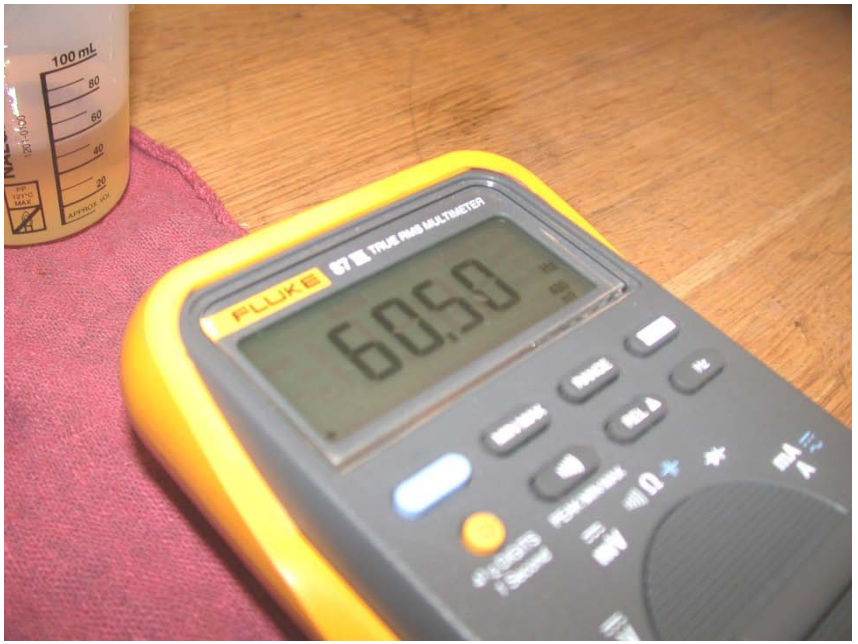
Gasoline: Dielectric

E-85 Shows Resistance

Checking using Kent Moore J44175



Kent Moore Alcohol tester



RVP test on E85

Gas Pump Nozzle Sizes

Fuel	Nozzle Diameter	Pump Handle Color (Varies—no established standard)
Gasoline	13/16 in. (21 mm)	Black, red, white, green, or blue
E10	13/16 in. (21 mm)	Black, red, white, green, or blue
E85	13/16 in. (21 mm)	Yellow or black
Diesel fuel	15/16 in. (24 mm)	Yellow, green, or black
Biodiesel	15/16 in. (24 mm)	Green
Truckstop diesel	1 1/14 or 1 1/2 in. (32 or 38 mm)	Varies

Gas Pump Nozzle Sizes

Gasoline

21 mm

Diesel

24 mm

Gasoline use and storage recommendations

- Most experts state that the shelf life of gasoline is 90 days.
- Shelf life means that it works like new for 90 days but after that the light ends start to evaporate and oxidation starts to occur that affects its performance.

Gasoline use and storage recommendations: Proper cans

Old oxidized gasoline results

Honda Odyssey Lab Vehicle: Very Bad Smell!

Use a gasoline stabilizer to help avoid oxidation

Use fresh Stabilizer in fresh gasoline

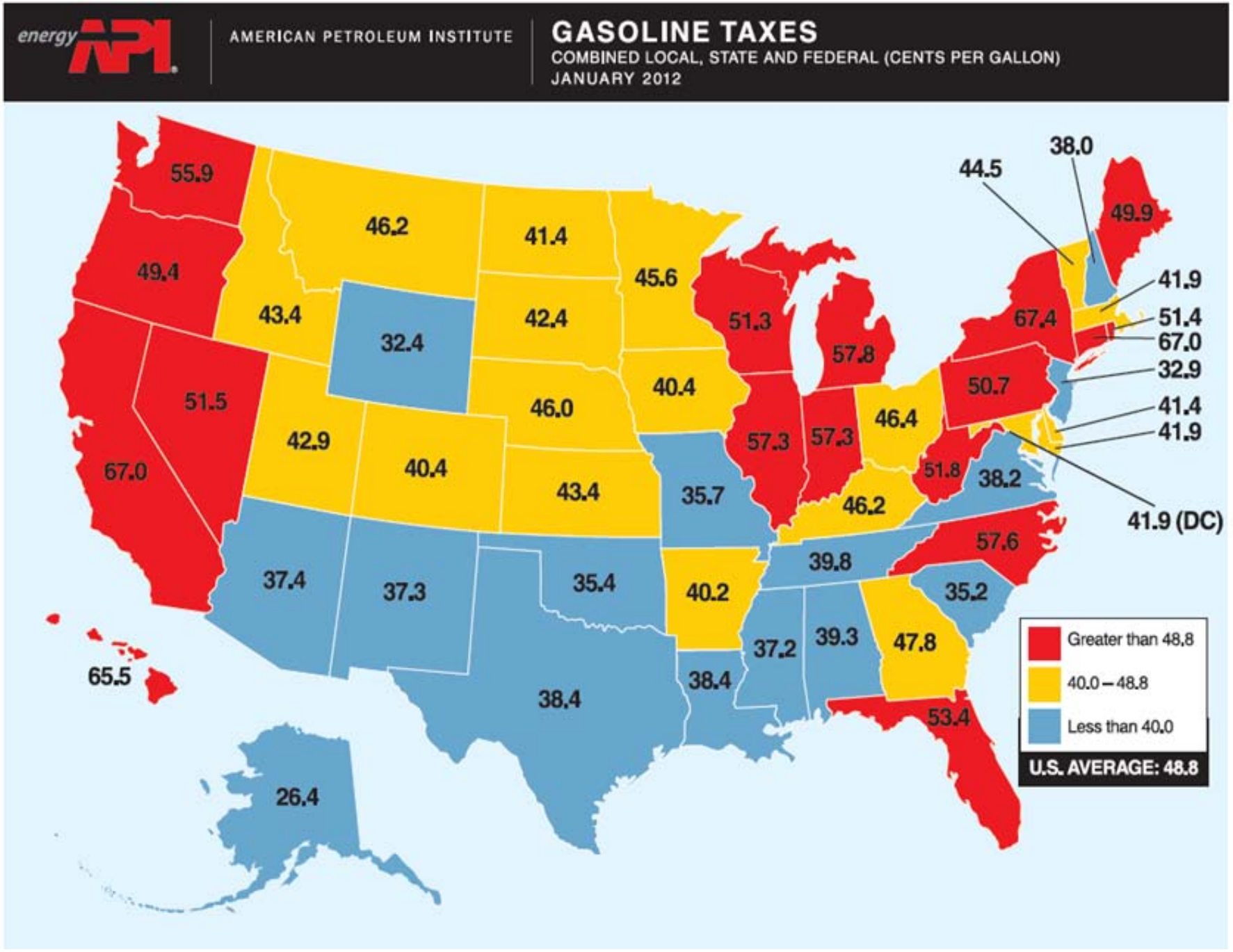
Use precautions when filling the tank

Gasoline taxes

Federal Excise Tax, currently: 18.4 cents per gallon

Each state also has excise and other taxes including sales tax

Combined State and Federal taxes are about **57.3 cents per gallon in Illinois** (one of the higher taxed states)


energy API
AMERICAN PETROLEUM INSTITUTE
GASOLINE TAXES
COMBINED LOCAL, STATE AND FEDERAL (CENTS PER GALLON)
JANUARY 2012
55.9
49.4
67.0
51.5
46.2
43.4
42.9
32.4
37.4
37.3
65.5
26.4
41.4
42.4
40.4
46.0
43.4
38.4
45.6
40.4
35.7
35.4
40.2
38.4
51.3
57.8
57.3
57.3
46.2
51.8
44.5
38.0
49.9
41.9
67.4
51.4
67.0
32.9
50.7
41.4
41.9
38.2
41.9 (DC)
46.4
57.6
39.8
35.2
37.2
39.3
47.8
53.4
Greater than 48.8
40.0 – 48.8
Less than 40.0
U.S. AVERAGE: 48.8

Taxes/tax credits: Ethanol

Current Federal Law provides for a 51cent/gallon credit for ethanol.

This translates to 43.3 cents for a gallon of E85 or about 5.1 cents for a gallon of E10

CAFE Flex fuel credits expire in 2020

Future regulations/ changes

- PM regulations (g's per mile)
- PM is a concern with GDI
- Reduction in sulfur?
- Sulfur measured in parts per million (PPM) or mG/KG
- Worldwide charter (2006) suggests 30 PPM or less perhaps down to 10 PPM in future
- Sulfur measured by ASTM D2622-98 method

Summary

- Gasoline is a blend of many hydrocarbons
- Weighs less than water, diesel, or ethanol
- Store fuels in correctly colored and labeled containers
- Use stabilizer if storing over 3 months

Summary

- Fuel volatility varies with both time of year and location of purchase
- Alcohol % varies with location of purchase and can be easily tested for
- Octane: R+M/2 anti knock rating, not all engines will benefit from higher ratings, refer to owner's manual: for correct grade
- Price, regulation, and taxes are likely to increase

Contact Information

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- dixonm@siu.edu