Biofuels and Emerging Issues for Emergency Responders

An introduction to basic response guides and case study examples from biofuel spills.

Jeff Kimble, OSC, Region 5
Kimble.Jeffrey@epa.gov

GOALS

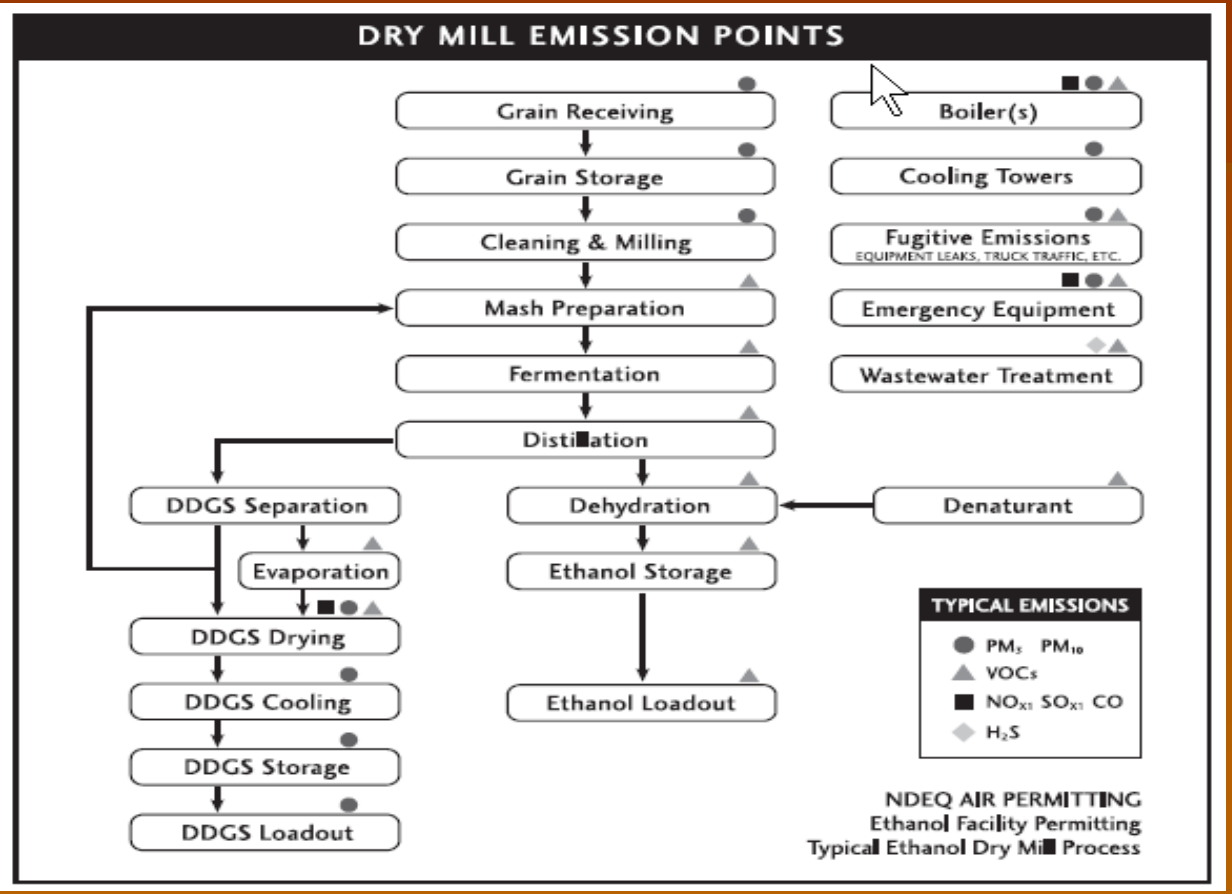
- Discuss hazards and clean up techniques for biodiesel and ethanol spills
- Discuss other biofuels hazards
- Look at what the response community is actually dealing with
- Present response guides as a tool for responders
- Discuss possible alternative approaches to response

ETHANOL MANUFACTURING FACILITY RESPONSE OVERVIEW

Description of Ethanol Fuel and the Production Process

- Ethanol, which contains hydrogen, carbon, and oxygen in its chemical structure, is also known as ethyl alcohol or grain alcohol.
- Ethanol can be used as a fuel for spark-ignited internal combustion engines. When burned in engines without active catalytic converters on the engine exhaust, the presence of oxygen allows ethanol to burn with lower carbon monoxide emissions than gasoline, although aldehyde emissions tend to be higher.
- In the U.S., ethanol is primarily produced from corn. To prevent ingestion, ethanol is denatured at the plant by mixing the ethanol with some type of hydrocarbon, such as gasoline. Denatured ethanol may contain 2-15 percent (%) gasoline, making it an ethanol and gasoline fuel blend. For example, ethanol E-85 contains 85% ethanol and 15% gasoline.
- The ethanol production process takes place through two methods: dry milling and wet milling. The dry milling method is more common and accounts for 82 % of U.S. ethanol production.

Dry Mill Process



- *Source: Nebraska Department of Environmental Quality*
- *CO – carbon monoxide*
- *DDGS - Dried Distillers Grains with Solubles*
- ***H2S – hydrogen sulfide***
- *NOx – oxides of nitrogen*

PM5 – particulate matter less than five micrometers
PM10 – particulate matter less than ten micrometers
SOx – oxides of sulfur
VOCs – volatile organic compounds

Major Chemicals Involved in Ethanol Production

- Corn – Used product
- Sodium Hydroxide – pH control during fermentation
- Ammonia – pH control and yeast nutrient during fermentation
- Sulfuric Acid – separates corn into starch, germ, fiber, and protein
- Fuel for process heat
- Yeast – used in fermentation
- Enzymes (amylase) – converts starch to dextrose
- Antibiotic such as penicillin – controls bacteria during fermentation
- Carbon Dioxide - byproduct
- Hydrogen Sulfide – process emission
- Sulfur dioxide – process emission
- Nitric oxide – process emission
- VOCs – process emission
- Ethanol – final product
- Gasoline – final product additive (if used)
- Denatured Ethanol – final blended product

Appropriate Mitigation Measures for Release of Ethanol Fuel

- **Proper Air Monitoring Equipment**
  - Combustible Gas Indicator (CGI) and Flame Ionizing Detector (FID) or MultiRAE Plus Five-Gas Air Monitoring Instrument; Photo Ionizing Detector (PID). Must review response factors prior to using PID.

- **Proper Spill Containment**
  - Ventilate area and eliminate ignition sources. Fire-fighting measures must use **ALCOHOL-RESISTANT FOAMS**. Containment/response should follow typical containment procedures. Example: use non-combustible oil-dry, absorbent socks, booms, etc that are **ALCOHOL-RESISTANT**. Avoid entry into sewers and waterways due to flammability hazards, potential aquatic toxicity, and potential microbial upsets at wastewater treatment plants. Waste generated from the clean-up may exhibit the flammability characteristic for hazardous waste.

Note: The Response Overview includes measures for the other major chemicals involved in the manufacturing process.

EXPECTED FATE OF ETHANOL

- **Release in Soil**
  -Ethanol is rapidly biodegraded in soil.

- **Release in Water**
  -Fuel ethanol will mix with water, and at high enough concentrations of water, the ethanol will separate from the gasoline. Ethanol is rapidly biodegraded in groundwater and surface water. However, some studies are focusing on the possibility of ethanol inducing the transport of other chemicals such as benzene.

- **Release in Air as result of spill/fire**
  -Ethanol vapor, like gasoline vapor, is denser than air and tends to settle in low areas. However, ethanol vapor disperses rapidly.

- **Release to storm/sanitary sewers**
  -Ethanol released to water will volatilize and rapidly biodegrade. The potential decrease in dissolved oxygen as a result of ethanol degradation can upset microbial functions at wastewater treatment plants. The potential flammability hazard must be addressed when ethanol is released to a sanitary or storm system.

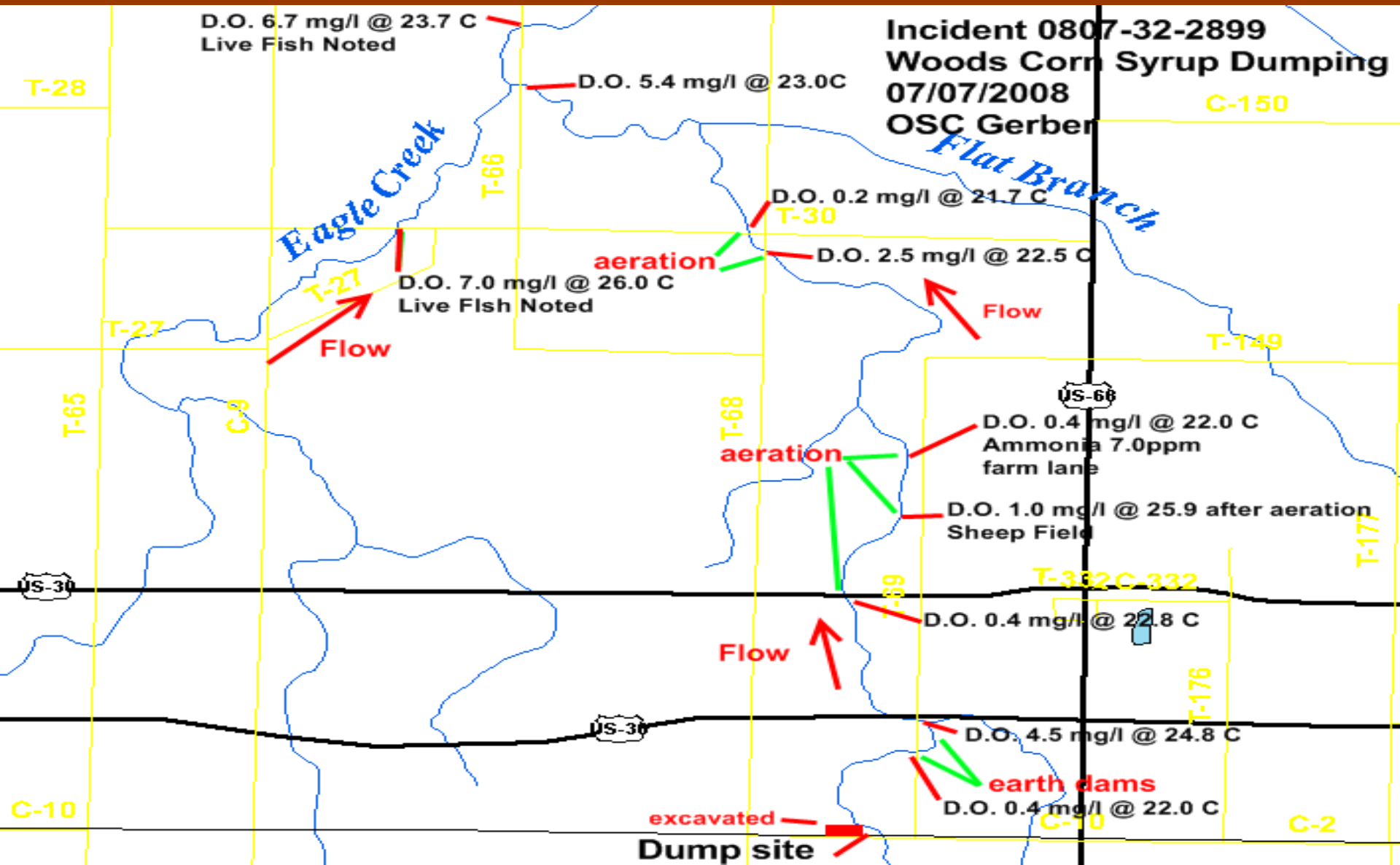
Overall Health Risks of Ethanol

- Human Health Effects
  - Exposure to fuel ethanol can occur by breathing its vapors (inhalation), getting it on the skin or in the eyes (skin absorption), or accidentally swallowing it (ingestion).
  - The following symptoms of exposure to fuel ethanol may appear immediately: Dullness of memory and concentration; impaired motor coordination; and drowsiness, stupor, and finally coma. May cause skin irritation as a result of defatting.
  - Carcinogenic compounds are not present in pure ethanol; however, because gasoline is used in the blend, E85 is considered to be potentially carcinogenic.
- **Ecological Effects**
  - Pure ethanol has demonstrated lethal concentrations for fish (rainbow trout) at 11,200 to 15,300 milligrams per liter (mg/L).
  - Pure ethanol is expected to biodegrade rapidly and bioaccumulation or concentration in the food chain is not expected. However, the biodegradation may decrease the dissolved oxygen in surface water resulting in fish kills.

Woods Ethanol Spill

- July 7, 2008-Report from Hancock Co. EMA of yellow substance in a roadside ditch
- Owner of adjacent property dumped 5,000 gallons of CDLS (byproduct of ethanol production)
- Corn distiller was rejected at disposal facility and sold to local farmer to feed deer
- Ethanol Plant on-site to provide “Technical Assistance”
- ODNR discovers up to 1,000 dead fish downstream of spill site
- PRP hired an environmental contractor to
  - **Remove gross contamination from spill site**
  - **Provide aeration to tributary**
  - **Remove dead fish from downstream**
  - **Dispose of contaminated soil**
- Direct reading in tributary showed
  - **DO Levels @ 0 mg/L**

Woods Ethanol Spill

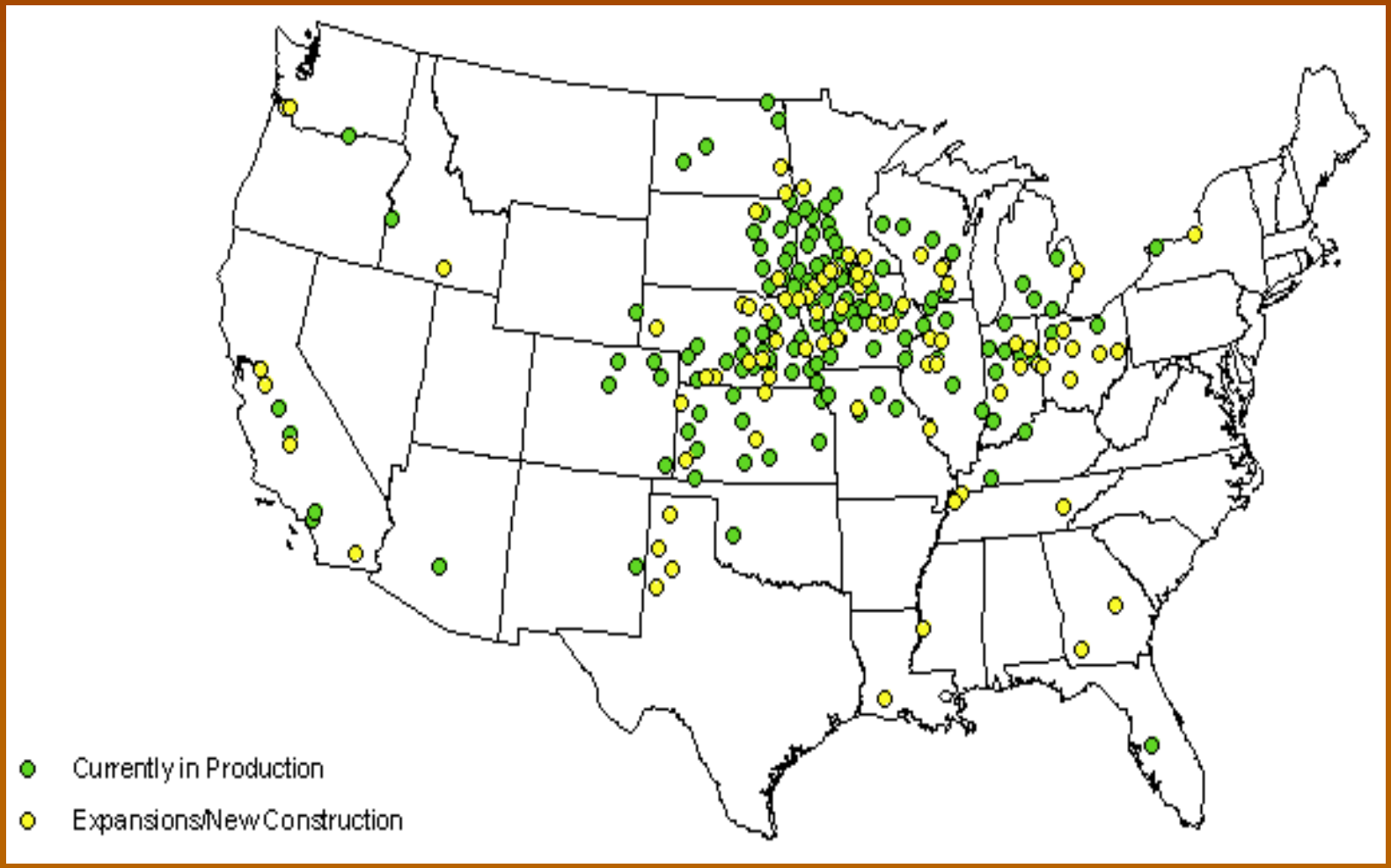


Woods Ethanol Spill

Woods Ethanol Spill

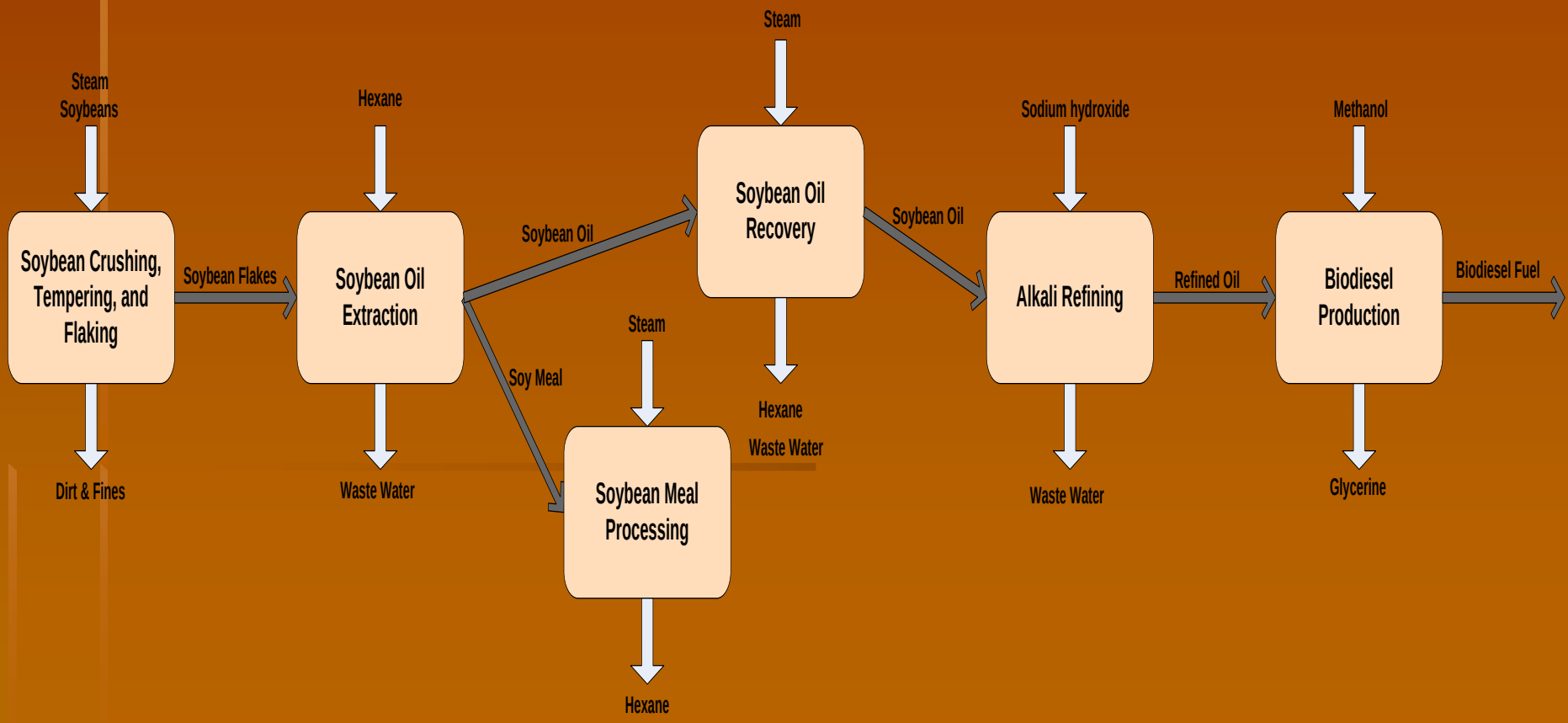
Current Ethanol Plants

http://www.card.iastate.edu/research/bio/tools/ethanol.aspx as of 01/16/2008



BIODIESEL MANUFACTURING FACILITY RESPONSE OVERVIEW

Description of Biodiesel Fuel and the Biodiesel Production Process



Major Chemicals Involved in Biodiesel Production

- Soybean hulls and fines
- Hexane – extracts soybean oil
- Sodium and Potassium Hydroxide – removes fatty acids from soybean oil
- Methanol – replaces glycerol in soybean oil to make oil less viscous (transesterification)
- Glycerol – byproduct of transesterification
- Fuel for process heat (i.e. natural gas, propane, etc.)

Appropriate Mitigation Measures for Release of Biodiesel Fuel

- **Proper Air Monitoring Equipment**
  - Biodiesel fuel has a very low volatility at normal ambient temperatures and vapors are not typically an issue. However, vapors/mists may be generated when heated above ~266 degrees Fahrenheit (°F).
- **Proper Spill Containment**
  - Containment/response should follow typical oil containment procedures. Example: use oil-dry, petroleum-compatible absorbent socks, booms, etc; the absorbent material used should be resistant to alcohol in the event methanol has further commingled with the biodiesel release. Disposal of biodiesel-contaminated soil or products can be considered non-hazardous provided methanol and/or hexane have not commingled with the release to meet the flammability characteristic for hazardous waste.

Note: The Response Overview includes measures for the other major chemicals involved in the manufacturing process.

EXPECTED FATE OF BIODIESEL

- **Release in Soil**
  -Biodegradation occurs rapidly, with faster rates under aerobic conditions than anaerobic conditions.
- **Release in Water**
  -Insoluble in water. Degrades rapidly and fairly extensively in aquatic environments. Estimated to degrade at a rate approximately four times faster than petroleum diesel – 85% of pure biodiesel expected to degrade within 28 days.
- **Release in Air as result of spill/fire**
  -Combustion produces carbon monoxide, carbon dioxide along with thick smoke.
- **Release to storm/sanitary sewers**
  -May be high in free fatty acids and glycerol, and can have a high biochemical oxygen demand (BOD). These can disrupt wastewater treatment plant operations.

Overall Health Risks of a Biodiesel Release

- **Human Health Effects**
  - Inhalation effects are negligible unless heated to produce vapors.
  - If biodiesel fuel were to be ingested, enzymes in the body called esterases would break the biodiesel fuel molecules into the component fatty acids and alcohol molecules. The alcohol is usually methanol and methanol is toxic. Thus, methanol toxicity could be a concern for ingestion of biodiesel fuel.
  - Neat biodiesel fuel is approximately 11 percent methanol by weight, so ingestion of 100 grams of biodiesel would release 11 grams, or 14 milliliters (mL) of methanol. For a 70 kilogram (kg) adult, the fatal dose of methanol ranges from 60 to 160 mL.
- **Ecological Effects**
  - Biodiesel biodegrades much more rapidly than conventional diesel.
  - When biodiesel is present in bulk in the environment, it can coat animals that come in contact with it and may reduce the ability of oxygen to reach aquatic systems. In this respect, its action is similar to petroleum diesel fuel.
  - Biodiesel does not have the toxicity and the solvent action that diesel fuel has, so its effects on animals are expected to be less severe.
  - The treatment of oiled birds and animals would be similar to the treatment provided when an oil spill occurs.
  - However, in water it has a high oxygen demand which can lead to massive fish kills

Defiance Biofuel Spill

- Initial report called in to state: *COMPANY HAD AN EXPLOSION. THERE ARE 2 LARGE TANKS ON SITE CONTAINING GYLCERIN. SEWER BEING IMPACTED WITH FF WATER*
- OHIO EPA OSC responded
- 2 tanks were in fire (10,000 gallons & 4,000 gallons)
  - **Only 1650 gallons of glycerin reported on hand**
  - **Also ~700 gallons of biodiesel**
  - **“Empty” 55-gallon drums**
- Release to ground and storm sewer
- Release to threatened creek and river via storm sewer

Defiance Biofuel Spill (cont'd)

Fire and release point

Defiance Biofuel Spill (cont'd)

- Ohio EPA responded and assessed situation
  - **Called EPA spill phone duty officer**
  - **Duty officer coordinated with OSC**
  - **Both told Ohio EPA to respond as if diesel spill**
  - **Were not sure what regulations applied to biodiesel production**
    - **Both continued research that night**
    - **Advised state on limited info obtained**
  - **Ohio determined spill contained, but not cleaned up**
  - **They decided to wait till morning for removal**

Defiance Biofuel Spill (cont'd)

-"fats" floated

- 3 layers in water observed

- some suspended in water

-"milky" layer observed

- Response Techniques
  - **Ohio EPA made PRP hire a contractor**
  - **On-land spills were excavated**
  - **Spill to ditch was collected and put in frac tanks**
    - **Analytical of frac tank water revealed styrene and perchloroethylene**
    - **Shows more than "glycerin" spilled**
  - **Some wastes suspended in water column were lost**

Renewable Energy (IDEM)

- Biofuels production facility
- Spill from 50,000 gallon tank
- Surface soils and ditch water impacted
- Water in ditch a “milky” white
- Soils excavated
- Tile field drains intercepted and plugged

Renewable Energy (IDEM)

Private Garage (IDEM)

- Small scale production
- Used vegetable oil
- No tanks large enough for regulation
- However, 20 gallons spilled, some to sewer
- IDEM advised resident on contingency plans and contractors

Michigan Paint Shop

- Reported as small biodiesel spill
- Actually a paint shop
- USCG was in area and offered to check on spill
- USCG and MDEQ met on site
  - **Small spill observed**
  - **Did not see any coming out of sewer**
- USCG left, conditions changed
- MDEQ noted emerging issues at shift change
- Noted entering waterway, low flow
- “Milky” white throughout the water column
- MDEQ and EPA discussed options
- Capture and removal not possible
  - **Little impact to fish observed**
  - **Conditions did not change much due to no flow**
- Decided to purge ditch and flush
- Flushing somewhat effective
- Heavy rains completed the flushing

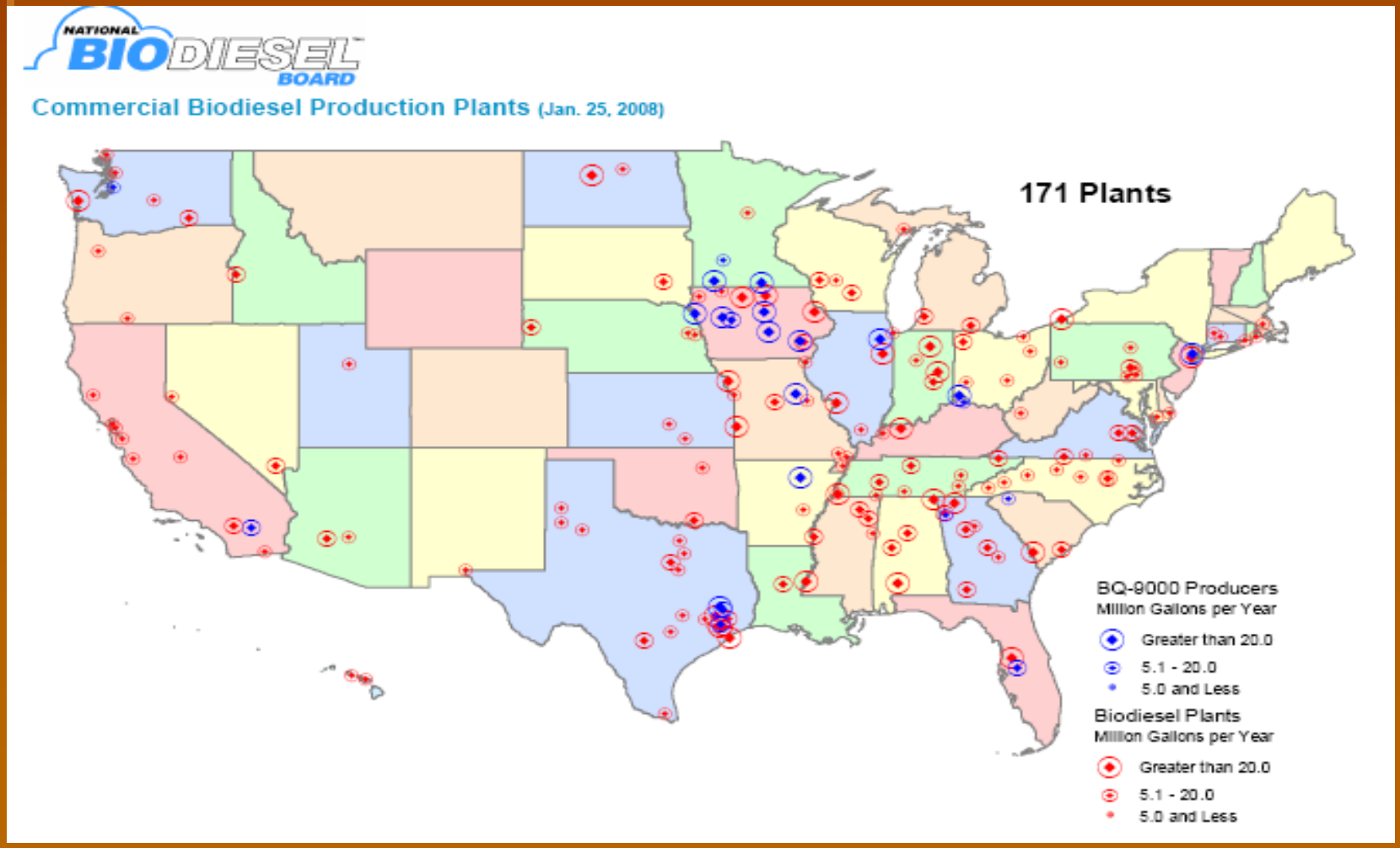
Michigan Paint Shop

Milky White

The following are Federal regulations that would apply to biofuels manufacturing facilities when they meet the thresholds for the requirements of the regulation. Note that state-specific regulations may also apply

- Emergency Planning and Community Right Know ACT (EPCRA)
- U.S. EPA Oil Pollution Control/Federal Water Pollution Control Act
- Clean Water Act
- Oil Pollution Act of 1990 (OPA 90)
- Resource Conservation and Recovery Act (RCRA)
- Clean Air Act (CAA)
- DOT Hazardous Materials Regulations (HMR); as amended by Homeland Security Act of 2002

Current Biodiesel Plants



Response Guides

Layout – intended for responders

- Description of Process
- The chemicals involved (1st important table)
- How releases may occur (what to look for)
- Responding to releases (and byproduct releases, 2nd table)
- Environmental receptors/concerns (3rd table)
- Health risks
- Summary of applicable regulations

Response Guides

Use – want more functionality

- Tables were included for quick location of info
- Many spills are not the end product
- Tables reflect the “may be” scenario of spills
- Need your input
  - got to http://www.epaosc.org/site_profile.asp?site_id=4022

Summary

- Biofuels degrade faster
- Causes extreme DO issues in creeks
- Not great for water treatment plants
- Other removal/cleanup techniques
  - Any ideas for treating “in stream” besides aeration?
  - Other sorbent technologies?
- Fast degradation can make cleanups faster
- Biofuel spills are many times not biodiesel or ethanol, but production products and byproducts

Summary

- Biofuel production can be anywhere
- "Manufacturers" are heavily ignorant of regulations
- In R5, many facilities are being abandoned or going bankrupt due to market fluctuations
- Glycerin spills seem to be prevalent
  - Output from the transesterification
  - Not that much use for it as product
  - People are storing it and not disposing of it
  - Some waiting for "value" to increase

QUESTIONS ???