Ethanol and Biodiesel Fuel Literacy

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Gasoline: Measures of quality

- Octane
- Volatility
  - Drivability Index
- Copper corrosivity
- Silver corrosivity
- Stability
- Sulfur content
- Metallic Additives

Energy Content?
Is not a measure of quality

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Ethanol and Gasoline BTU/gallon

Single Molecule, Short Chain, Contains Oxygen all lead to lower energy density per unit volume

Gasoline more volatile in winter to improve cold start and warm up. (more volatile means less dense = less btu/gal)

	Ethanol	Gasoline Summer	Gasoline Winter
Max	76,300	117,000	114,000
Min	76,300	113,000	108,500
Percent Difference	0	3.4	5.0
Difference between summer max and winter min 7.26%			

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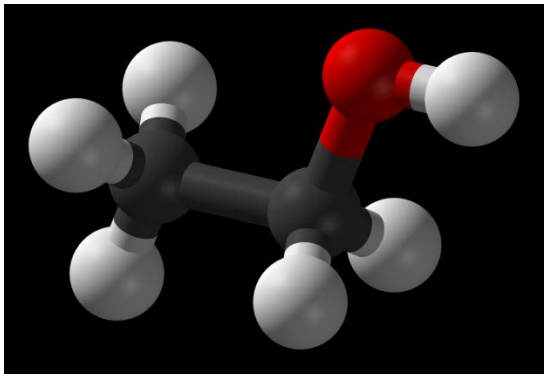
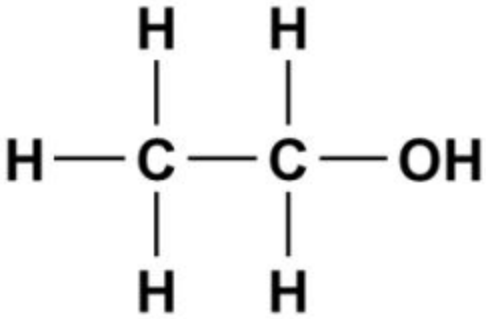
(Changes in Gasoline IV) RFA

Ethanol Properties

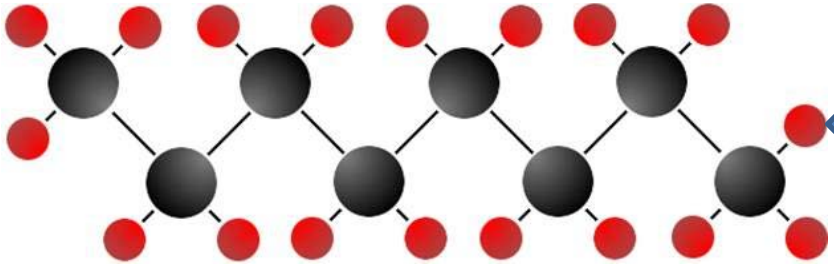
- Octane
  - Pure ethanol is 100 Octane
- Energy content 76,300 BTU/gallon
- Hygroscopic in nature
  - Gasoline is hydrophobic
- Volatility
  - Higher
- Mild Solvent

Ethanol vs Gasoline





Ethanol



Gasoline – 5-12 C chains

Carbon + Oxygen = Energy
Hydrogen + Oxygen = Energy
Oxygen + Oxygen = No Energy

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Ethanol vs Gasoline

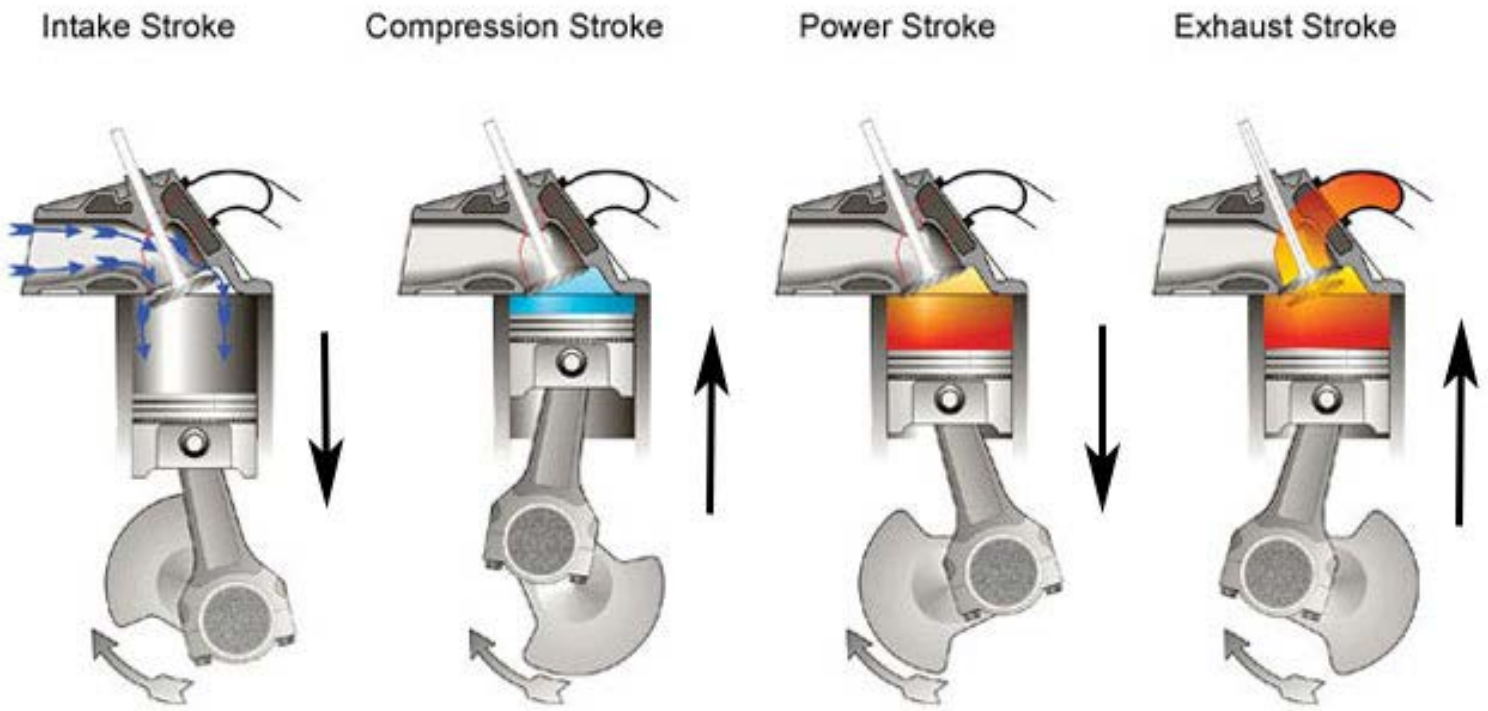
- Carbon + Oxygen = Energy
- Hydrogen + Oxygen = Energy
- Oxygen + Oxygen = No Energy
- Ethanol
  - C= 12 x 2 = 24
  - H= 1 x 6 = 6
  - O= 16 x 1 = 16
- 16/46=0.34
- Ethanol is 34% Oxygen by weight which gives no energy during combustion

How Ethanol Changes Gasoline

- Ethanol has less energy
- Ethanol contains approximately 33% less energy per gallon than gasoline
- Typical blend is 10% ethanol
- E10 would contain approximately 3.3% less energy than regular gasoline
- Hygroscopic nature causes ethanol to mix with water
  - Can be a positive in clearing water out of system
    - Can be a negative in fuel storage
    - Long term storage of ethanol blends can result in water in the fuel, formation of corrosive materials

Octane

- A relative value given to fuel to represent its ability to withstand compression without igniting
  - Premature combustion of fuel in a spark ignition engine causes knocking and can be damaging to an engine.
- Early anti-knocking agents / octane boosters
    - Tetra-ethyl lead (leaded gasoline)
    - With the phase out of leaded gas there needed to be a substitute anti-knocking agent / octane booster
      - Aromatic hydrocarbons
      - Ethers
      - Alcohol (ethanol or methanol)
      - Other
- Called octane because the compound (iso-octane) is the basis for comparison.
  - 87 octane fuel is some combination of fuels that has the same performance of the 87/13 combination of octane/heptane)


Intake Stroke
Compression Stroke
Power Stroke
Exhaust Stroke

Octane Ratings of Fuels

Fuel	RON	MON	AKI
Iso-Octane(RON and MON 100 by definition)	100	100	100
t-butanol	103	91	97
ethane	108		
toluene	111	95	103
E85 gasoline			100–5
xylene	117		
isopropanol	118	98	108
ethanol	106	89	100
methanol	133	105	119
methane	135	122	129
UK regular	95		
US regular	91-92	82-83	87

RON-
Research Octane Number (slow speed knock)

MON-
Motor Octane Number (high speed knock)

AKI-
Anti Knock Index (R+M)/2

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Volatility

- The fuel's ability to vaporize (change from liquid to vapor)
- Too low (1960's)
- Too high (1980's)

Volatility Too Low	Volatility Too High
Poor cold start	High evaporative emissions/ Canister overload & purge
Poor warm up performance	Hot driveability problems/ vapor lock
Poor cool weather driveability	Fuel economy may deteriorate
Increased deposits -crankcase -combustion chamber -spark plugs	
Unequal fuel distribution in carbureted vehicles	
Potentially increased exhaust emissions	

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Volatility

- To ensure proper volatility
  - Gasoline volatility is adjusted seasonally
  - Summer (less volatile)
    - Minimize vapor lock and hot drivability problems
    - Less evaporative losses
    - More energy dense (longer HC chains)
  - Winter (more volatile)(shorter HC chains)
    - Improved cold start and warm up performance
    - Low risk of evaporative losses
    - Less energy dense (shorter HC chains)

How Ethanol Changes Gasoline

- Ethanol contains oxygen
  - Oxygenates in gasoline lead to reduction in Carbon monoxide and soot emissions
    - Important to reducing smog formation in major cities. Reformulated gasoline containing oxygenates has improved air quality in cities.
- Ethanol increases Vapor Pressure or fuel volatility
  - Vapor pressure maximums are set for summer and winter fuel
  - Ethanol blends been granted 1 psi RVP allowance (not in reformulated gasoline or California)

How Ethanol Changes Gasoline

- Ethanol Increase Octane
- Ethanol is 100 octane
- Ethanol is 112 octane

Both are true

- Blending Octane Value "BOV"
- Blends of alcohols can be tested to determine what is called a "Blending Octane Value" or BOV. Basically, the octane rating of an alcohol/gasoline blend is compared to the octane rating of the gasoline without alcohol and some math is done to calculate what the effect of the alcohol was on the octane of the gasoline. http://www.racegas.com/article/11

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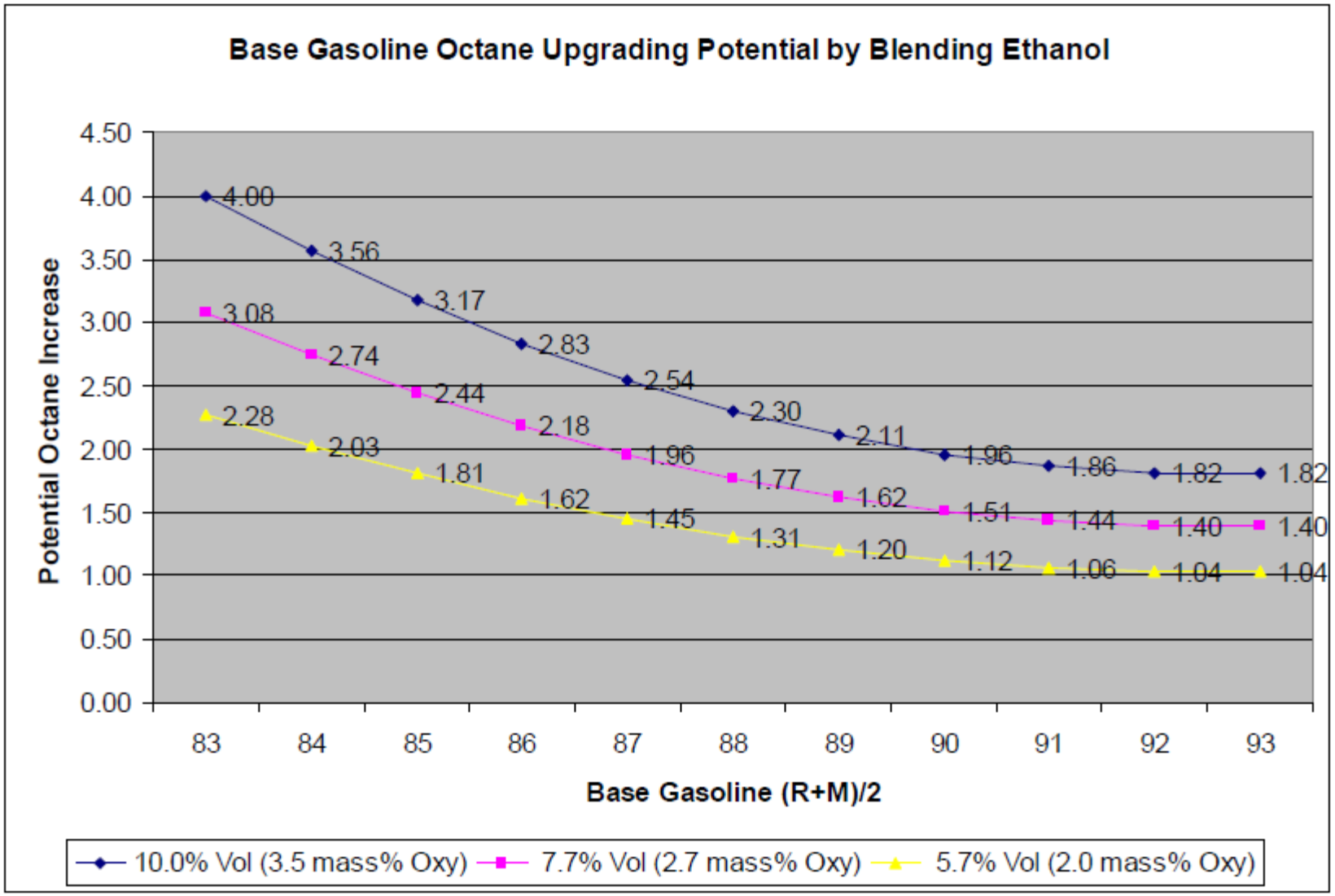
Blending Ethanol & Octane Boost



Tennessee Dept of Ag.

How Ethanol Changes Gasoline

- Ethanol is a solvent and can dissolve deposits in gas tanks
  - Positive because it is cleaner
  - Negative when dislodged deposits stick in carburetor or filters etc.
- Ethanol and component compatibility
  - True of old materials in older engines
    - Seals, gaskets, plastics. Swell, soften, harden etc.
  - Not an issue in modern engines

How Ethanol Changes Gasoline

Ethanol burns hotter?

Ethanol burns cooler?

Air/Fuel Ratio: Ethanol Combustion

$$A/F \cong 9.0$$

Air/Fuel Ratio: Gasoline Combustion

$$\frac{A}{F} \cong 14.11$$

$$A/F \cong 14.1$$

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How Ethanol Changes Gasoline A/F

- A/F ratio variation
  - Lean = less fuel, higher A/F ratio
  - Rich = more fuel, lower A/F ratio
- The air to fuel ratio in an engine is seldom (chemically) correct
  - Manufacturers often set engines to run “rich”
    - More power
    - Cooler operation
- Changes with Ethanol in mix
  - Enleanment
    - C_2H_5OH
- Symptoms
    - Power loss
    - Engine heating

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Diesel: Measures of Quality

- Cetane
- Flash Point
- Viscosity
- Ash%
- Sulfur
- Copper strip corrosion
- Cloud point or CFPP
- Ramsbottom carbon residue
- Lubricity
- Conductivity

Cetane

- Measure of fuels ignition delay
  - Low cetane has longer ignition delay
  - High cetane has shorter ignition delay
- Higher cetane
  - minimizes diesel knock and may be smoother running
  - Easier cold starting and faster warm up
- Higher cetane does not necessarily translate into greater efficiency or more power
- If cetane is too low
  - Engine may be hard or impossible to start
  - White smoke during start
- If cetane is too high
  - Incomplete combustion

ULSD: Typically 42-45 (min 40)

http://www.youtube.com/watch?v=WdQ4J-NFoU8

Cloud Point

- Cloud Point
  - Temperature at which crystals begin to appear in the fuel
- Pour Point
  - Highest temperature at which the fuel ceases to flow
- Pour Point is ~7 to 10°F lower than cloud point

How Biodiesel Changes Diesel

- Biodiesel (B100) has a high cetane
  - Biodiesel blends tend to increase cetane
    - 46-52 for veg oils
    - 56-60 for animal fat
- Increases lubricity even at very low blends such as 1%
- Increases cloud point and fuel gelling characteristics
- Significantly reduces emissions of particulate matter, CO, and hydrocarbons
  - Nitrous oxide may slightly increase

NOTE: new diesel engines (2010 and newer) with particulate filters and selective catalytic reduction systems all have very low emissions regardless of what fuel they run.

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How Biodiesel Changes Diesel

- Biodiesel may change the fuel gelling characteristics depending on level of blend and source of biodiesel
  - ULS Diesel and B5 Biodiesel perform similarly in cold temperatures
  - Higher blends are effected more
    - Cloud point of soy biodiesel is ~34°F (1°C)
    - Cloud point of ULSD is -18°F (-28°C) to + 20°F (-6°C)
      - Winter is lower summer is higher depends on location
  - Source of Biodiesel makes a difference (Cloud Point)
    - Soybean ~34°F (1°C)
    - Canola ~32°F (0°C)
    - Tallow ~59°F (15°C)

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How Biodiesel Changes Diesel

- Biodiesel has less energy
  - Biodiesel has about 8 percent less energy per gallon
  - B2 has ~0.17% less energy than #2
  - B5 has ~0.4 % less energy than #2
  - B20 has ~1.6 % less energy than #2
- Biodiesel acts as an cleaner and can clean fuel system deposits
  - B5 blends have little effect
  - B20 blends have shown short term filter clogging
- Long term storage of Biodiesel or blends can result in water in the fuel, oxidation, formation of corrosive materials

F. John Hay

Extension Educator – Energy

Nebraska Extension

Department of Biosystems Engineering

250 Chase Hall

Lincoln, NE 68538-0726

Jhay2@unl.edu

402-472-0408

http://bioenergy.unl.edu

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Gasoline - Octane

- The octane rating of gasoline tells you how much the fuel can be compressed before it auto-ignites.
- Octane is NOT a measure of the energy in gasoline
  - 87 octane gasoline - US gallon = 108-117,000 Btu
  - 92 octane gasoline - US gallon = 108-117,000 Btu
  - 100 octane ethanol - US gallon = 77,300 Btu
  - 87 octane unl (E10) - US gallon = 110,300 Btu

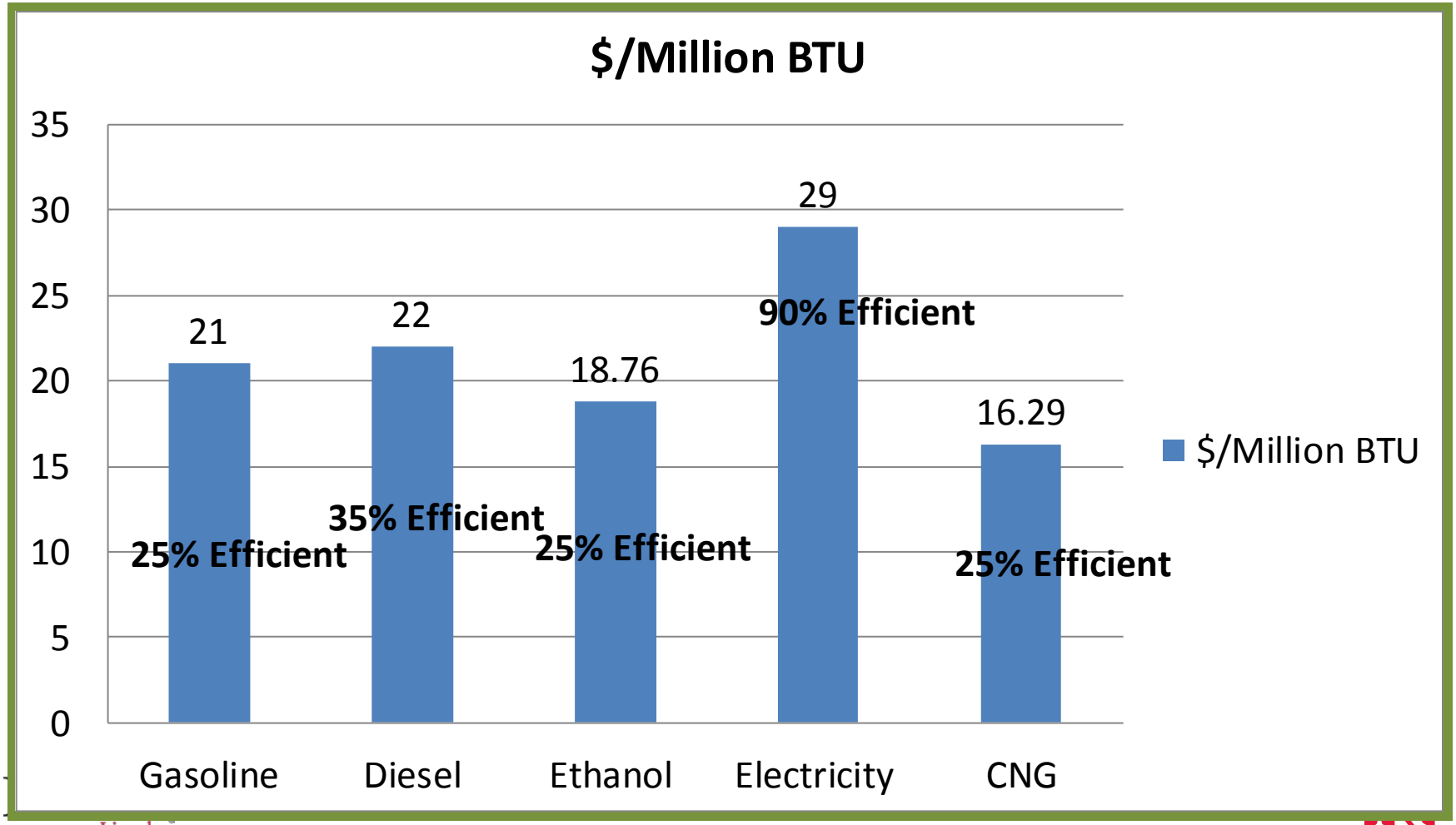
Time of Year Difference
Up to 7 % difference

~ 3.2 % difference from 117,000 BTU/ gal gasoline

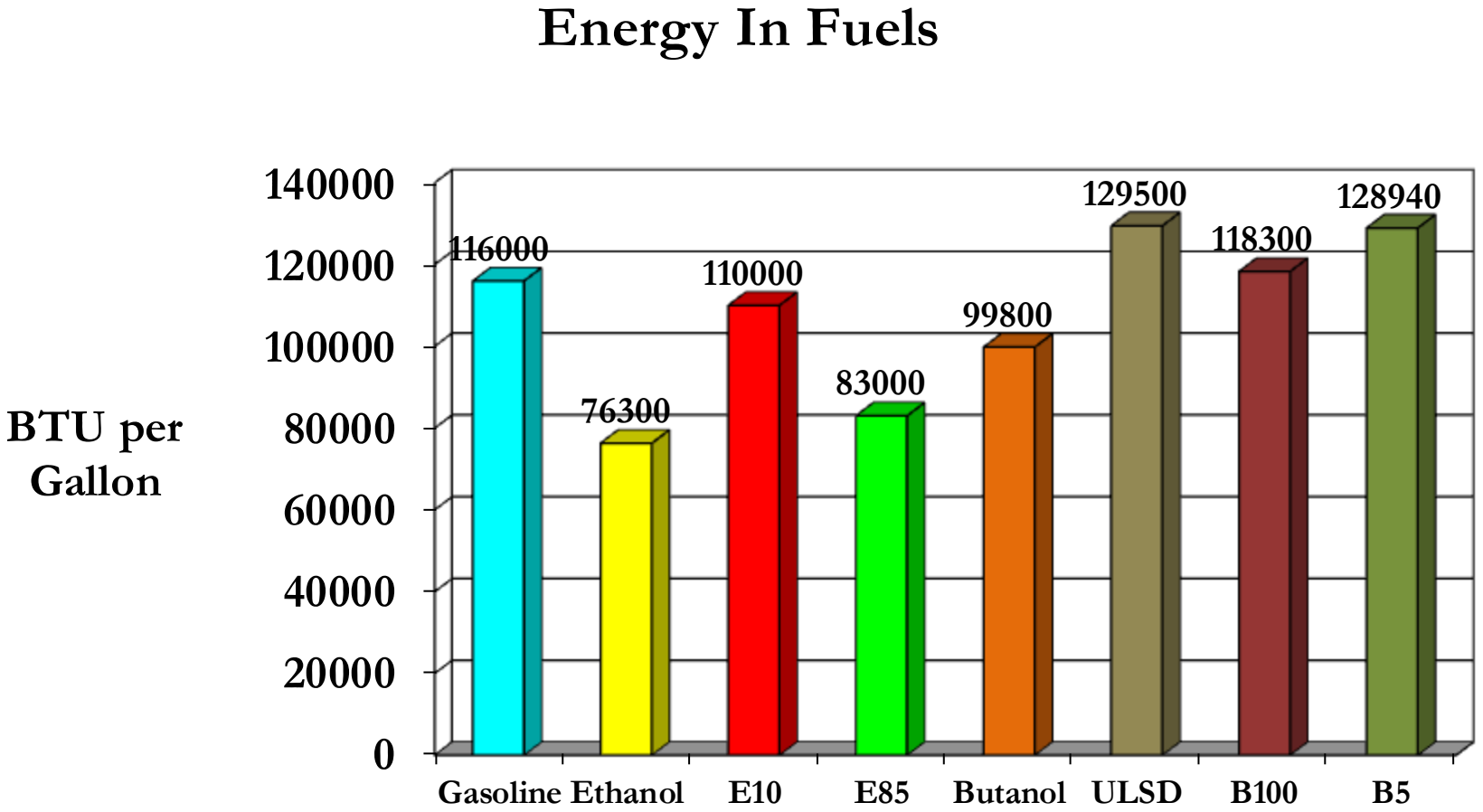
NOTE: octane numbers above are actually AKI (RON+MON/2)

Other Transportation Fuels

based on retail prices for fuel 2015



Energy Content of Fuels



Heating Value (HHV)

ΔH_c (heat of combustion in btu/lb)

$C + O_2 \Rightarrow CO_2$	$\Delta H_c = 14{,}500$ btu/lb
$2H_2 + O_2 \Rightarrow 2H_2O$	$\Delta H_c = 62{,}000$ btu/lb
$S + O_2 \Rightarrow SO_2$	$\Delta H_c = 4{,}000$ btu/lb

Therefore, the heating value of coal with measured percentage concentrations of the three elements (C, H, S) is:

HV(fuel) = (14,500 x [C] + 62,000 x [H] + 4000 x [S])/100

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Octane Ratings of Fuels

Fuel	RON	MON	AKI
diesel fuel	15–25		
Iso-Octane(RON and MON 100 by definition)	100	100	100
benzene	101		
"BP Ultimate 102	102	93–94	97–98
t-butanol	103	91	97
ethane	108		
propane	110		
toluene	111	95	103
E85 gasoline			100–5
xylene	117		
isopropanol	118	98	108
ethanol	106	89	100
methanol	133	105	119
methane	135	122	129
hydrogen*	> 130	very low	
UK regular	95		
US regular	91-92	82-83	87

RON-
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Motor Octane Number (high speed knock)

AKI-
Anti Knock Index (R+M)/2

Gasoline

- Spark ignition engine fuel
- Complex mixture of components
- Must run across a wide range of conditions
  - Engines
    - Different fuel systems, engine temps, fuel pumps, fuel pressure…etc
  - Climatic
    - Temperature, altitude…etc

Compounds in Gasoline

Gasoline is a complex mixture of over 500 hydrocarbons that may have between 5 to 12 carbons. Smaller amounts of alkane cyclic and aromatic compounds are present. Virtually no alkenes or alkynes are present in gasoline.

http://www.elmhurst.edu/~chm/vchembook/514gasoline.html

Paraffins or Alkanes	**Octane #**
n-butane	113
n-pentane	62
n-hexane	19
n-heptane	0
2-methylbutane	99
2,2-dimethylpropane	100
2,2-dimethylbutane	89
2,2-dimethylpentane	89
2,2,3-trimethylbutane	113
2,2,4-trimethylpentane (isooctane)	100
Olefins or Alkenes	
1-pentene	152
2-methyl-2-butene	176
3-methyl-2-pentene	130
2,4,4-trimethyl-1-pentene	164
Cycloalkanes or Naphthenes	
cyclopentane	141
methylcyclopentane	107
cyclohexane	110
1,2-dimethylcyclohexane	104
1,4-dimethylcyclohexane	66
Aromatics	
Benzene	99
Toluene or methylbenzene	124
m-xylene or 1,3-dimethylbenzene	145
Ethylbenzene	124
Propylbenzene	127
Isopropylbenzene	132

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High Compression Vehicles

- Higher-octane fuels allow for a higher compression ratio without knocking, resulting in a higher cylinder temperature, which improves efficiency
- High compression engines burn the fuel more efficiently – getting more power from same amount of energy

How Ethanol Changes Gasoline

- Ethanol burns hotter?
- Ethanol burns cooler?

How Ethanol Changes Gasoline -Water

- Student Intern Study 2014 (Igor Sousa, Ivan Mankino)
  - How much water will E0, E10, E15 hold in solution?
  - Will fuel additives which claim to remove water actually help?
- Study
  - 3 replicates of small 8 ml test tubes
  - Repeated with 2 replicates of 100 ml jars
- Tested 8 additives
  - STP, BG, Iso-HEET, Stabil, Rislene, HEET, Seafoam, Valvoline, (All claimed to remove water or help solve phase separation)
  - Additives used at labeled rate

How Ethanol Changes Gasoline –Water

Fuel	Water held in solution
E-0	Zero teaspoons per gallon
E-10	3.06 teaspoons per gallon (4 ml/liter)
E-15	6.47 teaspoons per gallon (8.55 ml/liter)

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How Ethanol Changes Gasoline -Water

Additive	Water held in solution
STP	No effect
BG – Ethanol Fuel System Drier	Increased water holding by 0.23 tsp per gallon (0.3 ml/L) ★
Iso-HEET	Increased water holding by 0.23 tsp per gallon (0.3 ml/L) ★
Stabil – Ethanol treatment	No effect
Rislene	No effect
HEET	Partial effect: Solution was more clear but did not clear phase separation layer
Seafoam	No effect
Valvoline – Nitro Shot	No effect

Observations: Iso-HEET contains isopropyl alcohol, Based on odor BG also contains high concentration of alcohol

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How Ethanol Changes Gasoline -Water

- E10 Water Study Conclusions
  - E10 can remove small amounts of water from fuel tank running it harmlessly through your engine
  - Small amounts of water can accumulate in a fuel tank with E0
  - Based on literature large amounts of water contamination is equally bad for E10 and E0 fuels.
    - Engines can not run on water or water ethanol phase.
  - The best way to avoid water contamination is to not let the water get in.
    - Sealed storage containers
    - Drain fuel or run equipment dry before winter storage or keep fuel tank full to limit air space for moisture to condense.