ETHANOL: WILL IT DRIVE YOU TO DRINK?

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Outline

- Coming soon to a station near you…
- The regulations and compatibility….
- Ethanol and the environment …..

Energy Policy Act of 2005

Title XV – Ethanol and Motor Fuels

Subtitle A – General Provisions

- **2% by weight oxygen content requirement of the Federal RFG program eliminated**
- **Requires gasoline sold in US to contain increasing amounts of renewable fuel**
  - **2006 4.0 billion gallons of renewable fuel**
  - **2012 7.5 billion gallons of renewable fuel**

Energy Policy Act of 2005

The Act does not:

- **Ban MTBE**
- **Clarify EPA or state authority to regulate/ban MTBE or other fuel additives**
- **Provide MTBE or renewable fuel product liability waivers**
- **Provide transition assistance to MTBE manufacturers**

Energy Policy Act of 2005

Title XV – Ethanol and Motor Fuels

Subtitle B – Underground Storage Tank Compliance

"Underground Storage Tank Compliance Act"

- Lots of additional tasks….
- Lots of additional money…..?

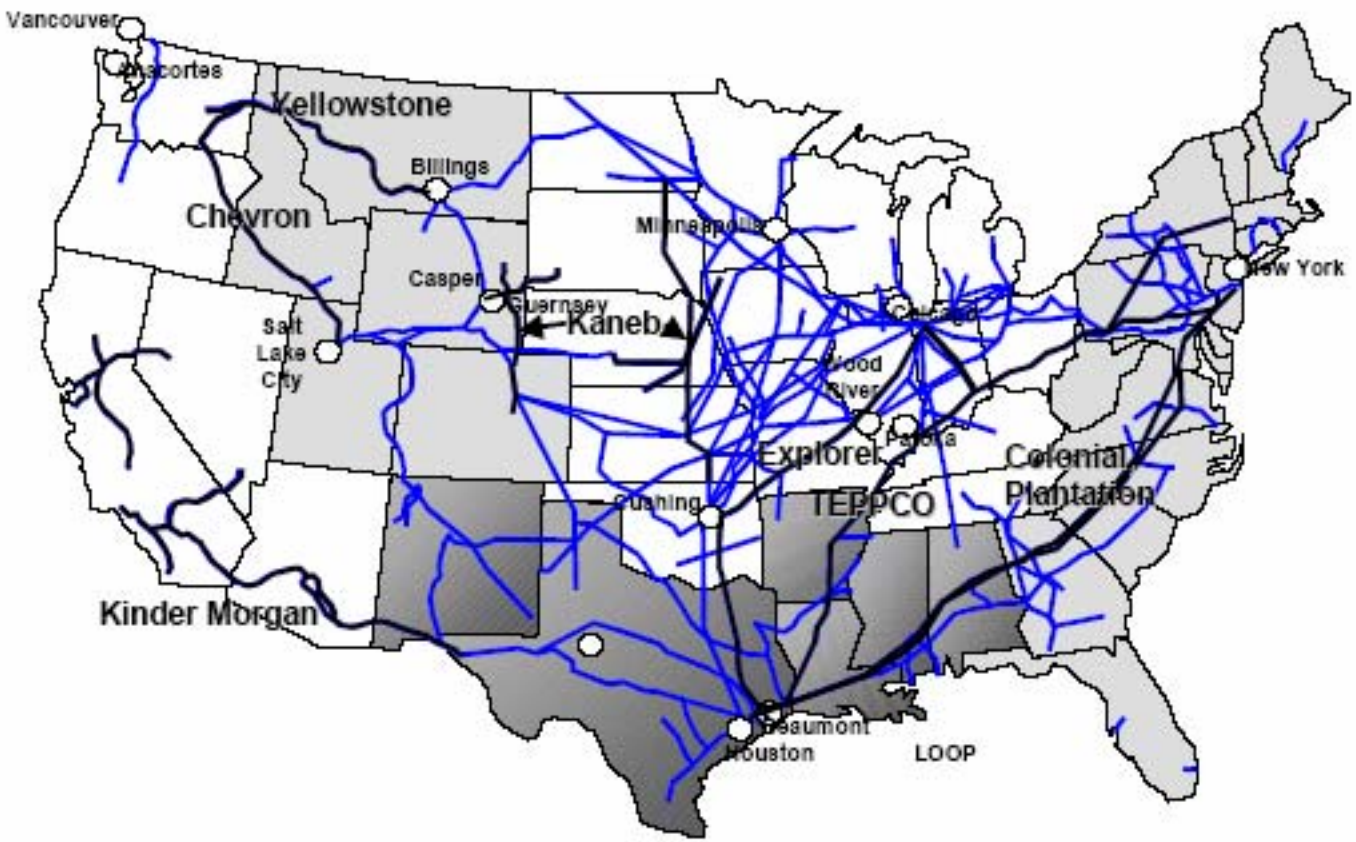
Coming soon to a station near you…

E10
UNLEADED
With 10% Ethanol

E10
UNLEADED
WITH 10% ETHANOL

MTBE is generally blended with gasoline at refineries and distributed by pipeline.

Petroleum Pipelines



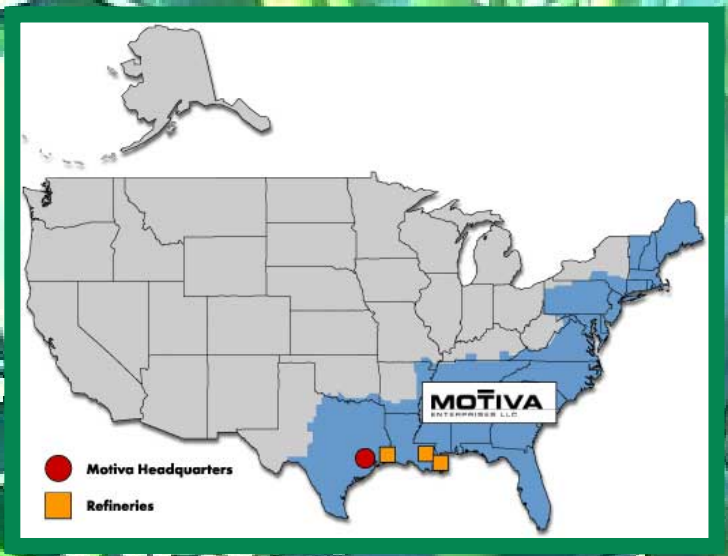
www.aopl.org/news/2003/ How%20Oil%20Pipelines%20Make%20the%20Market%20Work.pdf

What's Different about Ethanol?

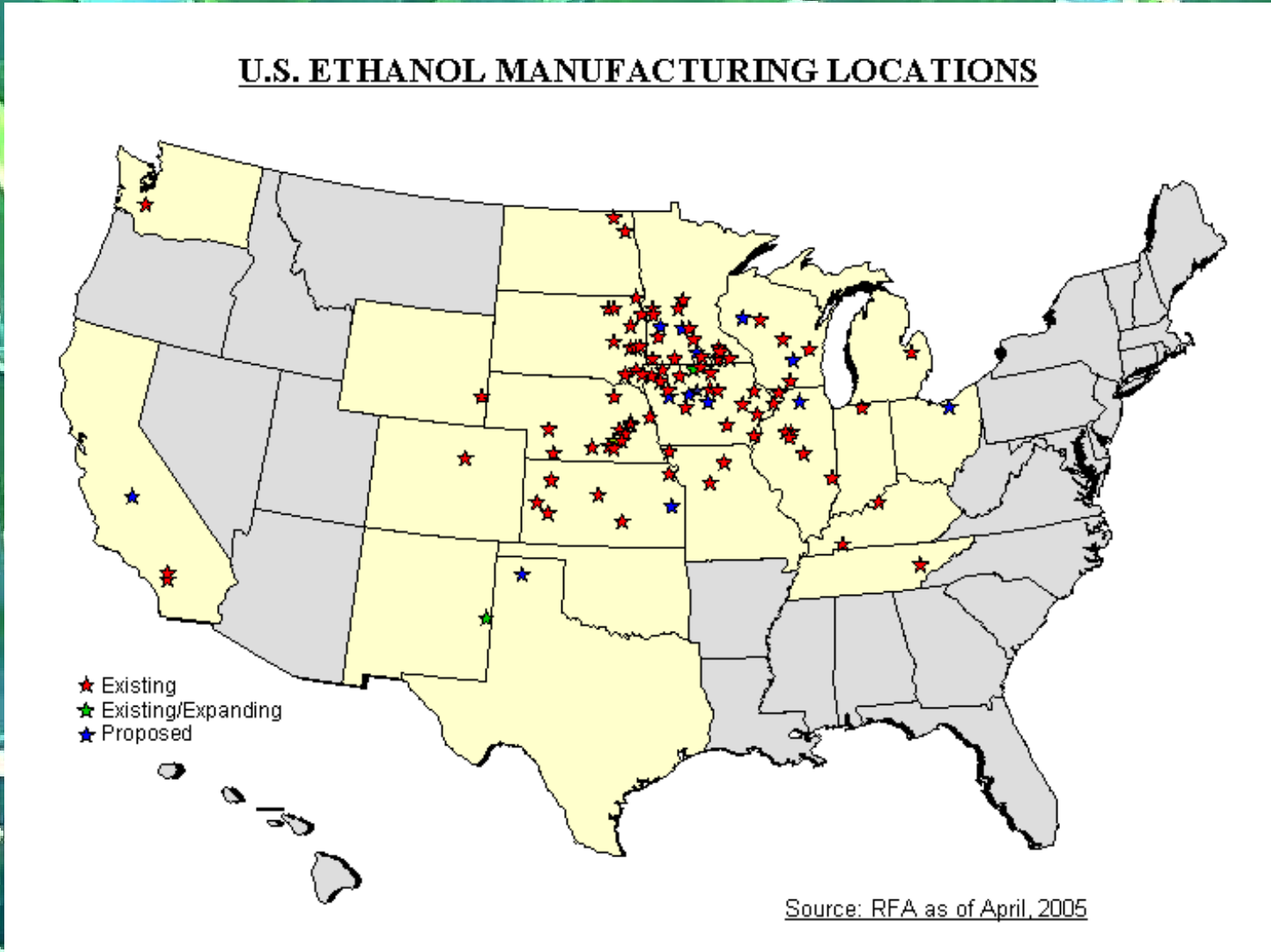
- Ethanol has a tendency to separate from gasoline because water will dissolve in the ethanol
- Therefore ethanol is typically blended into the gasoline at the distribution terminal, immediately before leaving the terminal for the gasoline station.

Blending Ethanol

- Approximately 155 oil refineries in the US (API)
- Example – Motiva has 3 US refineries and many terminals – each terminal would need storage and blending facilities

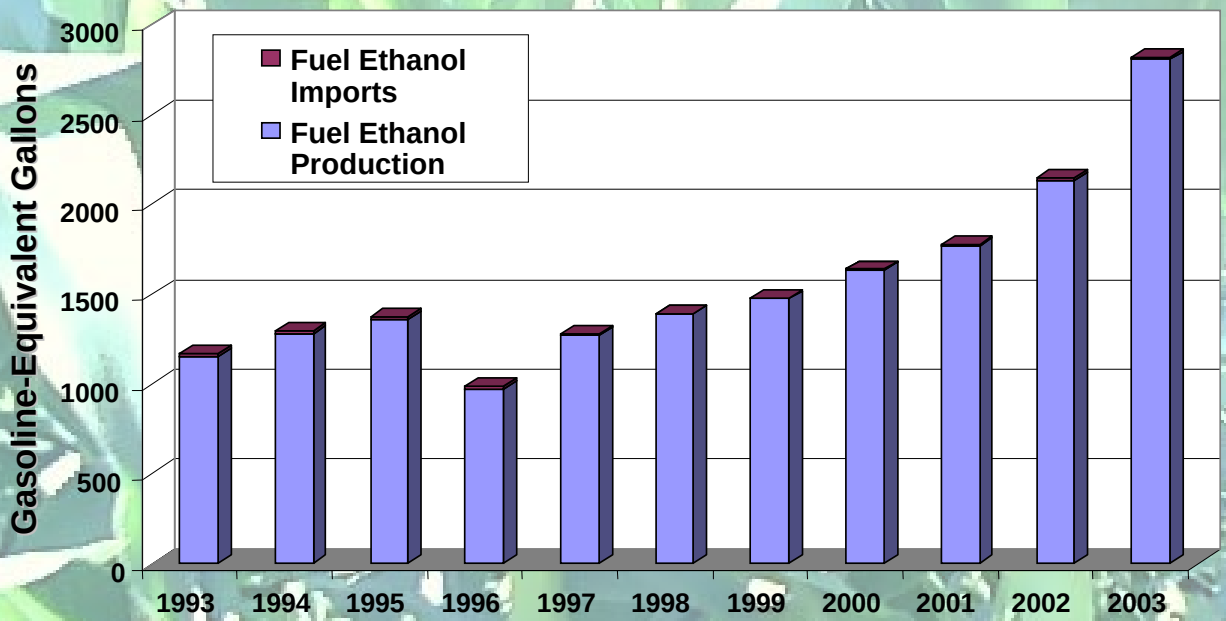


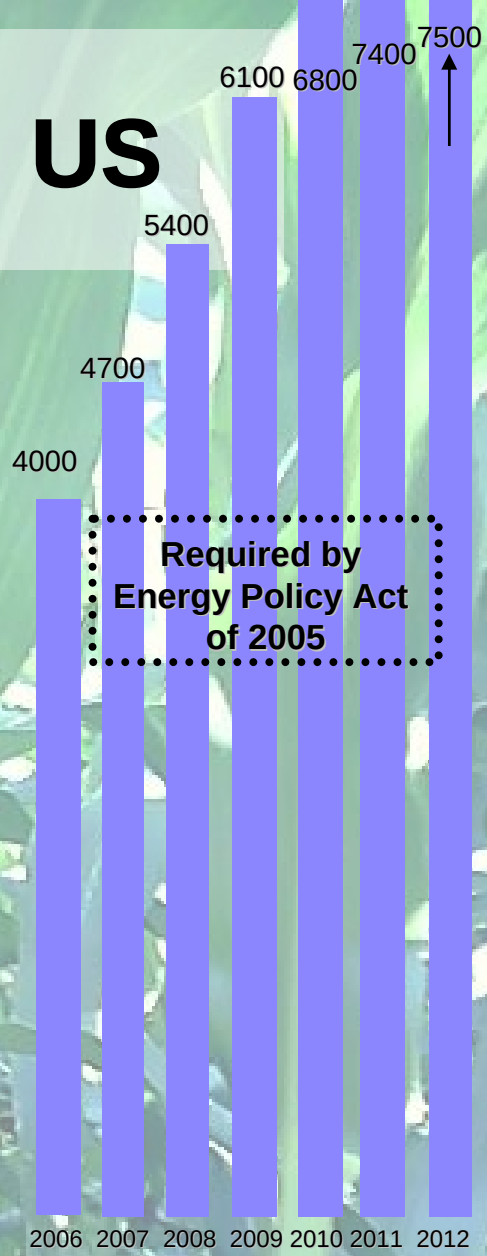
Ethanol Plants



Refineries in EPA Region 3

Fuel Ethanol Usage in the US





Transportation Energy Data Book, 2004

Ethanol Production

As of 10/18/05:

- 97 ethanol plants operational, with a capacity of producing 4175 million gallons per year
- 23 plants under construction, with a planned production capacity of 1151 million gallons per year.

U.S. Fuel Ethanol Industry Plants and Production Capacity

- Total Current Capacity 4381.4
- Total Under Construction/Expansions 2101.0
- Total Capacity 6482.4

(Millions of gallons per year)

Updated February 2006
http://www.ethanolrfa.org/industry/locations/

Credits/Tariffs

- 51 cents per gallon tax credit for blending 10% ethanol into gasoline
- Imports of ethanol into US subject to 2.5% ad valorem tariff and second duty of 54 cents per gallon
- US will allow 24 Caribbean Basin countries to ship up to 269 million gallons to US market this year duty free, but ethanol exports from the region are expected to amount to only 80 million gallons

Ethanol Prices

As of March 12, 2006…

- According to AAA, ethanol demand nationwide increased to 13 million gallons per day in December – 1.2 million gallons more per day than the U.S. daily production
- Ethanol futures for April are selling on the Chicago Merchantile Exchange for $2.47 per gallon, while gasoline futures on the New York Merchantile exchange are $1.66/gallon

Outline

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- Ethanol and the environment……

The regulations…

"……The material used in the construction and/or lining of the UST system must be compatible with the product stored……"

E10 Compatibility Issues

Fiberglass Tanks

- **Owens-Corning**
  - **Pre-1981 tanks not compatible with ethanol**
  - **1981-1990 - single and double wall tanks UL approved up to E10**
  - **1990-1995 – Up to E100 UL approved for double wall tanks only**
- **Fluid Containment (formerly OC)**
  - **1990-1995 – up to E100 approved for double wall tanks only**

E10 Compatibility Issues

Fiberglass Tanks

- **Containment Solutions**
  - **1995-Present – up to E100 UL approved for single and double wall tanks**
- **Xerxes (to be determined – certain years ethanol compatible tanks were only made to order)**
  - **At least 1993 to present – Up to E10 UL approved on single wall tanks and up to E100 UL approved on double wall tanks**

E10 Compatibility Issues

Steel Tanks

- Plasteel (steel tank with plastic outer coating)

  At least 1996 to present – Up to E10 approved for single and double walled tanks

- Permatank (steel with FRP outer coating)

  All their tanks (I.e. Permatank, ACT-100-U, etc.) have included the outer coatings in their UL testing so they are UL approved for ethanol. Waiting for confirmation for Sti-P3 tanks.

- All Highland Steel Tanks with external coatings

  All their tanks (I.e. Titan, ACT-100-U, etc.) have included the outer coatings in their UL testing so they are UL approved for ethanol.

E10 Compatibility Issues

Fiberglass Piping

- **Fiberglass piping manufactured before 1988 not UL approved for ethanol**
- **Fiberglass piping manufactured after 1988 is UL approved for ethanol for double wall systems only**

E10 Compatibility Issues

Flexible Plastic Piping

- **OPW Pisces flexible plastic piping system**
  - **Up to E10 UL approved for ethanol (awaiting information to establish date when this started)**
- **Environ plastic piping system**
  - **Compatible as per manufacturer (verbal). Awaiting written confirmation**

E10 Compatibility Issues

- Flexible Plastic Piping
  - APT flexible plastic piping system
    - Compatible as per manufacturer (verbal). Awaiting written confirmation. Sumps, boots, fittings, etc. are UL tested and approved for up to 50% ethanol only. APT piping is UL tested and approved for up to 100% ethanol (Note: Inner wall only on double walled pipe. If inner wall leaks, the outer wall is meant to contain and transmit the leak to a sump for detection. The outer wall is not designed for prolonged exposure to ethanol blends.). APT's poly-tech ducting pipe is not UL approved for any ethanol blend and is not to be considered secondary containment for any ethanol blend.

Other E10 Compatibility Issues…

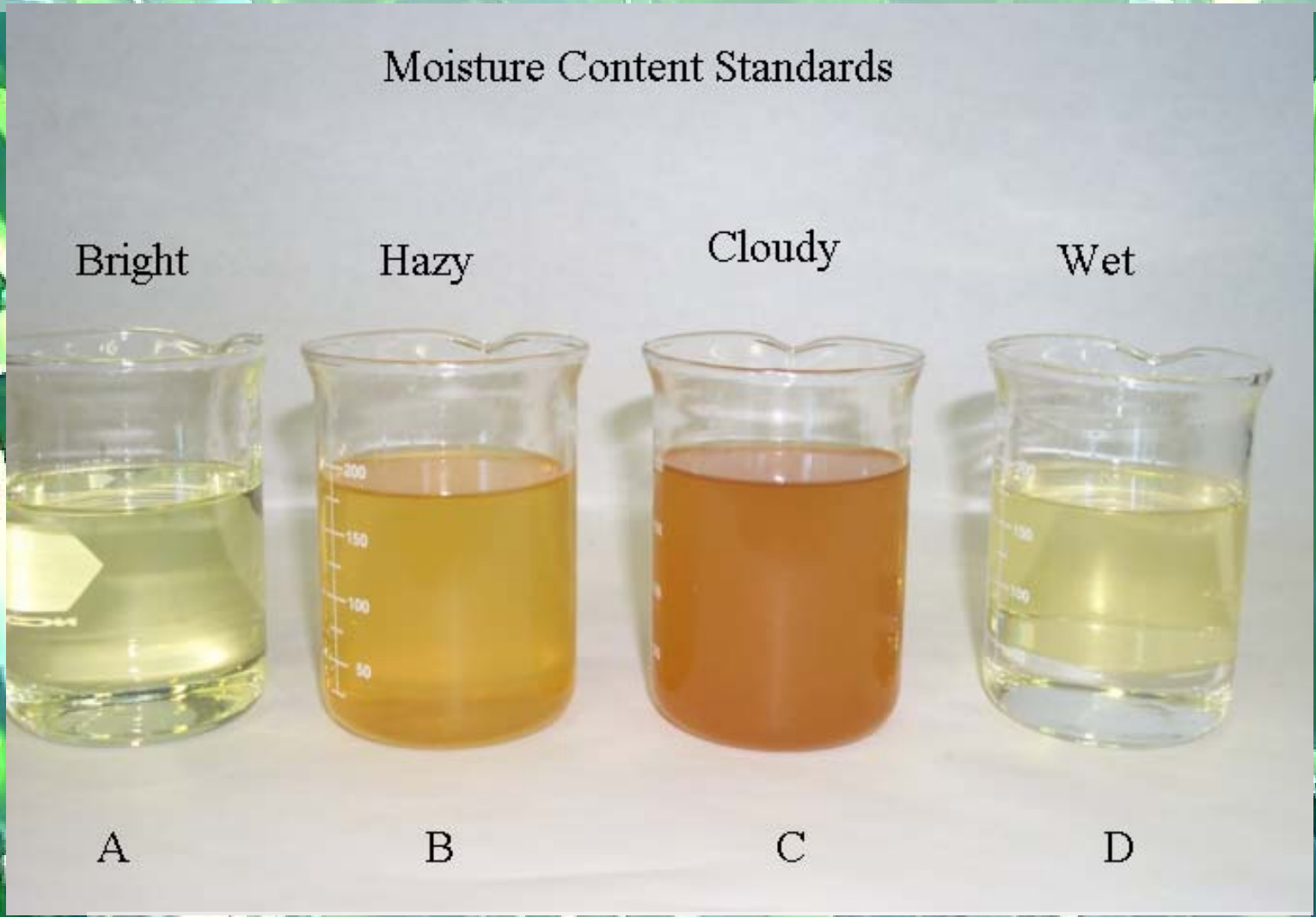
- Leak detection devices may not be compatible with E-blend fuels
- Automatic tank gauges that have capacitance probes will not work with E-blend fuels because these fuels are conductive, and capacitance probes must be used in a nonconductive product
- For magnetorestrictive tank probes, the fuel float must be changed for both chemical compatibility with ethanol and the change in specific gravities between the E-blend and the previous fuel

Delaware's Preparation for the Coming of Ethanol …

- Recommendation that owner/operator check compatibility of UST system components
- Tank cleaning to remove deposits, sludge, rust and scaling
- Filters – designed to remove water from gasoline
- Water detection paste specifically for ethanol blends
- Take care of water infiltration problems

Particulates in Gasoline

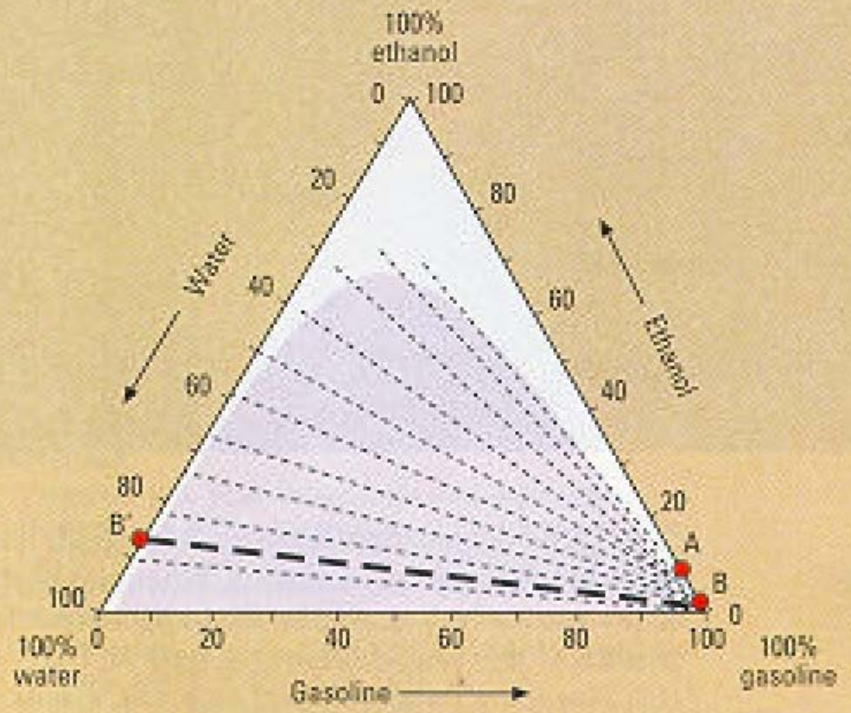
Water in Gasoline



Phase Separation

Ternary phase diagram for gasoline–ethanol–water system at 21 °C

The shaded portion of the diagram represents the region where the total mass fractions separate into two phases. The ends of the dashed (tie) lines indicate the composition of each phase at equilibrium. Axes represent mass percentages.



Source: Adapted from (8) with permission.

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Significance of Properties

▲ Properties	▲ Examples of Significance
– Aqueous Solubility	Rate of migration; bioavailability
– Vapor Pressure	Volatilization from LNAPL; Soil vapor extraction
– Henry's Constant	Volatilization from water; Air stripping
– Octanol/Water Partition Coefficient	Rate of migration; Adsorption Potential
– Biodegradability	Plume size; in-situ biodegradation
– Reactivity	Oxidation potential
– Structure	Biodegradability; oxidation potential

Ethanol Release Scenarios

- Denatured Fuel Ethanol Release
- Ethanol-Blended Gasoline Release
- Small Volume Release of Ethanol-Blended Gasoline

Denatured Fuel Ethanol Release

Will there be a dissolved ethanol plume?

- **Depends of volume of release, depth to groundwater, and soil type**
- **Depending on ethanol to water ratio in the area beneath the release, ethanol concentrations can exceed 10,000 ppm (1% by volume)**

Log K_{oc}

$$R = 1 + \frac{f_{oc} K_{oc} \rho_{bulk}}{\eta}$$

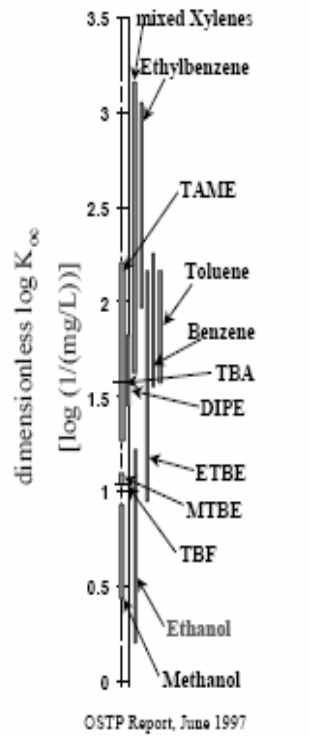
$$R = 1 + \left(\frac{\theta_w}{\theta_a} \frac{1}{H} \right) + \left(\frac{f_{oc} K_{oc} \rho_{bulk}}{\theta_a H} \right)$$

- Increasing Koc increases retardation (R) for constant soil properties

$$\frac{R_{benzene}}{R_{MTBE}} \cong 4.5$$

$$\frac{R_{ethanol}}{R_{MTBE}} \cong 0.25$$

- As R approaches unity, contaminant moves at speed of groundwater



Aqueous Solubility

- **Raoult's Law (holds for low contaminant concentrations)**

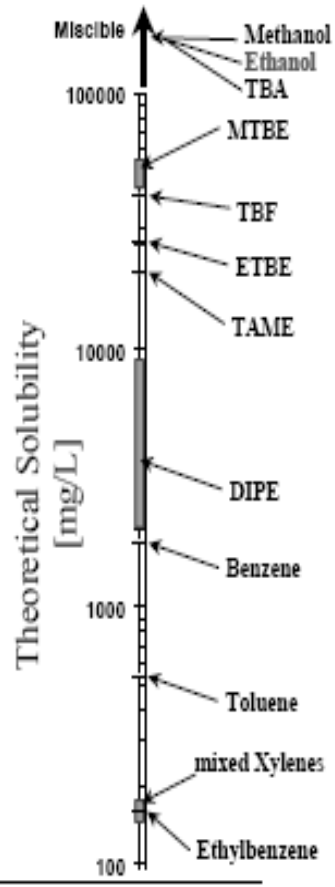
  $C_{gw} = Sol_{theoretical} X_{gasoline}$

  - $C_{MTBE,gw} \cong (48{,}000 \text{ ppm})(11\%) = 5{,}280 \text{ ppm}$
  - $C_{benzene,gw} \cong (1{,}750 \text{ ppm})(1\%) = 17.5 \text{ ppm}$

- **Does not hold for miscible contaminants (e.g. ethanol, TBA, methanol)**

  - $C_{ethanol,gw} \cong \frac{C_{ethanol,gasoline}}{MixingRatio * DilutionRatio}$
  - Actual source area ethanol concentrations higher than MTBE. i.e., <1,000 ppm

- **High solubility (> 10,000 mg/L)**
  - Fast dissolution
  - Lower sorption
  - Potential cosolvency effect



Denatured Fuel Ethanol Release

Will there be an impact on the mobility of nonaqueous phase liquid (NAPL) hydrocarbons, if present before the release?

Potential exists to impact NAPL mobility. Magnitude will depend on volume of release and pre-existing site conditions. Presence of ethanol can reduce interfacial tension which enhances NAPL mobility, which may result in reappearance of NAPL in wells and sumps

Cosolvency of Ethanol

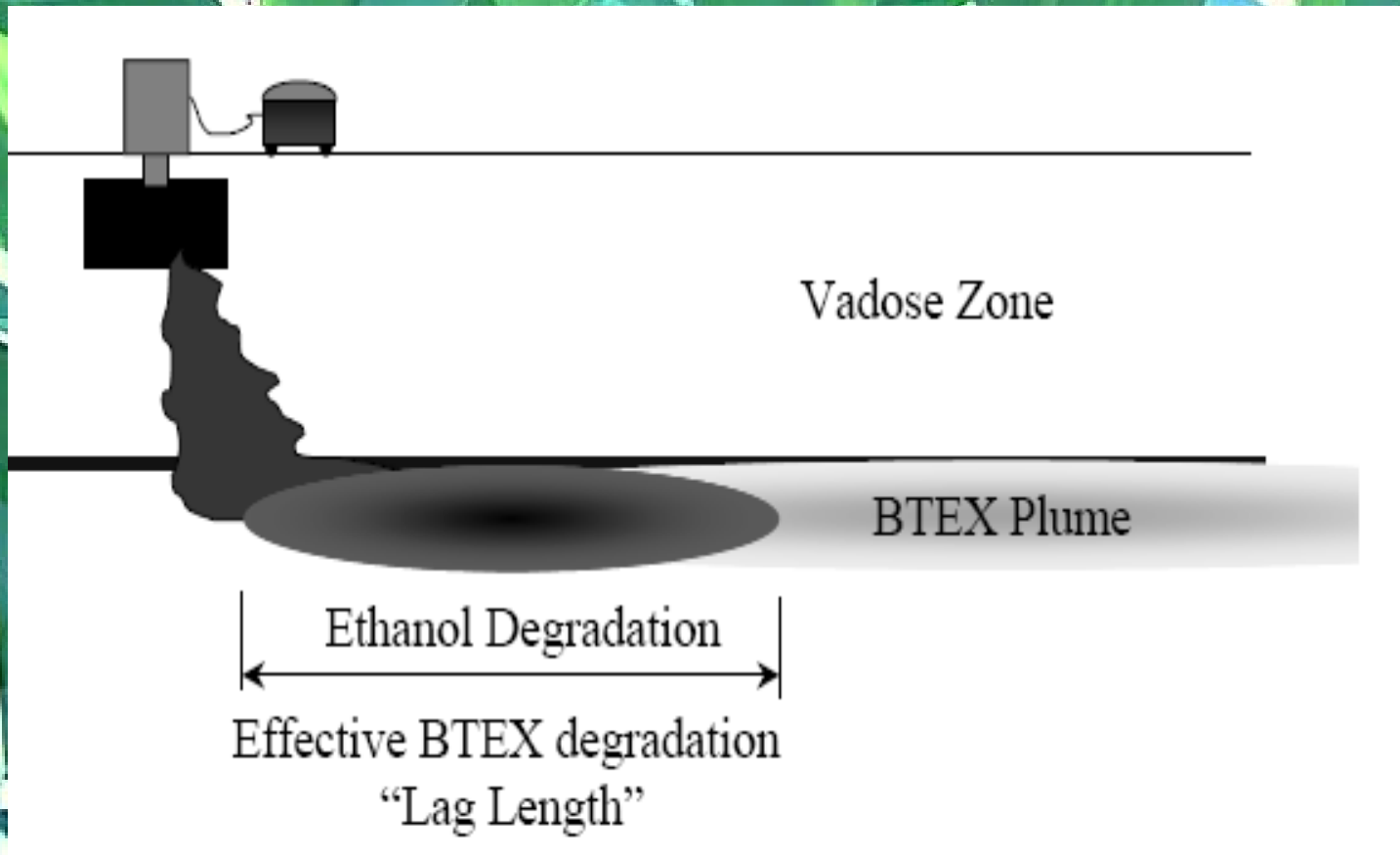
- Dependent on ethanol concentration in groundwater
  - Function of dilution factors
  - Concentration drops with distance from source
- Corseuil (1998) found ethanol concentrations >10,000 ppm will increase BTEX solubility
- 10% Ethanol in gasoline with 5-fold dilution factor results in groundwater concentrations of 20,000 ppm

Denatured Fuel Ethanol Release

Will there be an impact on BTEX plume length?

If the presence of ethanol increases BTEX solubilities. BTEX plume length is also likely to increase. The results of a modeling study suggest that benzene plume length could increase by as much as 150%. Ethanol constitutes a significant demand on oxygen (and other electron acceptors); the presence of ethanol can deplete electron acceptors, retarding BTEX degradation.

Conceptual Model of BTEX Plume Elongation



Denatured Fuel Ethanol Release

Can methane be a problem?

Ethanol biodegradation can produce elevated methane concentrations in groundwater and vapor phases that may persist for long periods. Thus, methane should be considered in groundwater sampling periods for monitoring wells in the vicinity of a denatured fuel ethanol release.

Ethanol-Blended Gasoline Release

Will there be a dissolved ethanol plume?

- **Depends of volume of release, depth to groundwater, and soil type**
- **Depending on ethanol to water ratio in the area beneath the release, ethanol concentrations can exceed 10,000 ppm (1% by volume)**

Summary of Literature Biodegradation Rates

Compound	Anaerobic Pseudo First Order Rate Constant	
	Electron Acceptor	Range of Rates (day^{-1})
Ethanol	NO_3^-	0.53 (1*)
	Fe^{3+}	0.17 (1*)
	SO_4^{-2}	0.1 (1*)
MTBE	Anaerobic Range	0.0062 - 0.00096 (3**)
Benzene	NO_3^-	0-0.045 (2*)
	Fe^{3+}	0-0.024 (2*)
	SO_4^{-2}	0-0.047 (2*)
	Methanogenic	0-0.052 (2*)
	General	0.0062-0.00096 (3**)

1) Estimated from Corseuil et. al., 1997; 2) Aronson et. al., 1997; 3) USGS, 1998; 4) Barker et. al., 1998;
*Determined in a laboratory;
** Estimated from first principles.

Ethanol Effect on BTEX Degradation

Corseuil et al., 1998

- Ethanol retarded BTEX aerobic biodegradation in laboratory; rapidly reduced oxygen concentrations
- No benzene degradation observed under anaerobic conditions
- Ethanol slowed toluene anaerobic degradation

Hunt et al., 1997

- Degradation of toluene completely inhibited until all the ethanol was degraded (aquifer microcosm)

Barker et al., 1990

- Methanol inhibits degradation of BTEX due to initial toxic levels; later due to depletion of electron acceptors

BTEX Plume Elongation: Possible Causes

- Increase in aqueous solubility of BTEX due to high ethanol concentration in water
- Preferential utilization of ethanol
- Larger volume of groundwater under anaerobic conditions; shift to methanogenic redox conditions

Ethanol-Blended Gasoline Release

Will there be an impact on benzene, toluene, ethylbenzene and xylene (BTEX) concentrations?

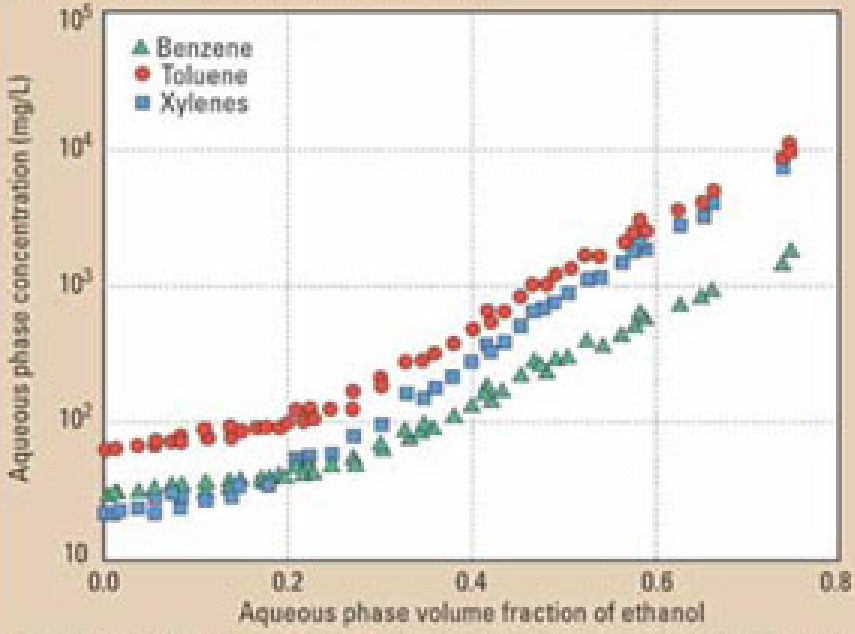
If the ethanol concentration exceeds 10,000 ppm, there can be an increase in BTEX concentrations.

Cosolvency

FIGURE 1

BTX and ethanol concentrations track logarithmically

Concentrations of BTX in an aqueous phase equilibrated with gasoline show a substantial increase in the effective solubility of these constituents with increasing concentrations of ethanol.



Source: Reprinted from *Journal of Contaminant Hydrology, 34*, S. E. Heerman, p. 377, 1998, with permission from Elsevier Science.

Ethanol-Blended Gasoline Release

Will there be an impact on (BTEX) plume length?

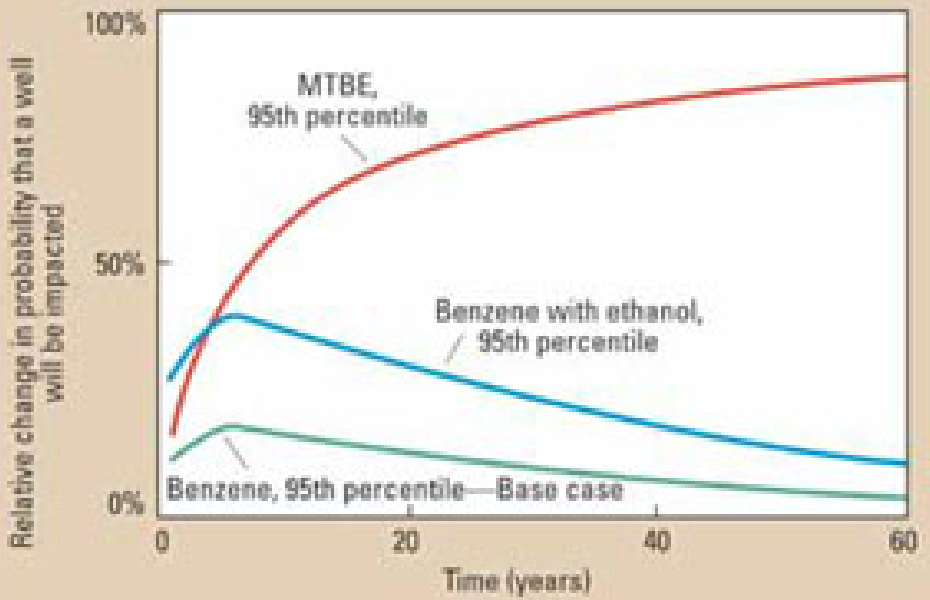
- Field study by Ruiz-Aguilar (2003) showed that presence of ethanol resulted in mean plume lengths that were 36% longer (70 feet); this difference was statistically significant.
- Mean toluene plume length was only slightly longer in the presence of ethanol (17% longer or 26 feet); this difference was not statistically significant.
- Study suggests that presence of ethanol could inhibit benzene biodegradation to a greater extent than toluene, but should not hinder application of natural attenuation as a remediation strategy.

Plume Length

FIGURE 2

Predicted contaminant plume length

Results of Monte Carlo simulations illustrate relative changes in the probability that a drinking water well will be affected following a spill of nonoxygenated gasoline (base case), ethanol-blended gasoline, and MTBE-blended reformulated gasoline. Analysis details are presented in (*4*).



Source: Adapted from reference (*4*).

Small Volume Release of Ethanol-Blended Gasoline

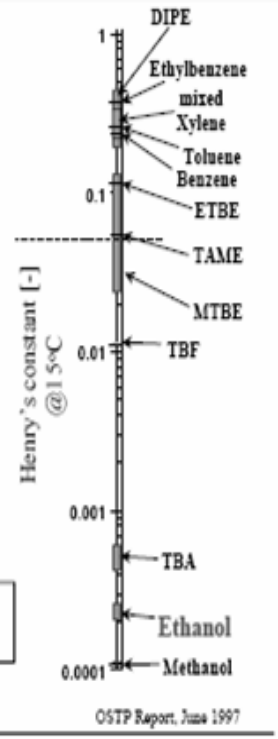
Small volume releases of ethanol-blended gasoline may be vapor or NAPL. In case of NAPL release, the volume is assumed not sufficient to contact groundwater.

Will ethanol impact groundwater?

- Field experiment simulating finite source showed no impacts to groundwater for a release more than one meter above the water table. If considerable infiltration (>0.5 cm/day) is applied, ethanol was detected in groundwater.
- Modeling results for steady state release (0.04 gal/day) indicate biodegradation likely to limit groundwater impacts. Actual infiltration rates associated with individual precipitation events could effect ethanol transport more than was demonstrated in study.

Henry's Law Constant (H)

- **Ethanol Henry's Constant = 0.000252**
- **Henry's Constant < 0.05**
  - Volatilization from surface waters unlikely
  - Off-gassing from groundwater unlikely
  - Vapor phase retardation will be high



OSTP Report, June 1997

H [(atm-m³)/(mole)] / RT = H[-]

R = 0.08206 [(atm-m³)/(mole-K)]; T = [°K] = °C + 273

Small Volume Release of Ethanol-Blended Gasoline

Will the presence of ethanol allow benzene vapor/leachate to impact goundwater?

Field experiment by Dakhel, et al. (2003) suggests any benzene impacts to groundwater would be localized and short-lived.

Modeling results for steady state release (0.04 gal/day) indicate that even in the presence of ethanol, biodegradation can significantly limit benzene transport to groundwater. Potential for benzene impacts to groundwater increases in fine-grained soils, because of limitations on oxygen availability.

Small Volume Release of Ethanol-Blended Gasoline

Is soil vapor monitoring needed?

No, the small volume releases detected in the Young and Golding (2002) study may go undetected by conventional soil vapor monitoring methods. However, there may be reasons to conduct conventional soil vapor monitoring for a large volume release of ethanol-blended gasoline.

Results of field and monitoring studies corroborate each other; ethanol and benzene impacts to groundwater associated with these small volume releases are not expected to be significant.

Summary

- Ethanol is miscible in water; does not adsorb or volatize – can result in high potential source area concentrations
- Ethanol will rapidly biodegrade following release to the environment – can result in rapid depletion of electron acceptors and suspected interference with hydrocarbon biodegradation
- Ethanol is preferentially biodegraded compared to other gasoline constituents (e.g., benzene, MTBE)

Wave of the future...?