Phase Behavior of Ethanol Biofuels

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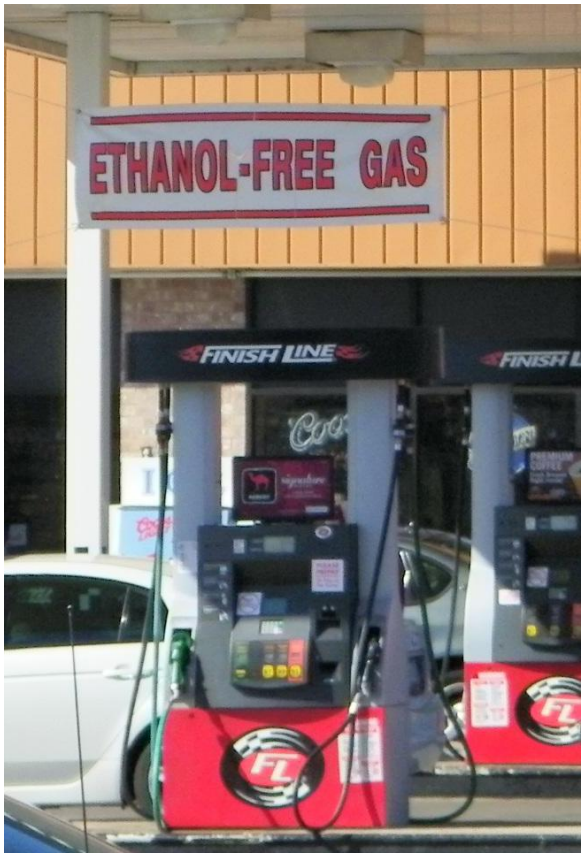
Outline

- Historical Usage of Ethanol
- Phase behavior of ethanol/gasoline blends
- Composition of Fuel Ethanol Samples
- Field Examples: Land and Water

Alternate Marketing Strategies



Ethanol Usage in Gasoline

- Historic
  - Known as an octane booster since the 1920s
  - Used in upper mid west at least during 90s
  - Oxygenates required in reformulated gasoline 1995-2006
  - Increased usage because of MTBE bans after 2000
- Mandated
  - Energy Policy Act 2005
  - Energy Independence and Security Act of 2007
  - Some state rules (Florida, Hawaii, Minnesota, Missouri, Oregon, Washington)

Terminology

- Following **ASTM D 4806 – 08a Standard Specification for Denatured Fuel Ethanol for Blending with Gasolines for Use as Automotive Spark-Ignition Engine Fuel.**

  - ***Denaturant*** -- a material added to fuel ethanol to make it unsuitable for beverage use, but not for unsuitable for automotive use.
  - ***Fuel Ethanol*** -- ethanol with impurities common to its production including water but not denaturants.
  - ***Denatured Fuel Ethanol*** – fuel ethanol made unfit for beverage use by the addition of denaturants.
  - ***Higher Molecular Weight Alcohols*** – aliphatic alcohols of general formula CnH2n+1OH with n from 3 to 8.

Ethanol and Gasoline Blends

- E100: Non-denatured fuel ethanol
- E95: Denatured fuel ethanol
  - ASTM 4806
    - Min 92% ethanol
    - Denaturants: 2% to 5%
      - Natural gasoline
      - Gasoline components
      - Unleaded gasoline
- E85: “Flex Fuel” ASTM D 5798
  - Three ethanol classes: 70%, 74%, 79%
- E10: “may contain 10% ethanol”
  - ~90% gasoline
- “E00” “ethanol free gasoline”

Overview from producers to consumers

- Producers
  - Distill to 190 proof
  - Dry to 200 proof (molecular sieve)
  - Denature
- Transporters
  - Not to go in U.S. pipelines (exception for Central Florida)
  - Therefore: barges, trucks, trains
- Distributers (from terminals)
  - Separate Ethanol Tank
  - Splash Blending
    - Add gasoline blending component (“RBOB”), ethanol, and additives let mix in tanker as delivery is made
- Users
  - Compatible Tanks, Pipes, Dispensers?
  - Water Bottoms?
  - Auto issues?

A Word on Taxes

- 2008 Food, Conservation, and Energy Act (Public Law 110-123)
  - January 1, 2009
  - full ethanol production credit only if denaturant content < 2%.
- U.S. Internal Revenue Service
  - temporarily allowing credits for denaturant(s) < 2.5% of the fuel ethanol
  - Notice 2009-06

Denaturants

- ASTM also specifies **prohibited** denaturants:
  - (adverse effects on fuel stability, automotive engines, and fuel systems)
  - hydrocarbons with an end boiling point above 225 ^{o}C,
  - methanol not meeting ASTM D1152,
  - pyrroles, turpentine, ketones, and tars.

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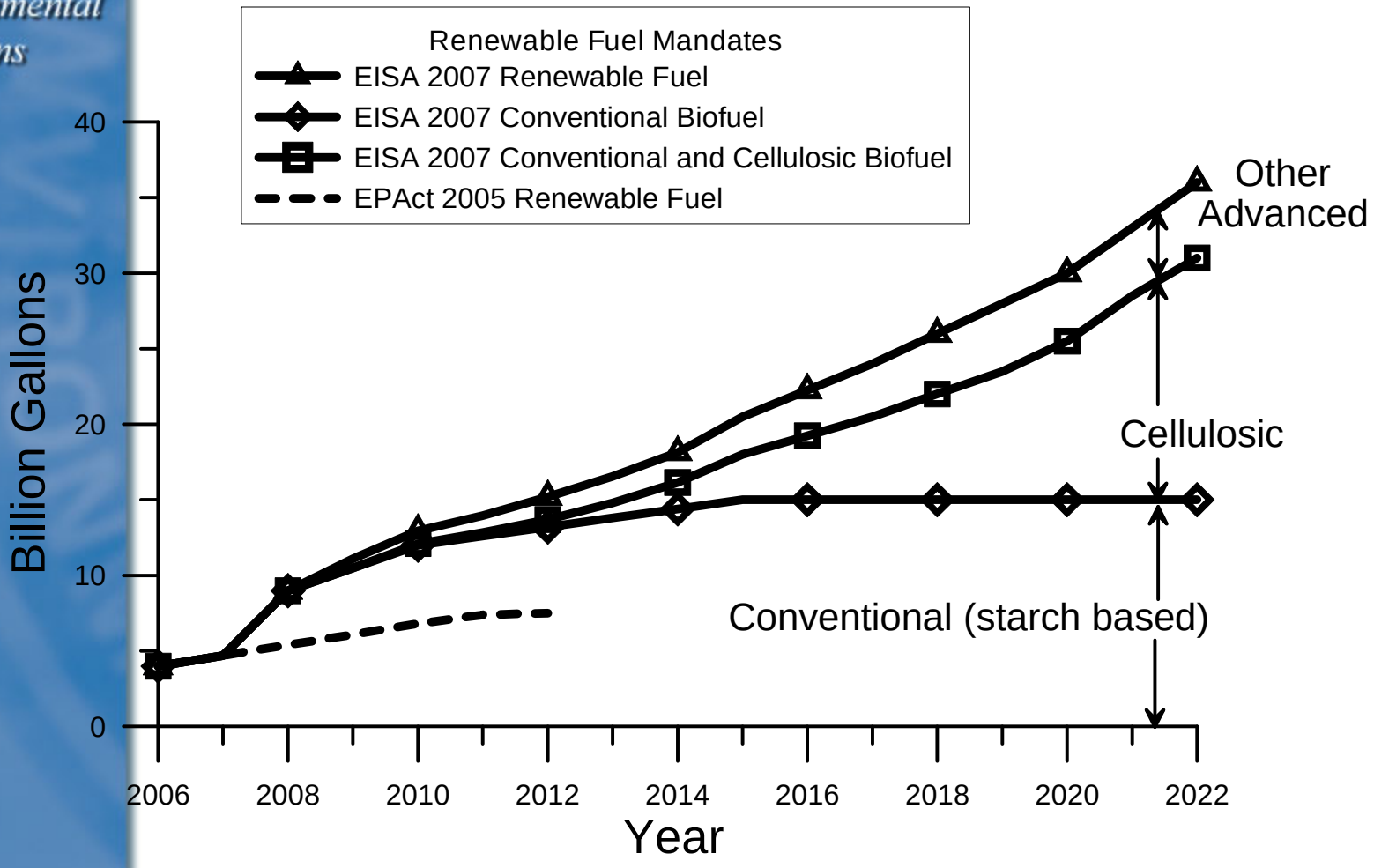
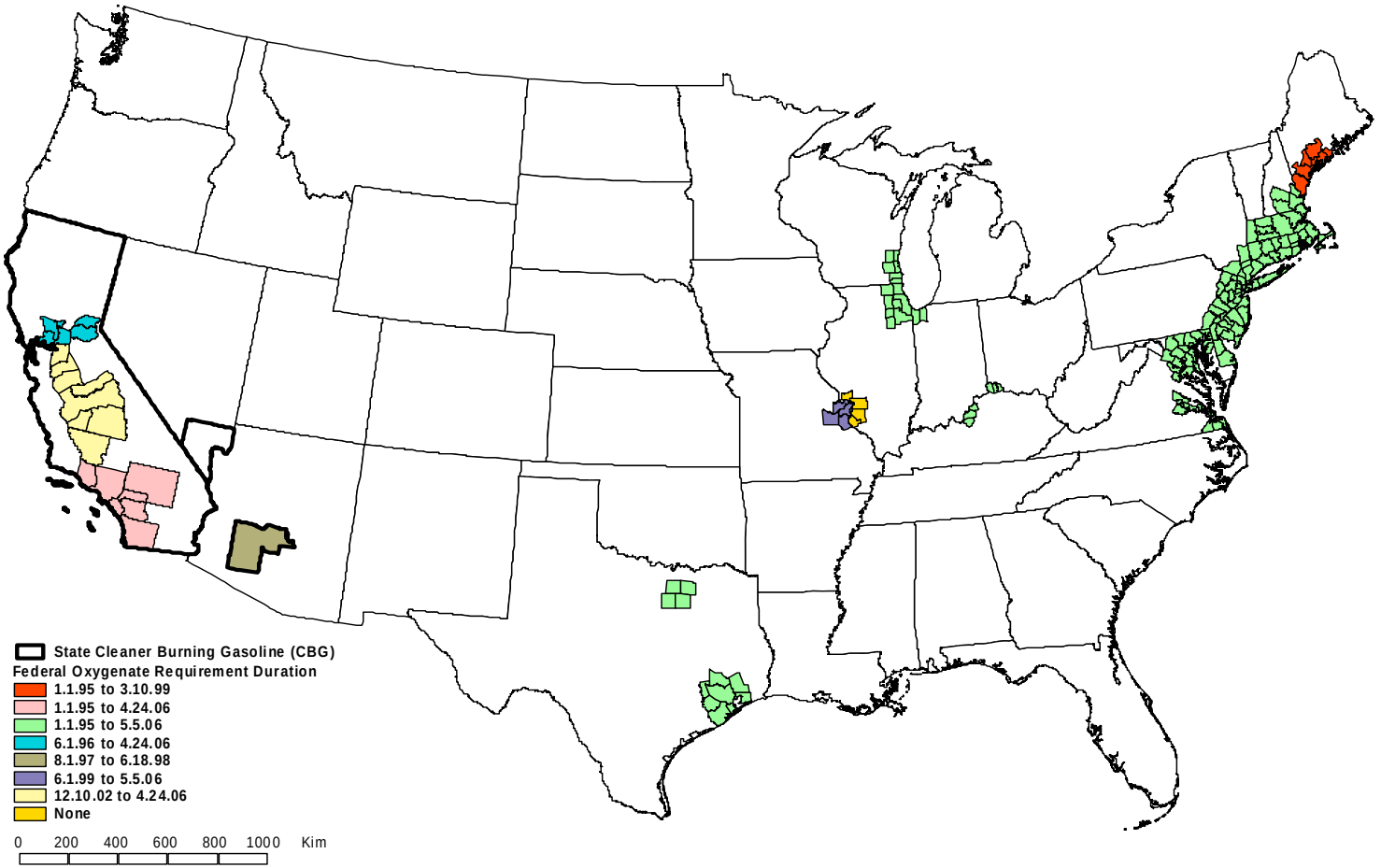
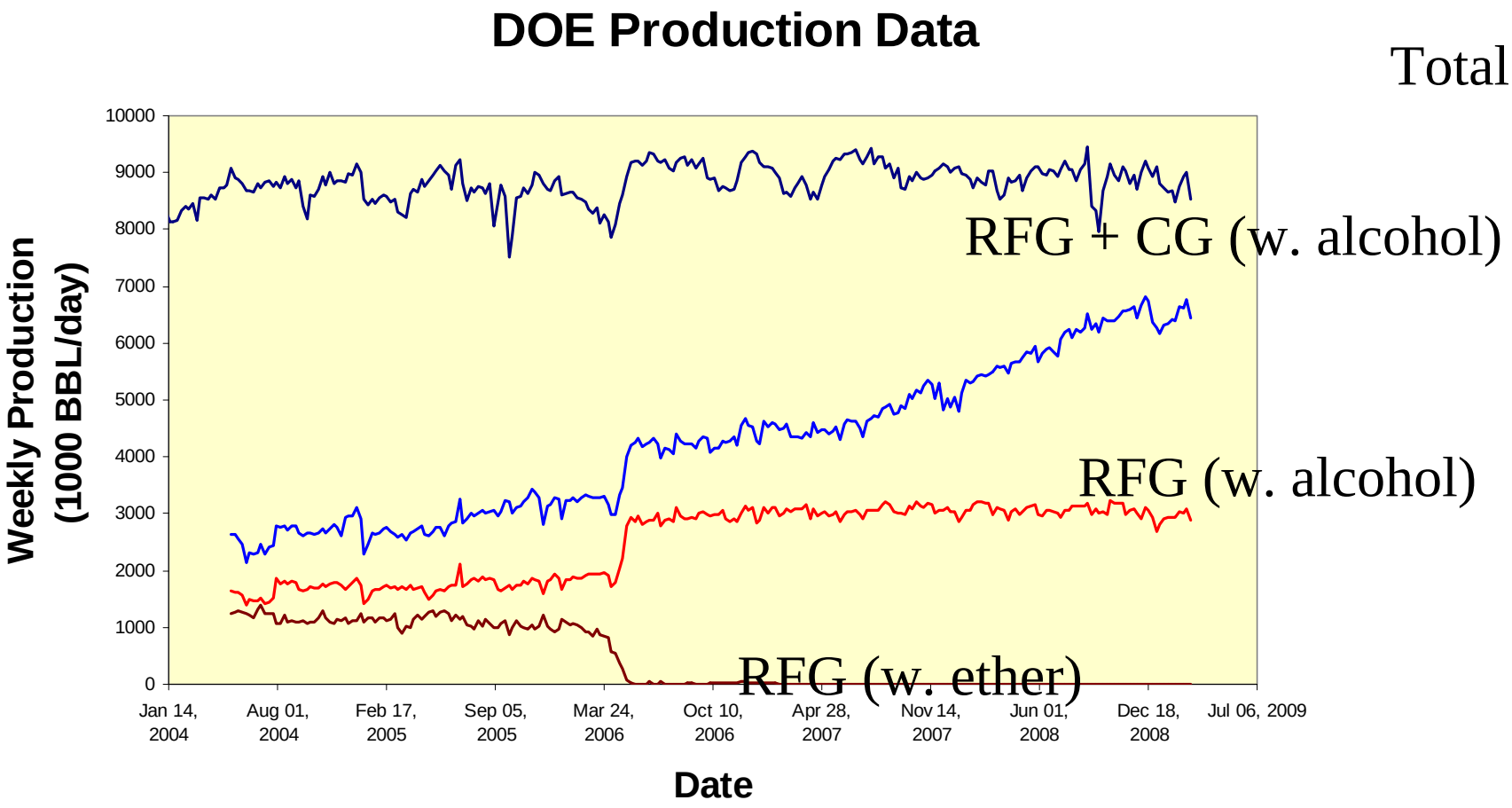


Terminology

- Following the **Code of Federal Regulations (40 CFR) Part 80 – Regulation of Fuels and Fuel Additives**:
  - ***Reformulated Gasoline (RFG)*** is any gasoline whose formulation has been certified under 40 CFR § 80.40 and which meets each of the standards and requirements prescribed under 40 CFR § 80.41.
    - From 1995 until 2006, RFG was required to contain 2 % by weight oxygen-containing compounds (“oxygenates”)
    - *Benzene < 1%*
  - ***Conventional Gasoline (CG)*** is any gasoline which has not been certified under 40 CFR § 80.40.
  - ***Oxygenated Gasoline (OG)*** is any gasoline which contains a measurable amount of oxygenate.

Reformulated and Conventional Gasoline in the US




DOE Production Data
Total
RFG + CG (w. alcohol)
RFG (w. alcohol)
RFG (w. ether)
Weekly Production
(1000 BBL/day)
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
Jan 14, 2004
Aug 01, 2004
Feb 17, 2005
Sep 05, 2005
Mar 24, 2006
Oct 10, 2006
Apr 28, 2007
Nov 14, 2007
Jun 01, 2008
Dec 18, 2008
Jul 06, 2009
Date

Phase Behavior

- Phase Separation
  - Gasoline adsorbs water up to a point where phase separation occurs
    - Gasoline ~0.1%
- Volume Changes
  - Ethanol/E85 volume reduction with water addition

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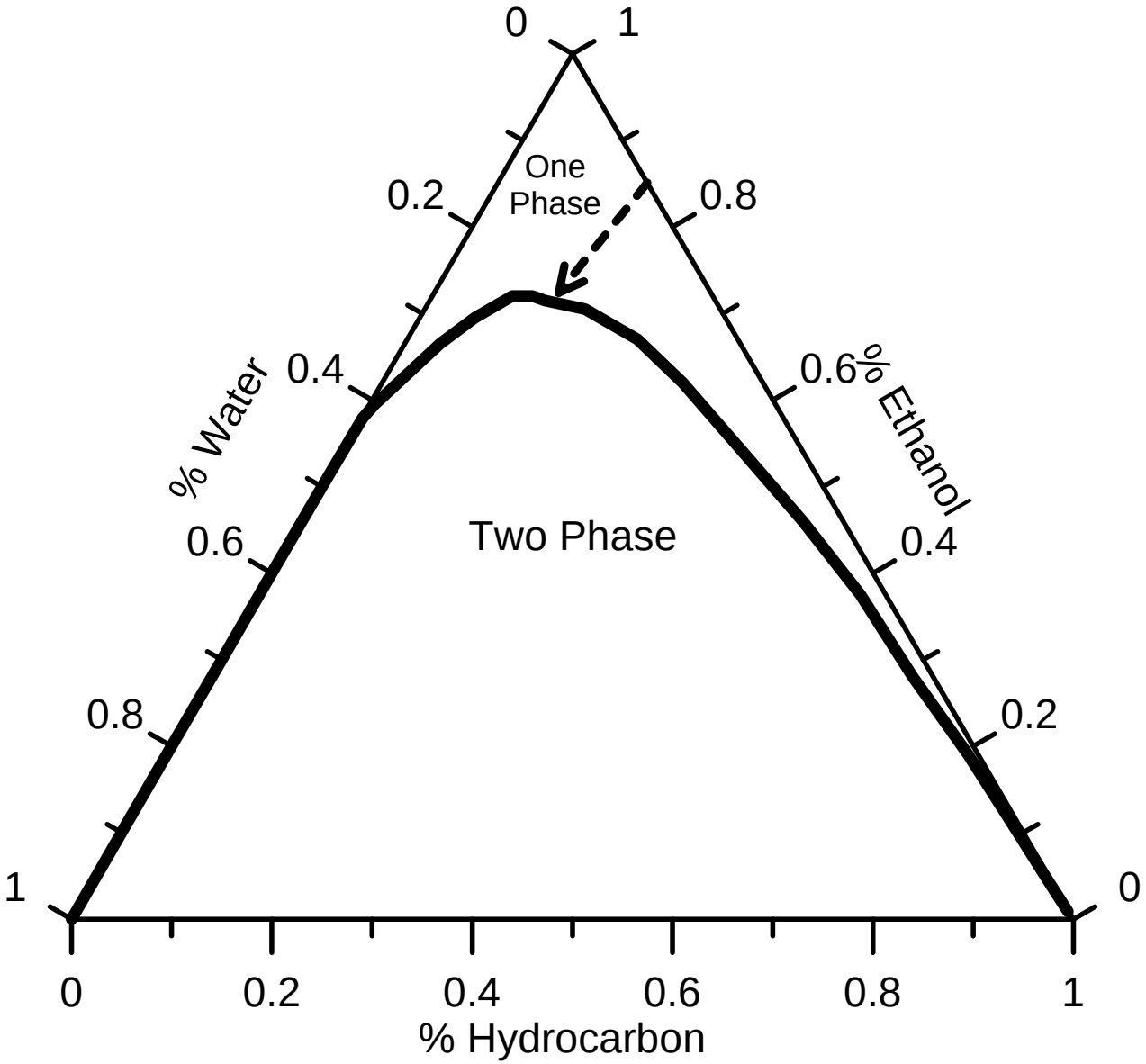

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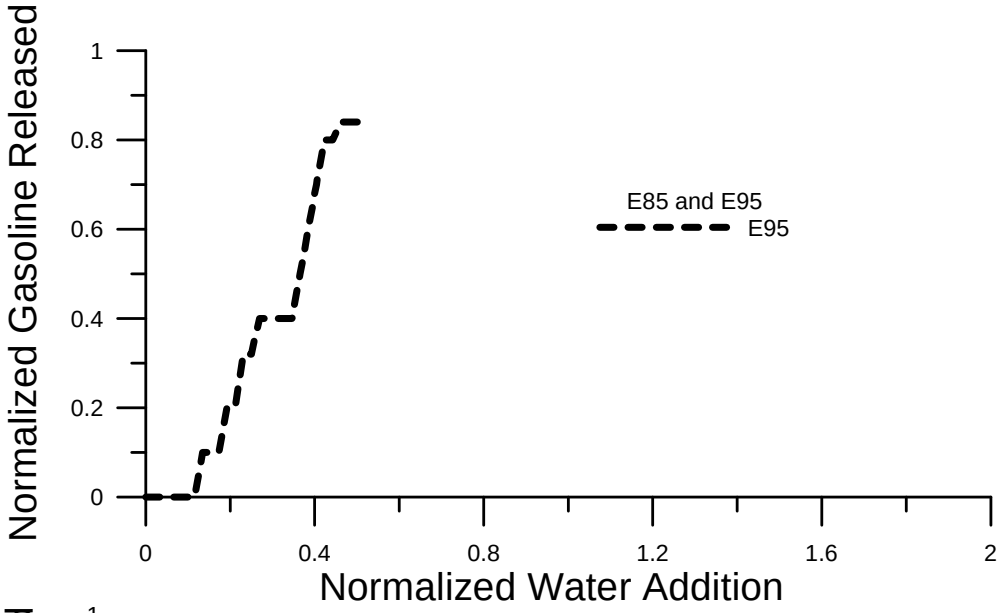

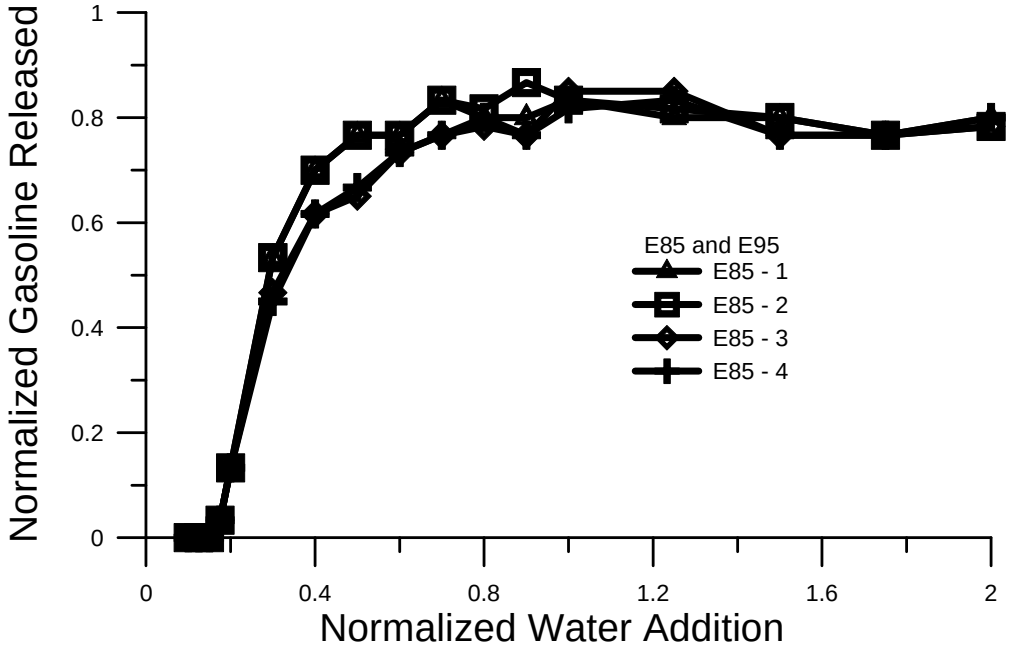

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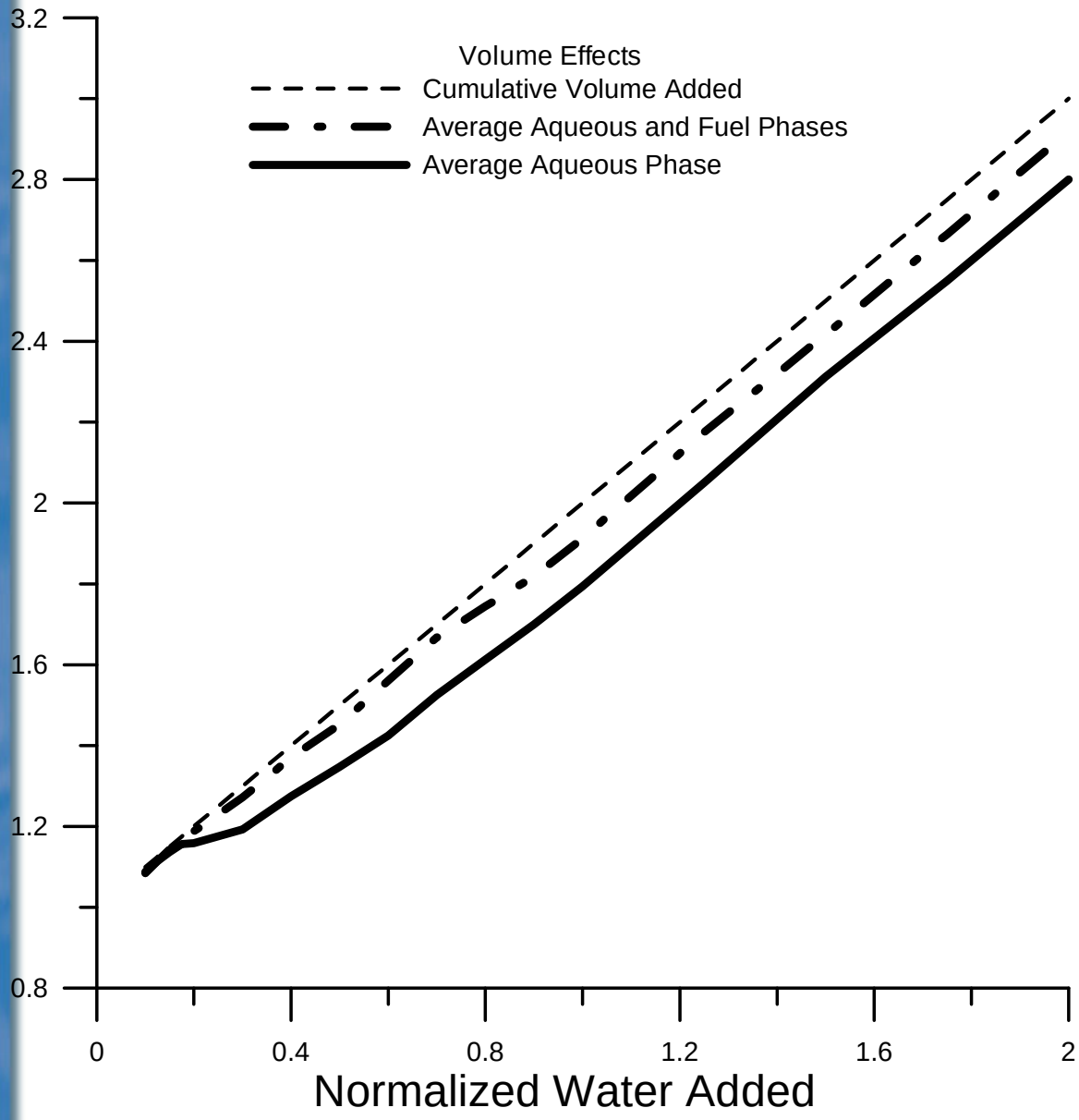
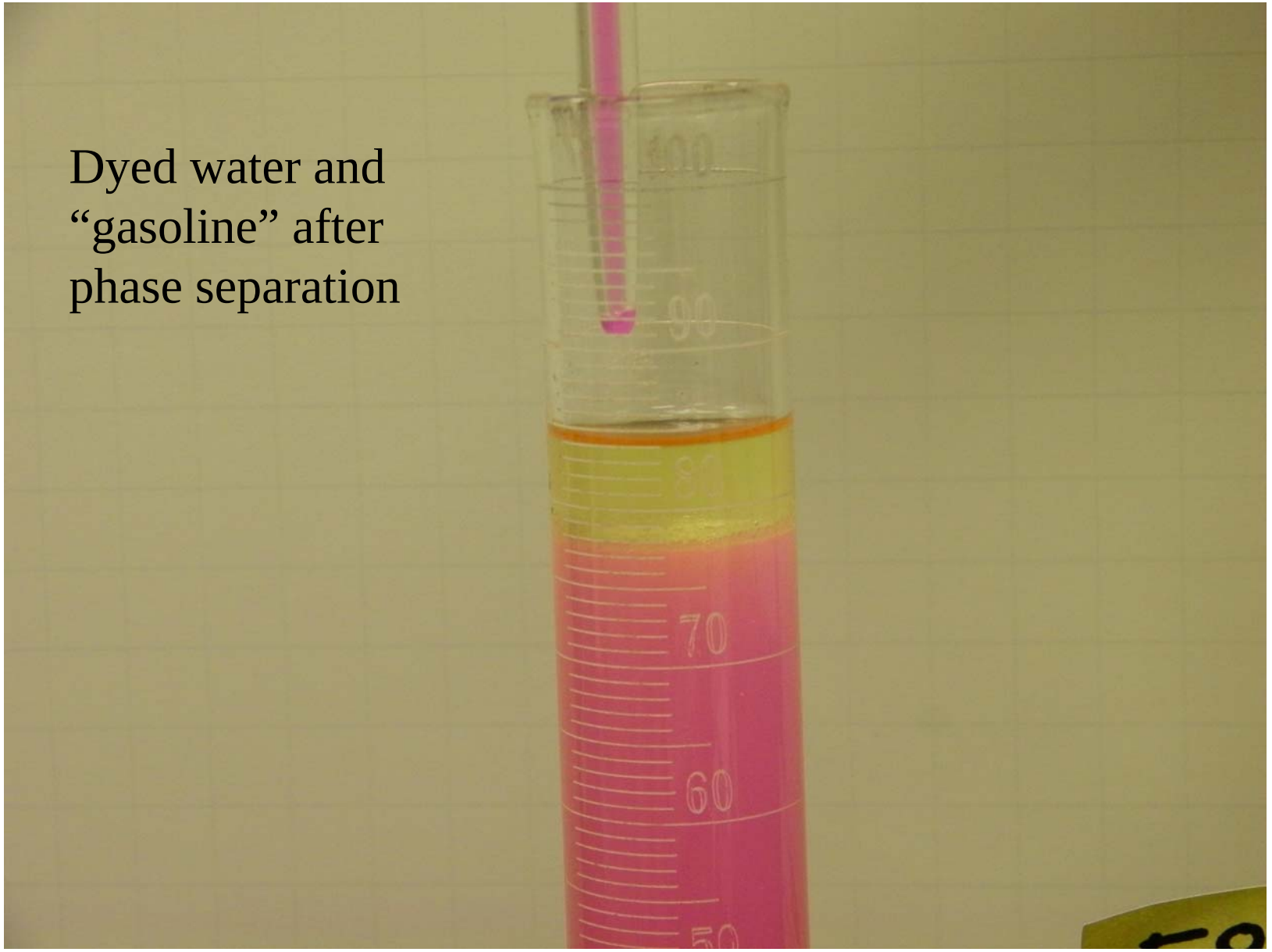


Videos

- Dyed Water Added to E85
  - Initially water is absorbed by E85
  - Initially no increase in volume
  - E85 breaks into “gasoline” and aqueous/ethanol phase
- E85 added to water
  - Quiescent E85 jets into water
  - Cloudy surfactant layer over clear water
  - Gasoline accumulates on surface
  - In moving system gasoline “rides” surface

Dyed water and “gasoline” after phase separation



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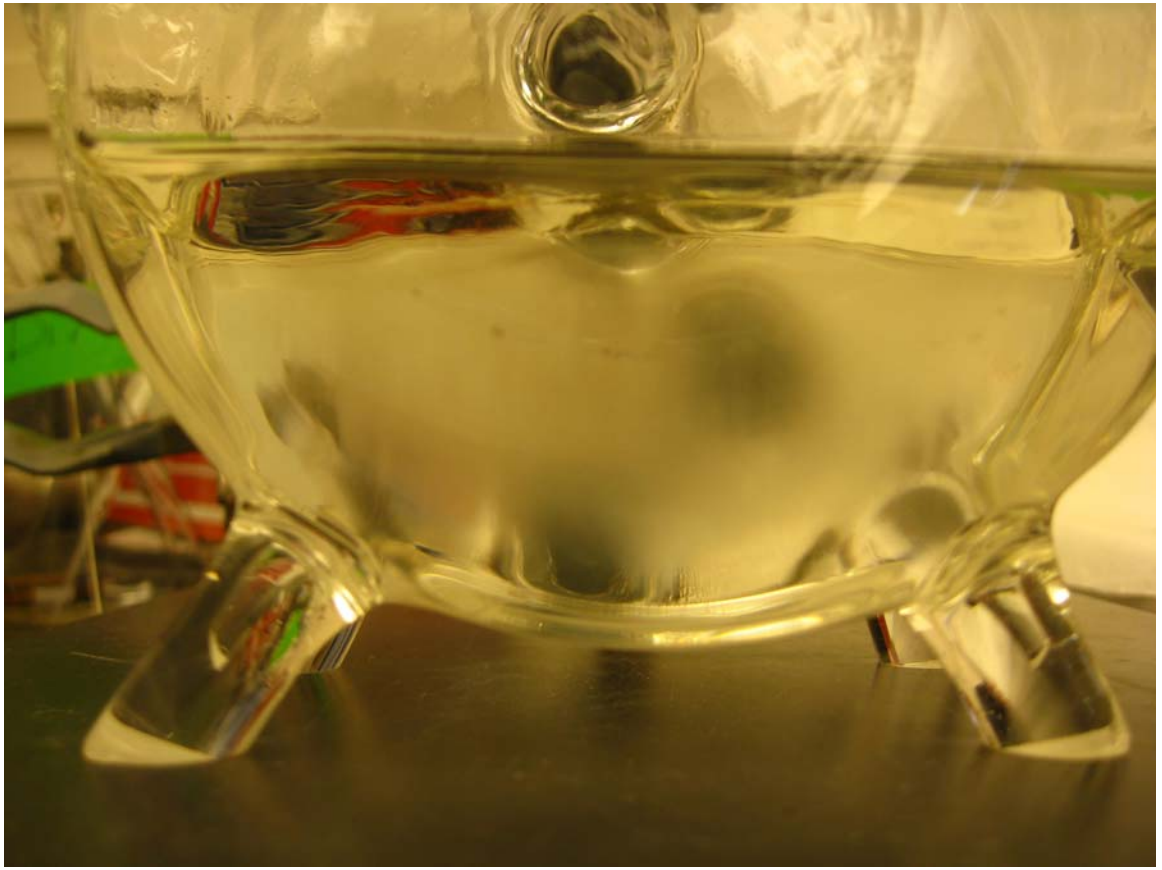
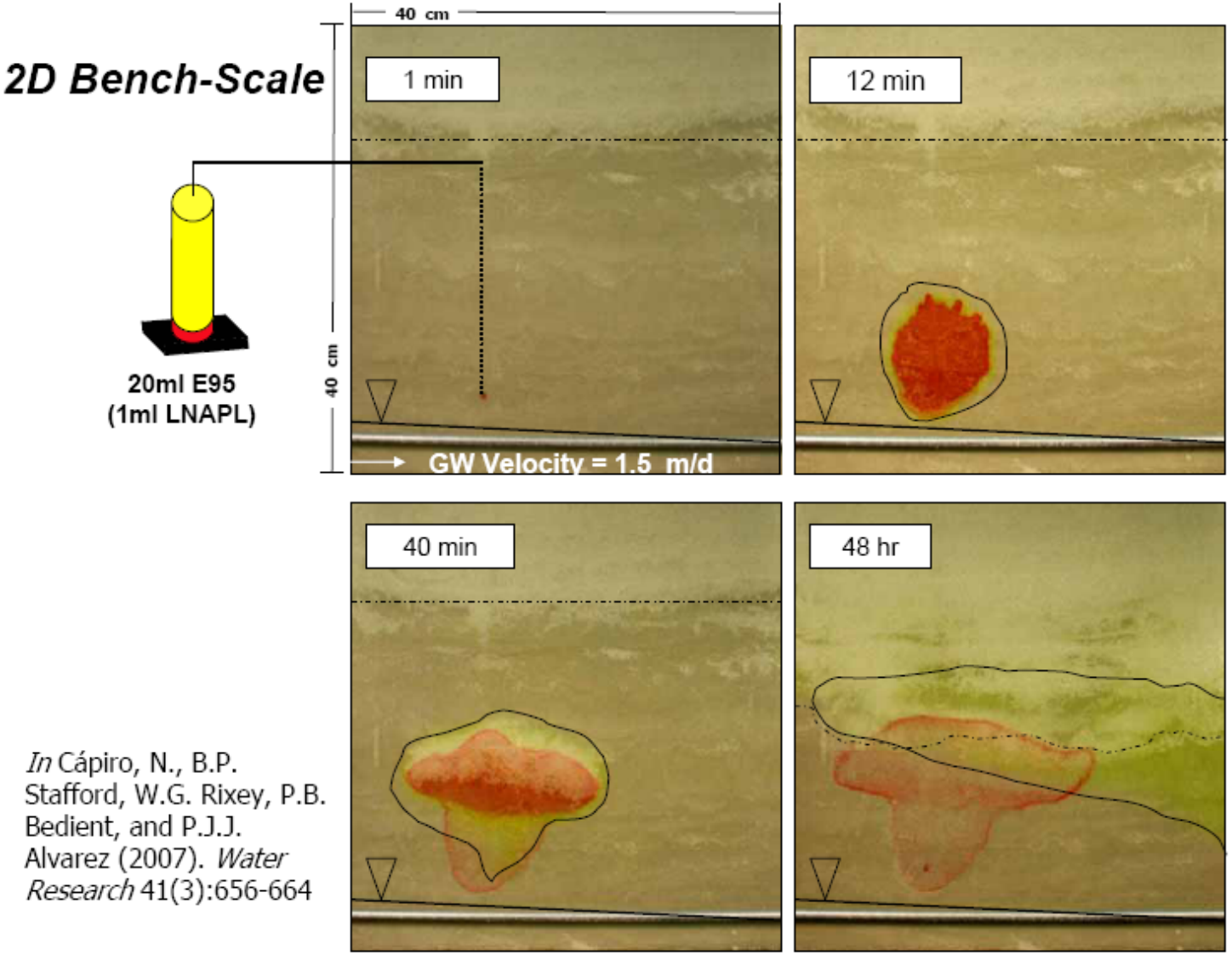


Thanks to Andrea Barbery, US EPA OUST

2D Bench-Scale



In Cápiro, N., B.P. Stafford, W.G. Rixey, P.B. Bedient, and P.J.J. Alvarez (2007). *Water Research* 41(3):656-664

Ethanol Components

Name	Formula	CAS. Number	Concentration (wt. %)	
			Wet Mill Sample	Dry Mill Sample
Water[1]	H_2O	7732-18-15	0.65	0.08
Methanol	CH_4O	67-55-1	0.07	0.06
Ethanol[2]	C_2H_6O	64-17-5	97.89	99.75
1-Propanol	C_3H_8O	71-23-8	0.03	0.08
Isobutyl Alcohol	$C_4H_{10}O$	78-83-1	0.10	0.08
2-Methyl 1-Butanol	$C_5H_{12}O$	137-32-6	0.06	0.01
3-Methyl 1-Butanol	$C_5H_{12}O$	123-51-3	0.21	0.02
Ethyl Acetate	$C_4H_8O_2$	141-78-6	0.02	--
1,1-Diethoxyethane	$C_6H_{14}O_2$	105-57-7	0.28	--

[1] Determined by Karl Fischer titration

[2] Determined by remainder of other compounds

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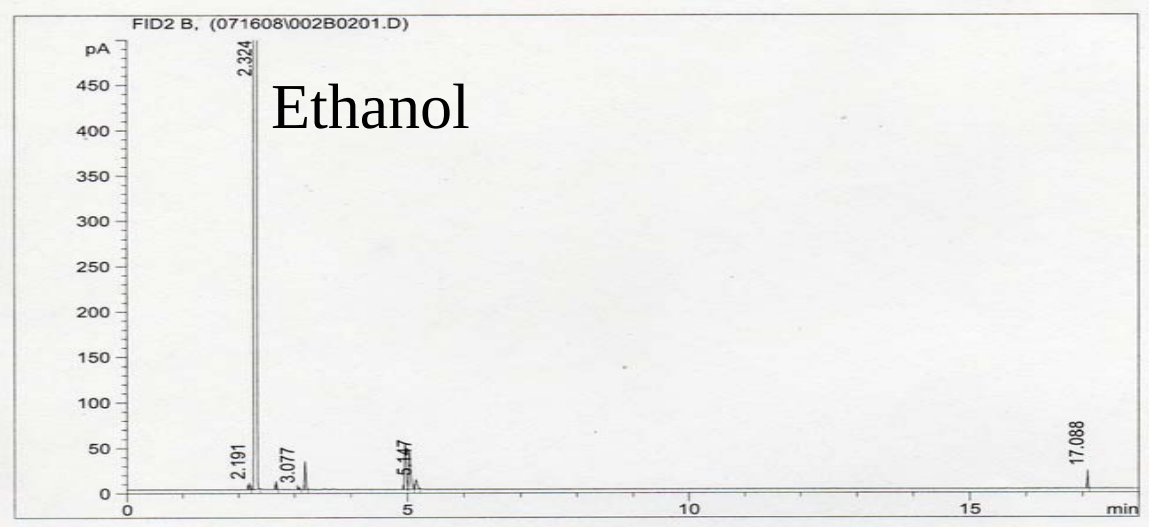
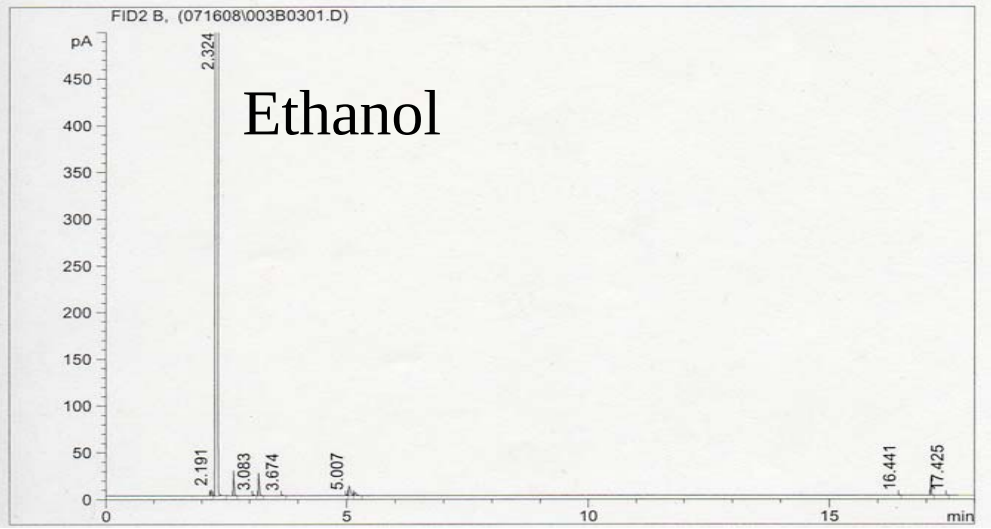


Ethanol



Ethanol

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Observed Ethanol Concentrations in Gasoline

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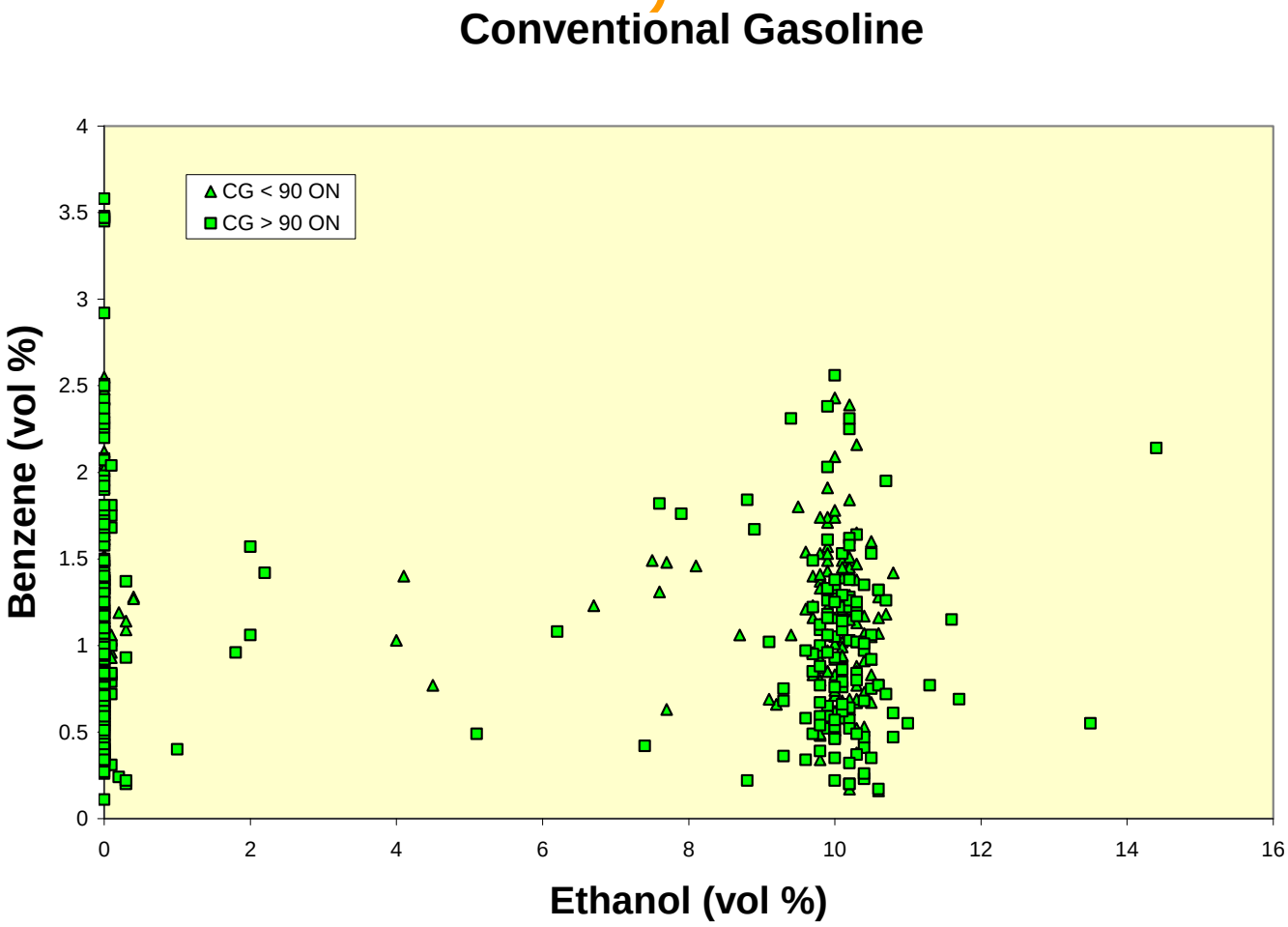
Northrop-Grumman (successor to NIPER) Bartlesville, Oklahoma



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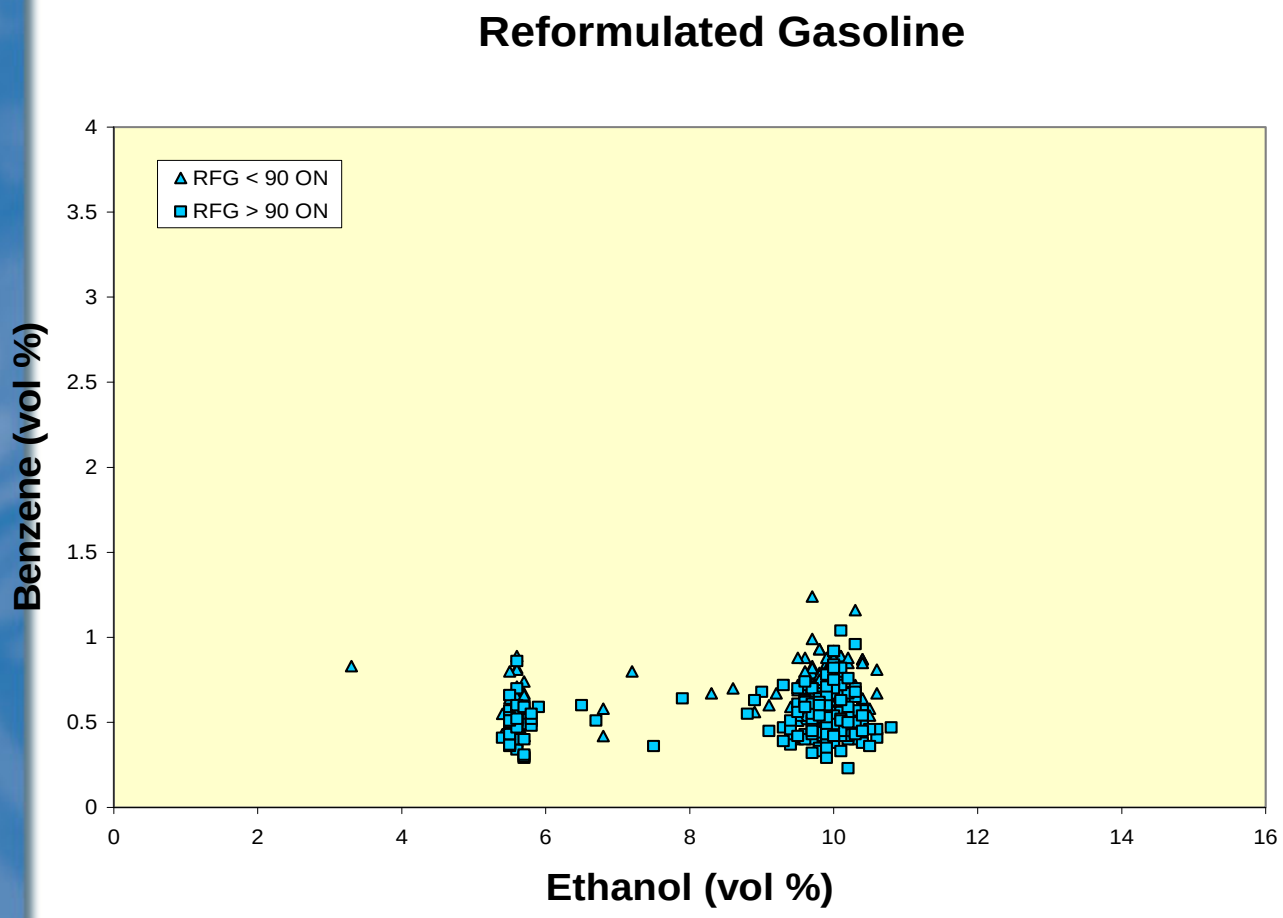

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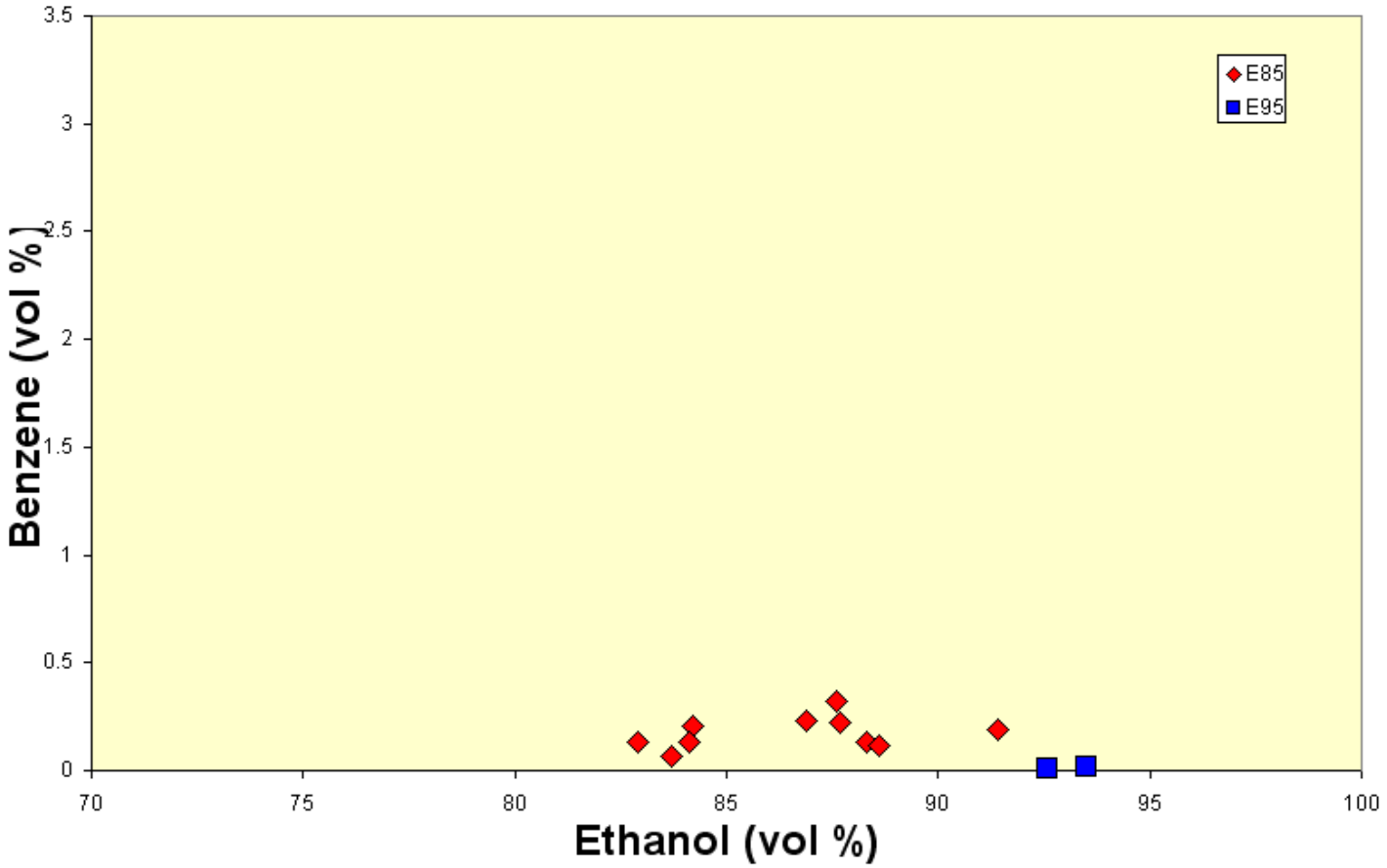
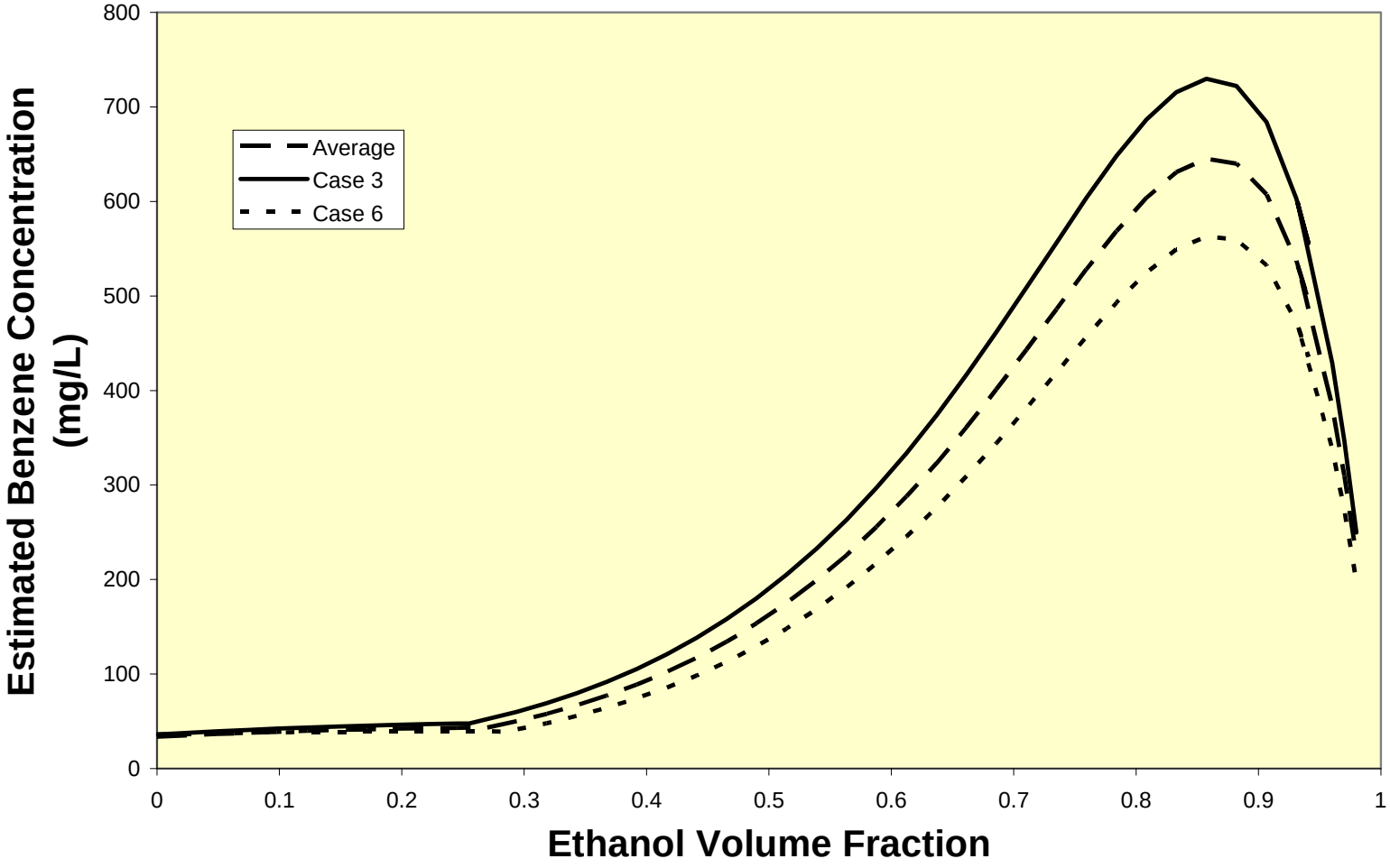


Cosolubility

- Ethanol increases the aqueous solubility of petroleum hydrocarbons
  - Dependent on
    - Ethanol concentration in water
    - Petroleum hydrocarbon concentration in gasoline
  - Theory developed by Heerman and Powers, 1998
    - Example:
      - Gasoline containing 1% benzene, mixed with denatured alcohol
      - Alcohol denatured with gasoline containing 1% benzene
      - Benzene mass not limiting

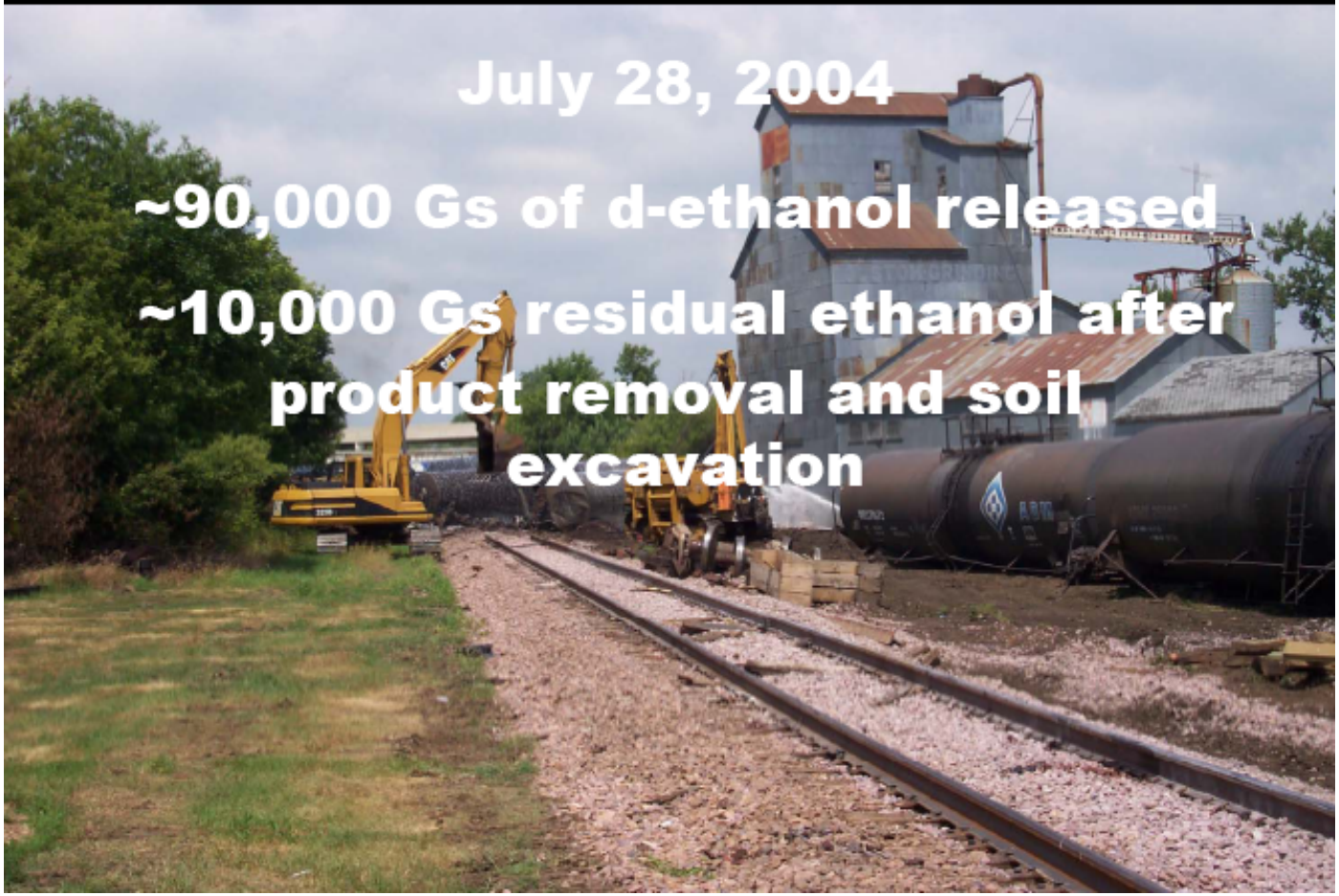
Estimated Benzene Concentration



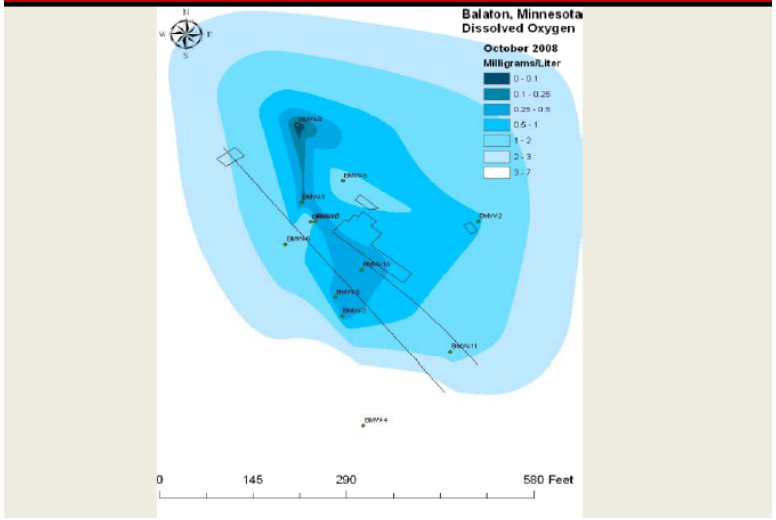
Spill to Land, Info. Courtesy of Dr. Roy Spalding, U of Nebraska

Balaton, Minnesota

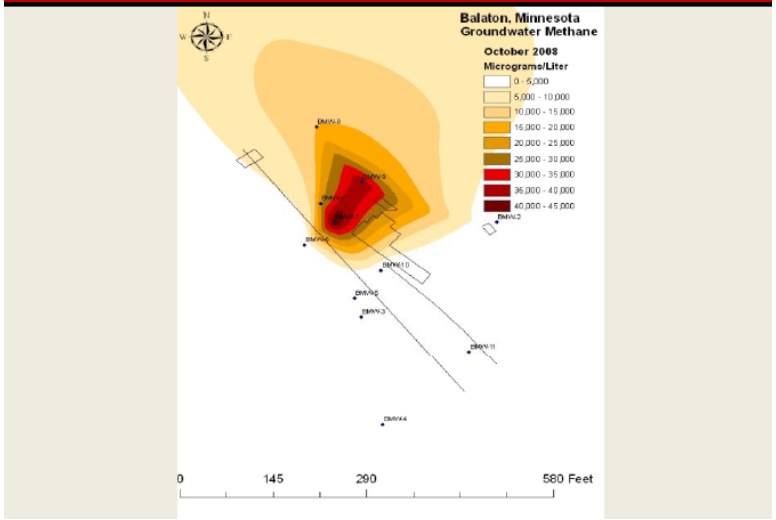
Balaton, Minnesota



D. Oxygen: 4.3 Years After Derailment

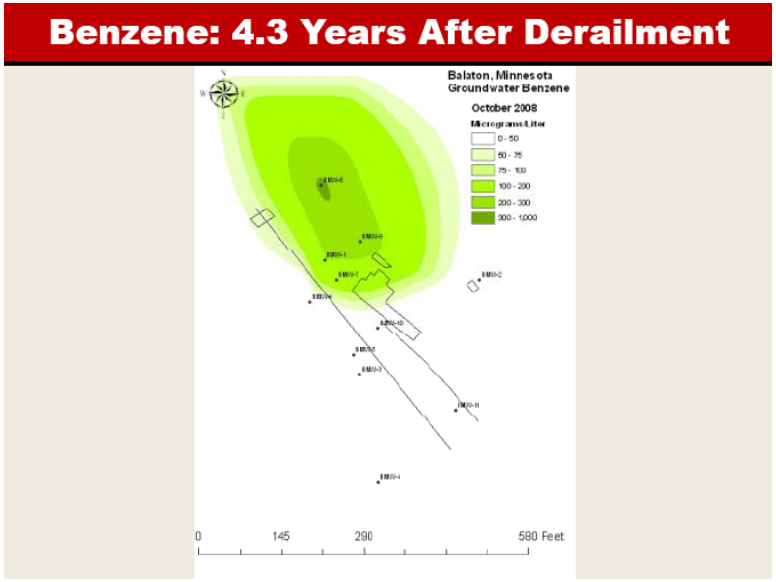


Methane: 4.3 Years After Derailment



- Long delay in ground water impact
- Ethanol hanging up in vadose zone for undetermined reasons
- Methane at water solubility
- Similar behavior to two other sites under investigation

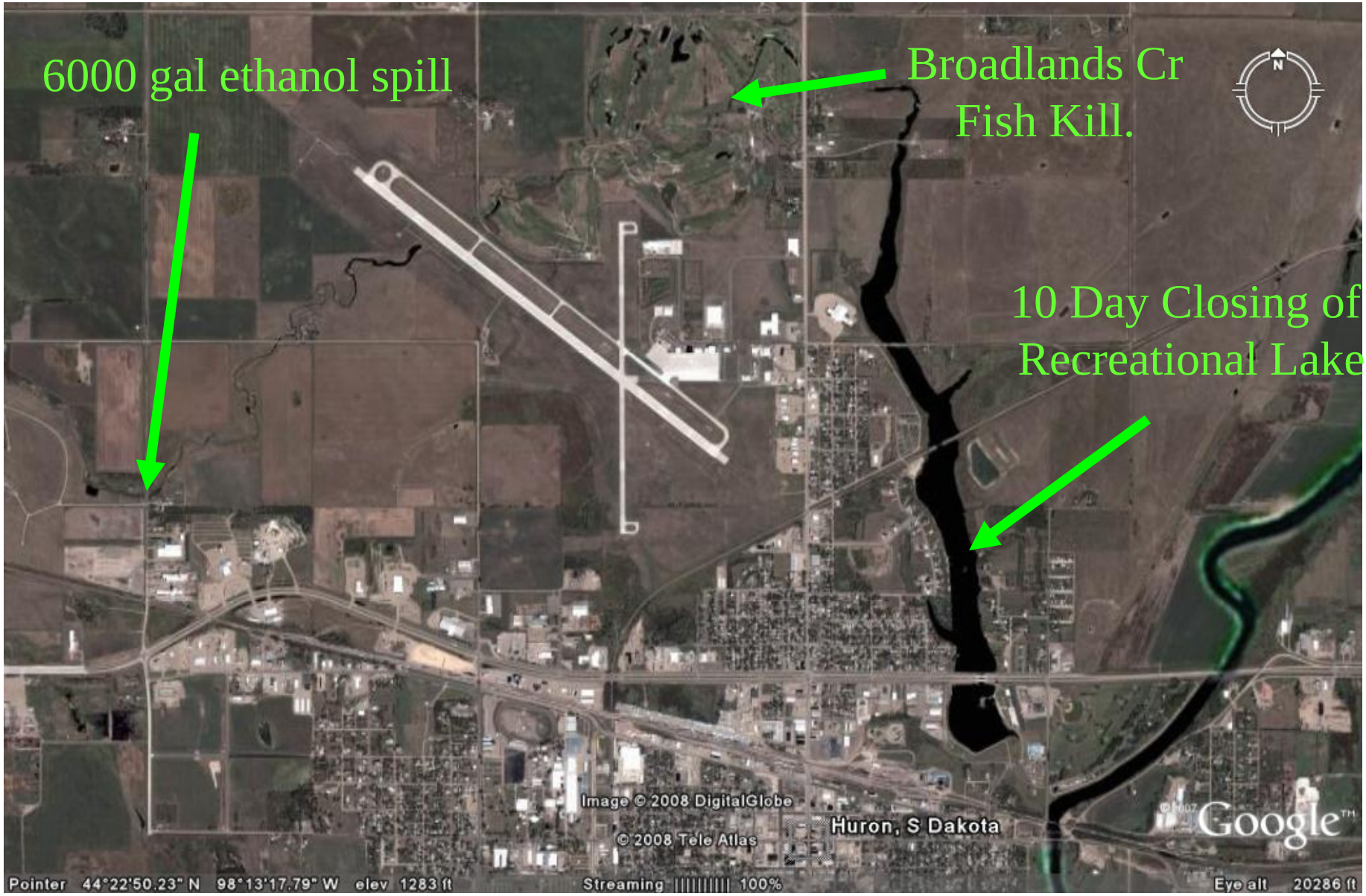
Benzene: 4.3 Years After Derailment



Spill to Broadland Creek May 17, 2008 Info. Courtesy of Kim McIntosh, SD-DENR

- Dry Mill plant in Huron, South Dakota
- Transfer line hose broke during filling of tank car
- Approx. 6000 gallons of ethanol released
- 100s of fish killed in creek
  - Minnows, bullhead, carp
- Recreational lake closed for 10 days

Huron, S.D., May 17, 2008



Comments

- No gasoline observed
- 4 water samples for VOCs 5/21
  - BTEX, tri-methylbenzenes, ethanol, methanol
  - Most results ND, one sample ethanol at 6800 ppb
- Generally increased D.O. by 5/27/2008
- Fish kill happened before oxygen sparging
  - Does the depletion of oxygen kill the fish?
  - Does the ethanol + hydrocarbons kill the fish?
    - (replenishing the D.O. may not save the fish)

Conclusions

- Ethanol rapidly replaced ethers in mid 2006 in reformulated gasoline
- Ethanol is used in about 75% of U.S. gasoline.
- Fuel ethanol contains several impurities including higher molecular weight alcohols
  - 3 to 5 carbon atoms
  - …But at concentrations < 1/4 percent

Conclusions

- E85 and E95 adsorb about 20%-30% of own volume in water before phase separating
  - Fuel Ethanol doesn't phase separate
  - E10 phase separates at about 0.5% water

Conclusions

- Spills of denatured alcohol to land based on three field studies:
  - Hangs up in the vadose zone
  - Methane at max solubility
  - Impacts to ground water delayed
- E10 Releases cause extended BTEX plumes
- Spills to water (Broadlands Ck)
  - No observed gasoline slick from denatured alcohol
  - Loss of dissolved oxygen major impact

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National Exposure Research Laboratory

- Although this work was reviewed by EPA and approved for presentation, it may not necessarily reflect official Agency policy.
- Thanks to:
  - Mark Toso, Minnesota PCA,
  - Cheryl Dickson, Northrop-Grumman,
  - Kim McIntosh, South Dakota DENR,
  - Dr. Roy Spalding, University of Nebraska,
  - Dr. Illena Rhodes, Shell Global Solutions
- Contact: *weaver.jim@epa.gov*
- EPA report, April 2009:
  - ***Composition and Behavior of Fuel Ethanol, EPA 600/R-09/037***
  - ***from www.epa.gov/athens/publications***