

Biodiesel and Ethanol



U.S. Environmental Protection Agency

Office of Solid Waste and Emergency Response

Office of Emergency Management

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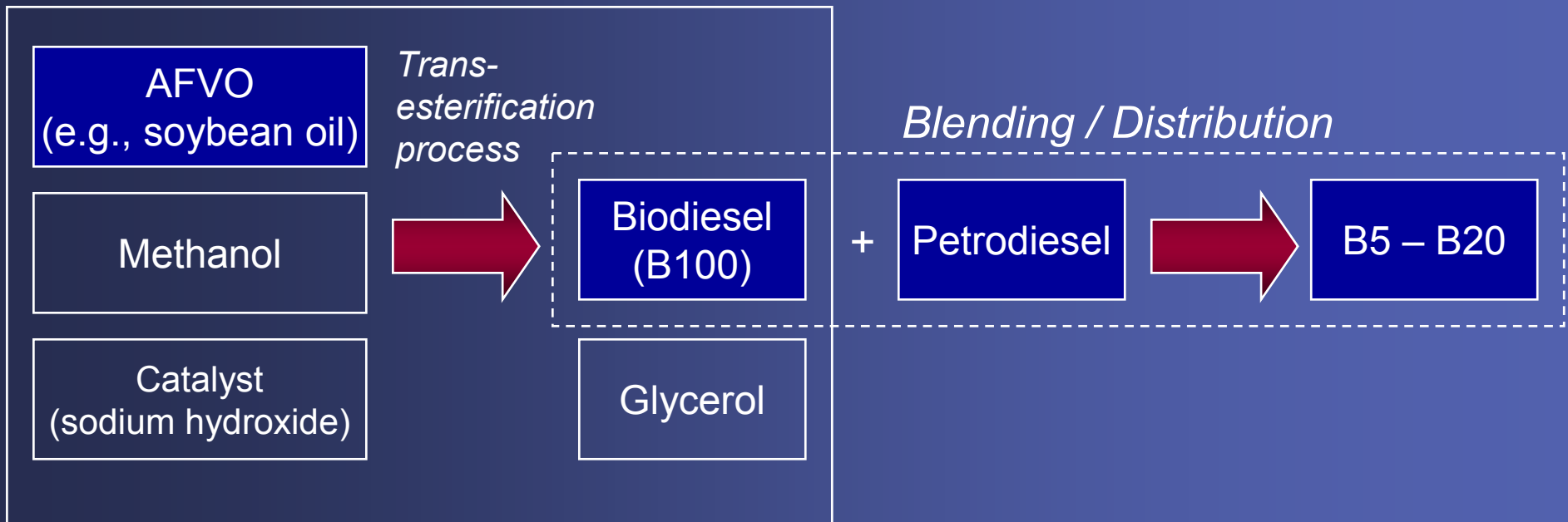
What is Biodiesel?

- ◆ **Mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats, e.g.:**
 - Oilseeds (soybean, canola)
 - Animal fats and trap grease
 - Cooking oils
 - Waste vegetable oil
- ◆ **Produced by combining organically derived oils with an alcohol in the presence of a catalyst.**
- ◆ **Resulting products are esters (biodiesel) and glycerol.**
- ◆ **Most of the biodiesel produced in the United States uses soybean as feedstock.**
- ◆ **Pure biodiesel is referred to as “B100”. Biodiesel is commonly marketed as blend of biodiesel and petroleum-based diesel (petrodiesel).**
 - Common blends: B5 (5% biodiesel; 95% petrodiesel) and B20 (20% biodiesel; 80% petrodiesel).



Biodiesel Schematic Product Flow

Production



Production Capacity

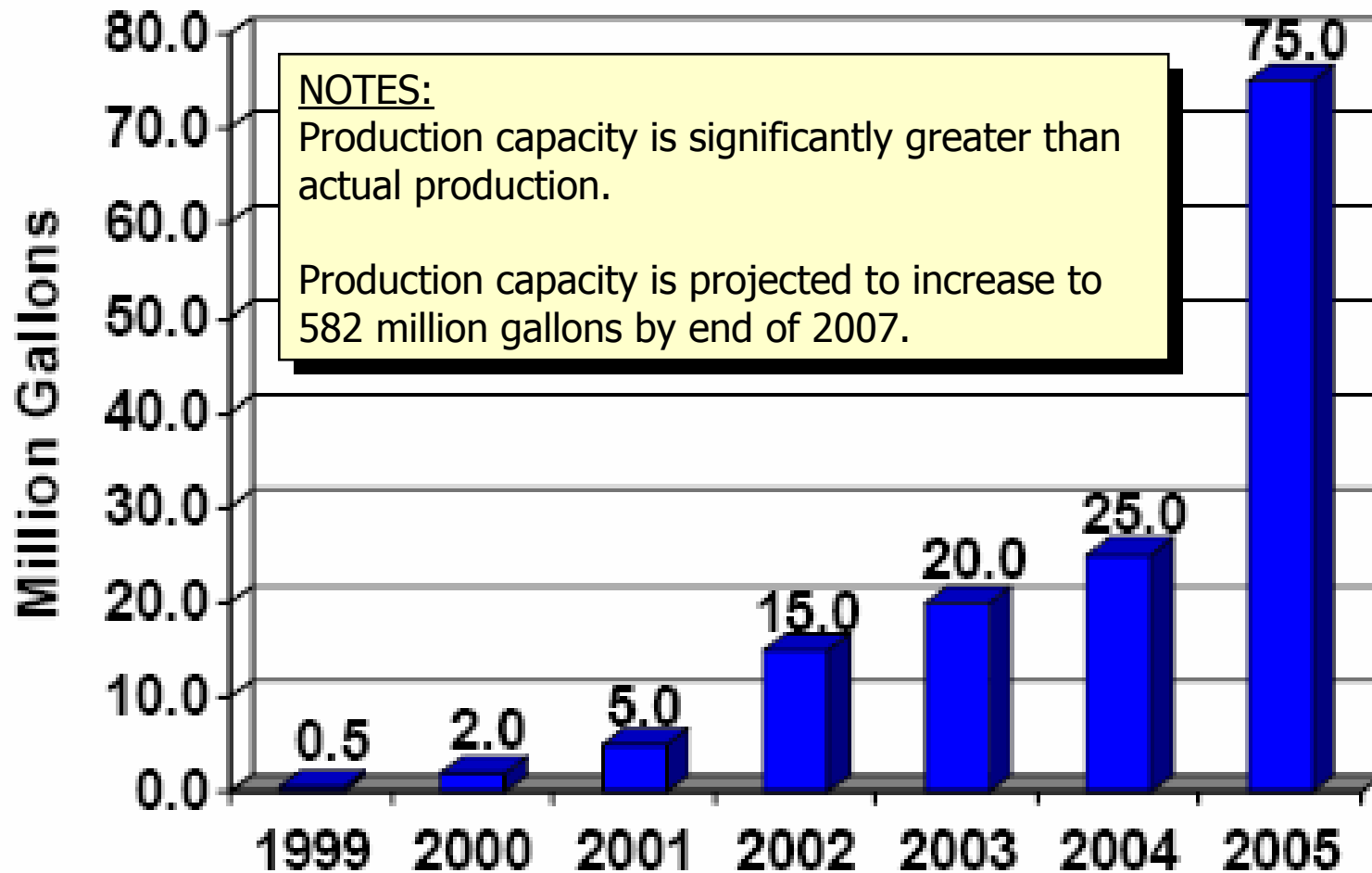
- ◆ **65 biodiesel plants currently in operation in the U.S.**
- ◆ **395 million gallons aggregate annual production capacity.**
- ◆ **Capacity expansion**
 - Domestic production capacity expected to increase to over 700 million gallons within the next 18 months with 58 plant construction/expansion projects in the United States.
- ◆ **Vertical integration of the production**
 - Traditional petroleum refiners are entering the business, e.g., AGE Refinery (TX) purchasing biodiesel from Gulf Hydrocarbons and selling B20 to its consumers.

Commercialization

- ◆ **Blending can be done at varying stages:**
 - In early days, biodiesel users (e.g., fleet owners) tended to “splash blend” B20 from B100 stored on-site.
 - As demand increased, pre-blended B20 became available. Petrodiesel suppliers receive and store B100 and blend biodiesel to the specified ratio, sometimes by carrying in separate compartments in one truck and blending when unloading at the customer’s site.
 - More recently, petroleum terminals and pipeline racks are adding biodiesel blending capability so that jobbers and distributors can receive a biodiesel blend directly at the rack and store and distribute only the pre-blended biodiesel.

Biodiesel

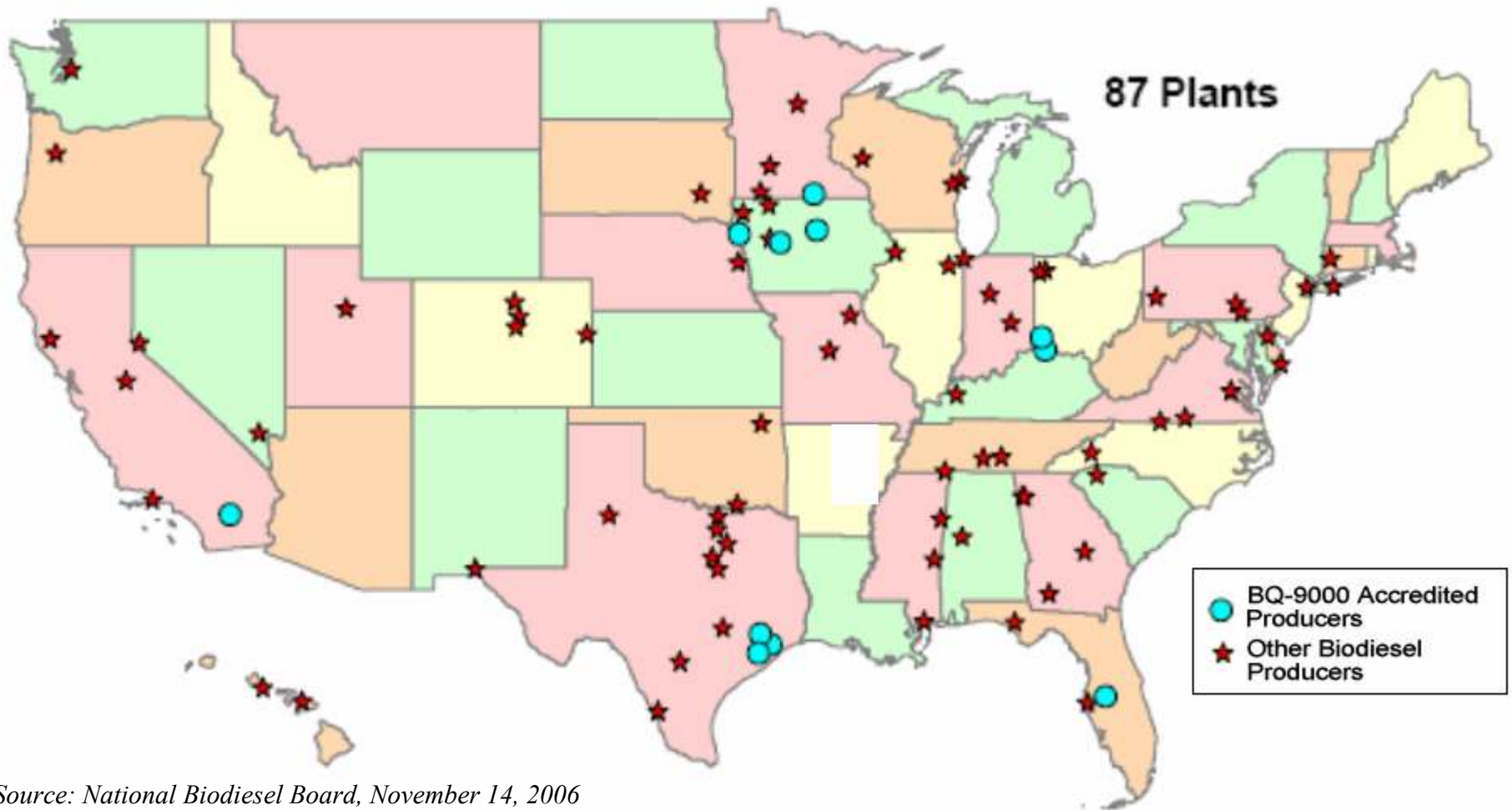
Annual Biodiesel Production



Source: National Biodiesel Board

Biodiesel Distribution of Existing Producers

Commercial Biodiesel Production Plants



Source: National Biodiesel Board, November 14, 2006

Biodiesel

Transportation and Infrastructure

- ◆ **Can generally use the same infrastructure as petrodiesel with only minor modifications.**
- ◆ **Vessel**
 - Possible, depending on plant location. In practice, uncommon since most plants are located inland in closer proximity to their feedstock. A few plant receive feedstock from foreign suppliers via vessels.
- ◆ **Railcar**
 - Most dominant mode. Biodiesel loaded onto rail cars at the plant
- ◆ **Truck**
 - Most flexible mode. Biodiesel loaded to tanker trucks at the plant or at intermediate distribution points
- ◆ **Pipeline**



Technical Considerations

◆ Higher solvent characteristics.

- Cleans fuel system and may flush residues. More frequent filter changes may be needed.
- Can damage rubber lines. Use steel, aluminum, fluorinated polyethylene, fluorinated polypropylene or Teflon.

◆ Higher gelling point and decreased cold flow characteristics.

- May require additives, blending with #1 diesel, storage in underground storage tanks, and/or tank heaters.

◆ Fuel oxidation stability and algae growth.

- May require the use of additive to improve stability.
- May require use of anti-microbial agents to reduce potential for microbially-influenced corrosion (MIC) in metallic storage tanks.

Oil Storage at Biodiesel Plants

◆ Types of Oil

- Vegetable oil or other feedstock
- Methyl esters (biodiesel) (B100) finished product

AND, if facility is blending on-site:

- Petroleum diesel
- Blended biodiesel (e.g., B5 or B20) product

Biodiesel

Facility Case Example: Grays Harbor, WA

- ◆ **Largest biodiesel plant in the country (currently under construction, expected to be online in second quarter of 2007)**
- ◆ **Production capacity: 100 million gallons per year**
- ◆ **Feedstocks: Virgin vegetable oil**
- ◆ **Storage Tanks**
 - Vegetable oil and biodiesel: 25 million gallons total (14 tanks)
 - Methanol: 500,000 gallons (1 tank)
 - Other substances:
 - 100,000 gallons sodium methoxide (product of NaOH and MeOH)
 - 300,000 gallons glycerine
 - 100,000 gallons tank bottoms
- ◆ **Transportation Infrastructure**
 - Receipt of feedstock by ships and/or rail
 - Finished products (B100, glycerine) transported by rail or tanker trucks

Regulatory Requirements

- ◆ **As an oil, biodiesel is subject to Federal oil spill reporting and prevention, control, and countermeasure requirements (e.g., 40 CFR part 110, 40 CFR part 112)**
 - Oil or fat feedstocks are also oils and are subject to the same requirements.
- ◆ **A number of states specifically address biodiesel (pure or blended) as an oil, including in regulations commonly targeted at “petroleum tanks” such as USTs.**

Considerations for Response

- ◆ **Key parameters (“Pure” Biodiesel, B100):**
 - **Solubility:** Insoluble (Saturation concentration: approximately 7 ppm (seawater) and 14 ppm (freshwater) at 17°C)
 - **Specific gravity:** 0.88 Floats on water
 - **Volatiles:** less than 2% per volume
 - **Biodegradation:** may degrade faster than petroleum diesel.
 - **Biological oxygen demand (BOD):** greater than petroleum diesel.
- ◆ **Given the above, and considering that biodiesel is most often used as a blend of bio/petro diesels:**
- ◆ **Response strategy and equipment generally expected to be similar to those used for spills of petrodiesel**

Biodiesel

Considerations for Response (cont'd)

- ◆ **Fire hazard**
 - Flashpoint: >270 °F (compared to petrodiesel 125 °F)
 - Burns readily once ignited
- ◆ **At biodiesel production plant, risk is compounded by presence of methanol**
 - Methanol Flashpoint: 55 °F
- ◆ **Eliminate ignition sources**



*Fire at biodiesel plant in Canby, OR (06/24/2006)
Source of the blaze was the biodiesel. Methanol tanks were unaffected.*

Biodiesel

Response Equipment

- ◆ **Same equipment as used for responding to petrodiesel spills, e.g.:**
 - Containment booms
 - Appropriate size/type for affected waterway
 - Skimmers and pumps
 - Absorbent material
 - Pillows, pads, socks, sorbents
 - Containers for collected materials
 - Additional Supplies (e.g, personal protection equipment)



Ethanol



- ◆ Ethyl alcohol made by fermenting and distilling simple sugars (most commonly from corn).
- ◆ Used as an additive to gasoline where it acts as oxygenate, octane booster, and extender.
- ◆ May also be used in pure form (denatured) as an alternative to gasoline in engines that are especially designed for its use.
- ◆ Currently produced and consumed predominantly in the Midwest where corn (most common feedstock) is grown.

Ethanol Production Capacity



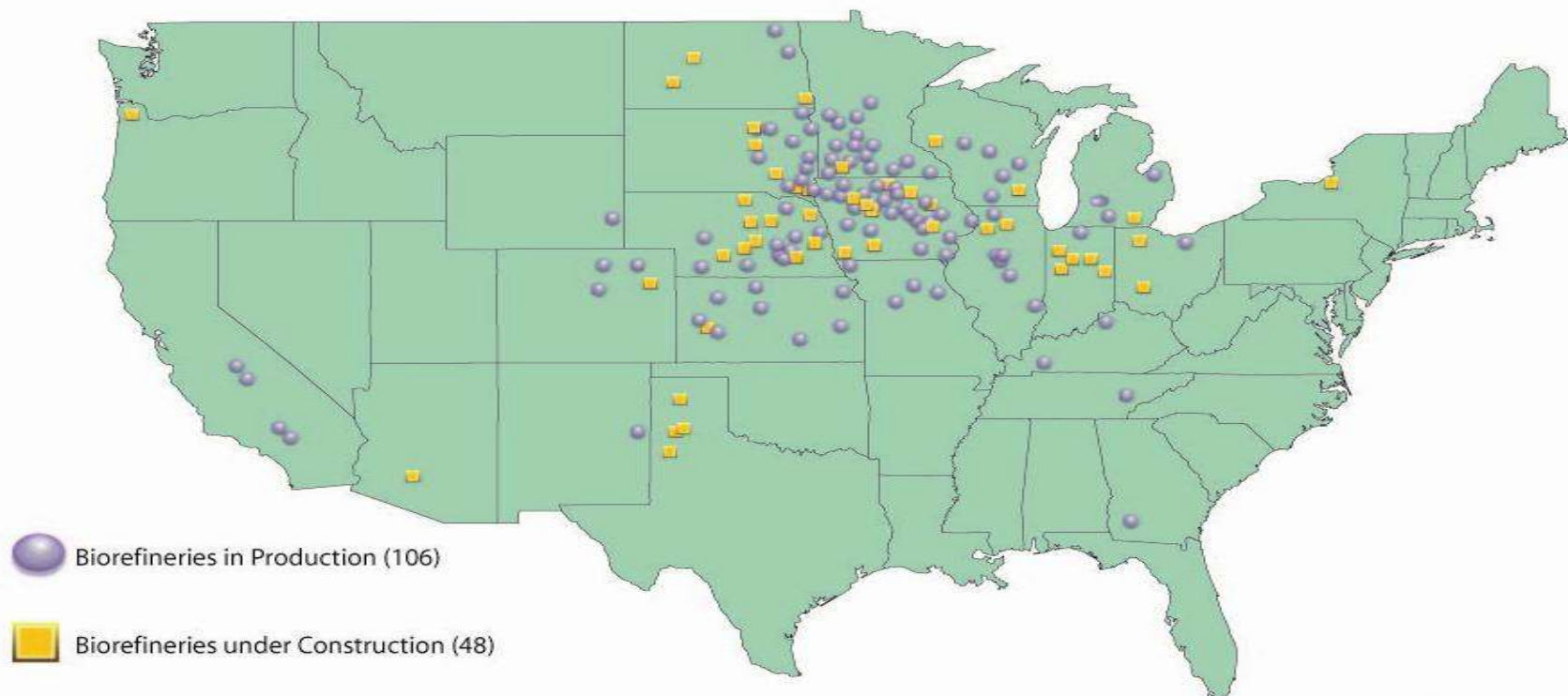
- ◆ **Total current annual production capacity**
 - 101 existing ethanol plants; 4,718 million gallons
- ◆ **Construction/expansion projects currently underway**
 - 41 projects; 2,222 million gallons in additional capacity
 - Total planned capacity: 7,040 million gallons.
- ◆ **90% of current output produced in five states: Illinois, Iowa, Nebraska, Minnesota, and Indiana.**

Top 5 Ethanol Producers (No. Plants)	2006 Capacity (million gallons/year)
Archer Daniels Midland (7)	1,070
VeraSun Energy Corp. (3)	230
Hawkeye Renewables (2)	200
Aventine Renewable Energy (2)	150
Cargill (2)	118

Ethanol

Distribution of Ethanol Producers

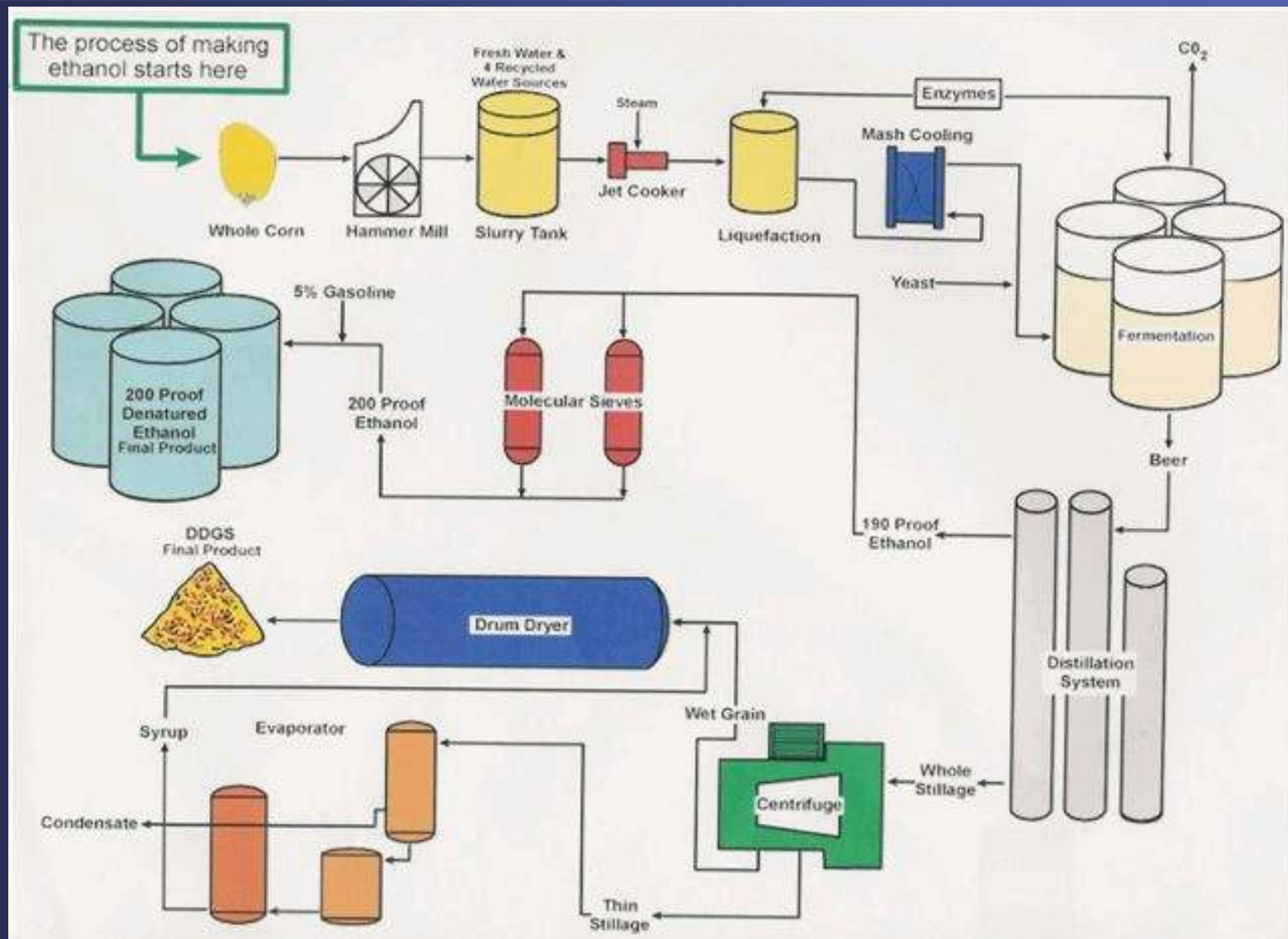
U.S. Ethanol Biorefinery Locations



Source: Renewable Fuels Association, December 29, 2006

Source: Renewable Fuels Association

Ethanol Production Process



Ethanol

Production Process (cont'd)

1. **Cleaned corn is ground, mixed with water, and cooked with enzymes to convert the starch into sugar.**
2. **Yeast is added to the mash in batch fermentation tanks. The yeast breaks down sugar into alcohols, primarily ethanol, and carbon dioxide (CO₂).**
3. **When fermentation is complete, ethanol is distilled to produce 190 proof ethanol (97.5% ethanol). The ethanol is further purified in a molecular sieve to 200-proof (100% ethanol).**
4. **The 200-proof ethanol is denatured with gasoline (5% gasoline) and stored pending load out to customers.**
5. **The solids-rich material recovered from the bottom of the beer still is dewatered mechanically. This “wet cake” contains about 67% water. The wet cake can be further dehydrated in heated dryer to produce dried distillers grain with solubles (DDGS), which only contains about 10 percent water.**

Oil Storage at Ethanol Plants

- ◆ **Average bulk storage capacities (based on review of characteristics of 19 plants):**
 - *140,000 gallons 190-proof ethanol stock tank*
 - *140,000 gallons 200-proof ethanol stock tank*
 - **90,000 gallons denaturant (gasoline) tank**
 - **1,500,000 gallons denatured ethanol tanks (5% gasoline)**
- } Oil
- ◆ **Common storage tank capacity**
 - Gasoline: 60,000 and 100,000 gallons
 - Denatured ethanol: 750,000 gallons
 - ◆ **Plants have on average approximately 11 days of gasoline at site**
 - ◆ **Plants have an average of approximately 12 days of finished product (E95) storage capacity at site.**

Ethanol

Transportation

- ◆ **Cannot be transported through petroleum pipeline (susceptible to water).**
- ◆ **Transported primarily by truck, rail or barge, except for a few proprietary pipelines, according to Association of Oil Pipelines.**
- ◆ **Requires dedicated equipment and infrastructure.**
- ◆ **Appropriate shipping name for E85 ethanol fuel is currently “Flammable Liquid, N.O.S. (Ethanol, Gasoline)”**
 - PHMSA is working on revising the shipping description for alcohol and gasoline mixtures for clear identification.

Ethanol

Facility Case Example: Aventine Renewable Energy, Fairbanks, IA

- ◆ **Facility was completed in May 2006**
- ◆ **100 million gallons capacity**
- ◆ **Receives corn by railcar and truck; sends product by railcars and trucks.**
- ◆ **Ethanol and oil storage:**
 - One 100,000-gallon 190-proof ethanol tank
 - One 100,000-gallon 200-proof ethanol tank
 - **One 100,000-gallon denaturant (gasoline) tank**
 - **Two 750,000-gallon E95 ethanol blend tanks (1.5 million gallons total)**
 - **One 1,000-gallon diesel tank**
 - One 2,300-gallon fuel additive tank

Ethanol

Regulatory Requirements

- ◆ **Denaturant, denatured ethanol, and ethanol fuel contain gasoline and may be considered oil substances**
 - Feedstocks (grains/seeds) and intermediate products (pure 190-proof or 200-proof ethanol) are not oils.

Considerations for Response

◆ Key parameters (E85 ethanol blend):

- **Solubility:** Fuel ethanol mixes with water. At high enough concentrations of water, the ethanol will separate from the gasoline.
- **Specific gravity:** 0.76-0.78 Floats on water, but is slightly heavier than gasoline.
- **Volatiles:** volatile. Vapor pressure: 340-560 mm Hg
- **Vapor density:** 2.0-4.0 (air = 1) Denser than air and tends to settle in low areas.
- **Fire hazard:** Flashpoint: -20 to -4 °F. Eliminate ignition sources.
 - At low temperature (32°), E85 vapor is more flammable than gasoline vapor. However, at normal temperatures, E85 vapor is less flammable than gasoline.

Considerations for Response (cont'd)

◆ Fire Hazard

- Fires involving E85 and other ethanol/gasoline mixtures containing more than 10% ethanol **should be treated differently than traditional gasoline fires** because these mixtures are polar/water-miscible flammable liquids (i.e., they mix readily with water) and will degrade the effectiveness of fire-fighting foam which is not alcohol resistant.
- **PHMSA recommends use of alcohol-resistant foam to fight fires involving these fuel mixtures.**

Considerations for Response (cont'd)

- ◆ **Department of Transportation Hazmat Guide 127: Flammable Liquids (Polar/Water-Miscible)**
- ◆ **Emergency response in the event of spills or leaks**
 - Eliminate all ignition sources (no smoking, flares, sparks or flames in immediate area).
 - All equipment used when handling the product must be grounded.
 - Do not touch or walk through spilled material.
 - Stop leak if you can do it without risk.
 - Prevent entry into waterways, sewers, basements or confined areas.
 - A vapor suppressing foam may be used to reduce vapors.
 - Absorb or cover with dry earth, sand or other non-combustible material and transfer to containers.
 - Use clean non-sparking tools to collect absorbed material.
- ◆ **Emergency response for large spills:**
 - Dike far ahead of liquid spill for later disposal.
 - Water spray may reduce vapor; but may not prevent ignition in closed spaces.

Future Considerations

- ◆ **Drills and exercises**
- ◆ **Response training**
- ◆ **For more information, see:**
 - Biodiesel:
 - National Biodiesel Board: www.biodiesel.org
 - Ethanol
 - Renewable Fuels Association: <http://www.ethanolrfa.org/>
 - Handbook for Handling, Storing, and Dispensing E85, U.S. Department of Energy, NREL, July 2006 (includes MSDS for E85 ethanol fuel) (<http://www.eere.energy.gov/afdc/pdfs/40243.pdf>)
 - Department of Transportation Hazmat Guide 127: Flammable Liquids (polar/water-miscible) (<http://hazmat.dot.gov/pubs/erg/g127.pdf>)