

# BIODIESEL: RESPONSE CONSIDERATIONS PARTICIPANT MANUAL



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# Module 0 Introduction

## About This Course

**Course Goal** Upon the successful completion of this course, participants will have the knowledge related to biodiesel fuels, including their use, chemical and physical characteristics, transportation, and transfer.

### **Course Overview**

Course topics include:

- Module 0: Introduction
- Module 1: Chemical and Physical Characteristics of Biodiesel Fuels
- Module 2: Production and Manufacturing
- Module 3: Terminal Objective
- Module 4: Fire Fighting Foam Principles and Biodiesel Fuel
- Module 5: Personal Protective Equipment (PPE) and Decontamination

### **Target Audience**

This course is designed for individuals who will respond to biodiesel-related emergencies as well as those who work at fixed facilities and transport fuel.

**Delivery Method** Course delivery method consists of:

- lecture with PowerPoint presentations,
- case studies, and
- participant discussions.

**Course Prerequisites** None

**Course Length** 4 hours

## Administrative Information

Instructors will use this portion of the course time to familiarize you with facility safety and convenience features as well as any additional resources or equipment available to you.

# Module 1 Chemical and Physical Characteristics of Biodiesel Fuels

## Terminal Objective

Upon the successful completion of this module, participants will be able to describe the chemical and physical differences between pure gasoline, petrodiesel, and biodiesel.

## Enabling Objectives

1. Compare the chemistry of gasoline, petrodiesel, and biodiesel.
2. Describe the characteristics of biodiesel-blended fuels.
3. Discuss how biodiesel fuels react in fire situations.

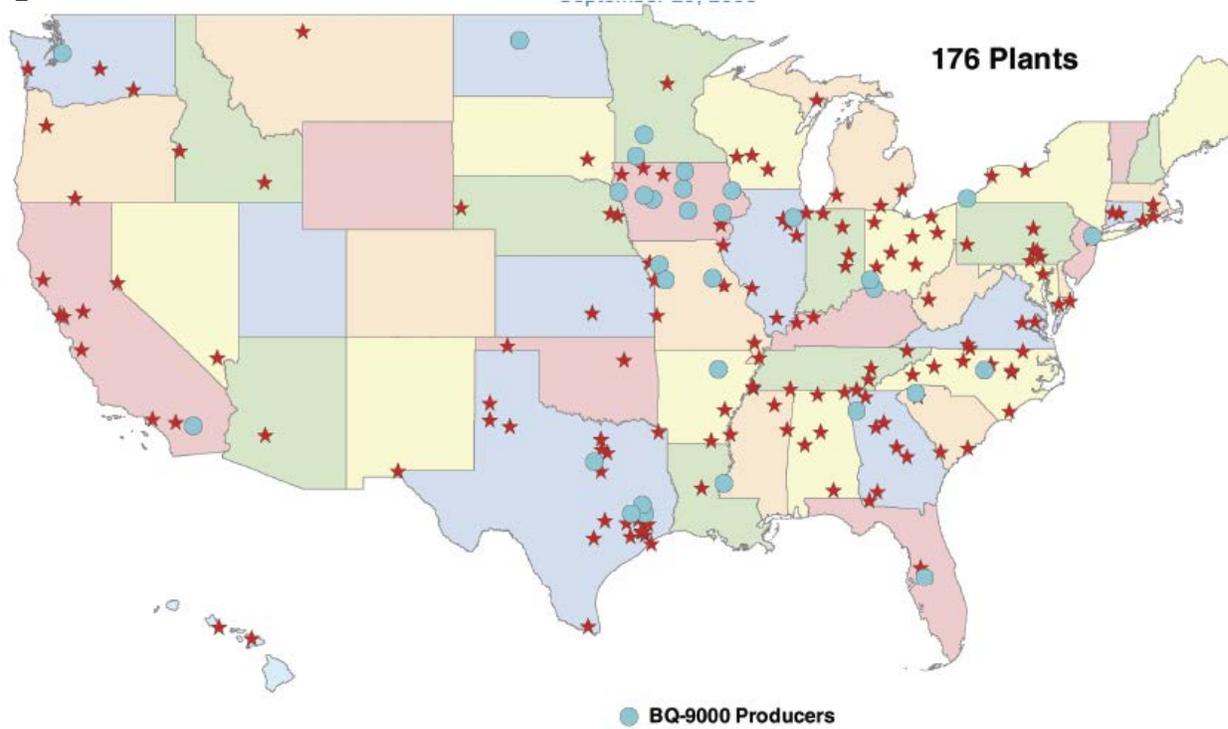
## Introduction

What is biodiesel? Biodiesel is a fuel that can be:

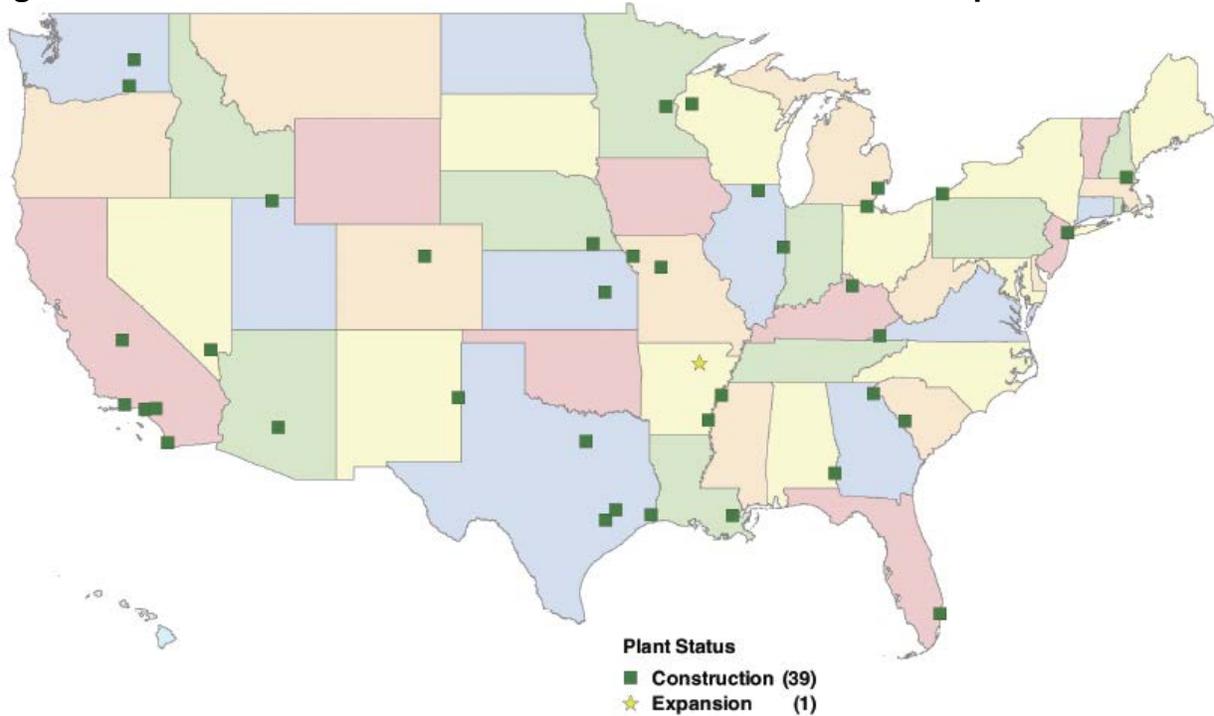
- domestically produced,
- renewable, and
- made from new and used plant oils, animal fats, and recycled restaurant grease.

The physical properties of biodiesel are similar to those of petroleum diesel (petrodiesel), but when burned as fuel, biodiesel significantly reduces greenhouse gas emissions and the release of toxic air pollutants. Biodiesel is also biodegradable. All of these characteristics make biodiesel an attractive alternative to petrodiesel. Biodiesel is also adaptable to a variety of uses since it can be blended in many different concentrations. They include B100 (pure biodiesel), B20 (20 percent biodiesel, 80 percent petrodiesel), B5 (5 percent biodiesel, 95 percent petrodiesel), and B2 (2 percent biodiesel, 98 percent petrodiesel). The most common biodiesel blend is B20, which qualifies for fleet compliance under the Energy Policy Act (EPA) of 1992 and Executive Order 13423. The EPA requires that certain federal fleets of light-duty vehicles (those containing twenty or more vehicles) operating in large metropolitan areas be converted to the use of alternative energy fuels. There are numerous exceptions to the policy, including military tactical, emergency, and law enforcement vehicles. Biodiesel and biodiesel-blended fuels are in use in growing quantities in the United States, and volumes have become substantial. Consumers in the United States use more than 62 billion gallons of diesel fuels per year. Today, there are more than 500 million gallons of biodiesel produced in the United States. Although biodiesel can be produced in small quantities for individual use, its acceptance has been such that commercial production facilities have spread across the United States (see Figures 1.1 and 1.2).

**Figure 1.1: Commercial Biodiesel Production Plants**



**Figure 1.2: Biodiesel Production Plants Under Construction or Expansion**



In September of 2008 there were 176 commercial biodiesel production facilities at work and another 40 were under construction or in the process of being expanded.

## Uses of Biodiesel and Biodiesel Blends

Biodiesel is most commonly used as fuel for vehicles. However, it can also be used as a heating fuel in domestic and commercial boilers. This is sometimes referred to as bioheat. While traditional methods of fire fighting against hydrocarbon (gasoline) fires have been found to be effective against these type fuels, the scope of fire fighting and spill cleanup efforts is extended to include potential incidents at production facilities, storage facilities, transportation facilities and routes, distribution centers, businesses, and even homes.

## Ethanol Versus Biodiesel

Americans often think of ethanol and biodiesel as the same thing, given that they are both “alternative fuels” and can both be made from plants such as corn. Some clues to their differences can be found in their names. Ethanol is made by combining alcohol with food sugars. It can be used in gasoline engines. Biodiesel, by contrast, is made by using alcohol to remove glycerin from plant oils. It can only be successfully used in diesel engines. It is interesting to note that ethanol is miscible with water, while biodiesel is not miscible with water. This difference in characteristics will have an impact on how fires can be effectively fought and how spills can be effectively cleaned.

## The Nature of Biodiesel

In order to understand the nature of biodiesel-blended fuels, emergency responders will need to understand the characteristics of polar solvents and hydrocarbons, their differences, and how these types of products interact. Under some conditions, biodiesel-blended fuels will retain certain characteristics as if they were petroleum-based fuels and under others they will exhibit polar solvent-type characteristics. Understanding these conditions will help emergency responders mitigate the various incidents according to the conditions found. When the biodiesel is still “natural” (before the plant oils and animal fats are converted to biodiesel through a process called transesterification), they are still a fuel because they are oils. These oils have an ignition temperature of more than 600°F (315.6°C) and, once lit, these oils will burn just like a petroleum oil. Once the methanol is added the polar solvency comes into play: first the ignition temperature is lowered dramatically, and second at mixing there is the hazard of the methanol vapors igniting, causing the methanol to separately burn.

## Activity 1.1—Definitions

### ***Purpose***

To allow participants to identify the definitions related to biodiesel.

### ***Participant Directions***

1. A list of definitions is provided in Worksheet 1.1.
2. Write in the appropriate definition for each in the space provided.
3. You will have approximately 5–10 minutes to complete the activity.

### Worksheet 1.1: Definitions

Oleophobic	Hydrophilic (water miscible)
Toxicity	Flash point
Hydrocarbon	Combustible liquid
Specific gravity	Flammable liquid
Vapor density	Hydrophobic (immiscible)
Auto-ignition temperature	Boiling point
Flammable range (Upper Explosive Limit [UEL]–Lower Explosive Limit [LEL])	

1. \_\_\_\_\_: A compound composed of only carbon and hydrogen and commonly obtained through the refining of crude oil; these are the primary constituent parts of both gasoline and diesel fuel.
2. \_\_\_\_\_: Has an affinity to water; “water-loving”
3. \_\_\_\_\_: Repels water; “water-fearing”; apparent when oil and water separate or when a drop of water beads on a coat of wax
4. \_\_\_\_\_: Lacks affinity for oil; will not readily mix with oil
5. \_\_\_\_\_: The lowest temperature at which a flammable liquid can form an ignitable mixture in air near the surface of the liquid; the lower the value is, the easier it is to ignite. This is the minimum temperature at which a liquid gives off vapor in sufficient concentrations to allow the substance to ignite.
6. \_\_\_\_\_: The minimum temperature required to ignite a gas or vapor to spontaneously combust in air without a spark or flame being present
7. \_\_\_\_\_: The ratio of the density of a substance to the density of water
8. \_\_\_\_\_: Relative weight of a gas or vapor in comparison to air
9. \_\_\_\_\_: The temperature at which the vapor pressure of a liquid equals the environmental pressure surrounding the liquid
10. \_\_\_\_\_: Concentration range for a gas or vapor within which a fire may result if an ignition source is introduced; includes an upper and a lower limit between which the danger lies.

11. \_\_\_\_\_: The degree to which a substance can harm humans or animals

12. \_\_\_\_\_: Any liquid with a flash point under 100°F; referred to as Class I liquids; examples are gasoline and ethanol

13. \_\_\_\_\_: Any liquid with a flash point above 100°F but below 200°F; examples include diesel fuel and kerosene

## Characteristics of Gasoline (Hydrocarbon)

Hydrocarbon fuels (gasoline, petrodiesel fuel, kerosene, and jet fuel) generally have similar characteristics whether they are flammable liquids or combustible liquids. In this program we will specifically identify the characteristics of gasoline as they relate to biodiesel and biodiesel blends. Gasoline is a hydrocarbon produced from crude oil by fractional distillation. It is immiscible and has an ignition point (flash point) of approximately -45°F (-43°C), varying with octane rating. Gasoline has a vapor density between 3 and 4. Therefore, as with all products with a vapor density greater than 1.0, gasoline vapors will seek low levels or remain close to ground level. Gasoline has a specific gravity of 0.72–0.76, which indicates it will float on top of water since it is immiscible or insoluble. Its auto-ignition temperature is between 536°F and 853°F (280°C and 456°C), and it has a boiling point between 100°F and 399°F (38°C and 204°C) depending on fuel composition. Gasoline is not considered a poison but does have harmful effects after long-term and high-level exposure that can lead to respiratory failure. Smoke from burning gasoline is black and has toxic components. Gasoline's greatest hazard is its flammability even though it has a fairly narrow flammability range (LEL is 1.4 percent and UEL is 7.6 percent).

## Characteristics of Petroleum Diesel (Petrodiesel)

Petrodiesel is produced from petroleum and is a product of the distillation of crude oil. Its color is generally amber. It is immiscible with water, has a high boiling point (typically greater than 300°F [149°C]), and low vapor pressure (0.40 millimeters of mercury [mmHg]). The flash point of petrodiesel is between 100°F and 160°F (38°C and 71°C). The product has a specific gravity between 0.82 and 0.95, less than that of water, and a vapor density greater than 1, making it heavier than air. Exposure to petrodiesel can cause irritation to the eyes and damage to the respiratory system. Petrodiesel fires are considered to be Class B fires. These fires will render thick, black smoke that is filled with toxic components.

## Characteristics of Biodiesel

Biodiesel is a liquid that varies in color, ranging between water white to pale gold and dark brown. However, it is most commonly seen as a water white to pale golden liquid with a slight odor. It is immiscible with water, has a high boiling point (360–640°F [182–338°C]), and low vapor pressure (less than 2 mmHg). The flash point of biodiesel (199°F [93°C]) is significantly higher than that of petrodiesel (100°F [38°C]) or gasoline (-45°F [-43°C]). Biodiesel has a specific gravity between 0.86 and 0.90, less than that of water, and a vapor density in excess of 1, making it heavier than air. With its high flash point, biodiesel is considered to be less hazardous in terms of flammability. But, as with all combustible liquids, *it will burn*. It is a matter of the liquid being exposed to heat that will raise the temperature of the material to its

flash point. At this point the material will be giving off vapors and ignition will be likely to occur. Another property of combustible liquids is with high flash points they tend to have a high British Thermal Unit (BTU) output when they burn, producing large amounts of heat.

## Activity 1.2—Comparison of Gasoline, Petroleum Diesel (Petrodiesel), and Biodiesel

### *Purpose*

To allow participants to discuss the differences and similarities in the chemical and physical properties of biodiesel, petrodiesel, and gasoline.

### *Participant Directions*

1. Review the information in module 2.
2. Fill in Table 1.1.

**Table 1.1: Gasoline, Petrodiesel, and Biodiesel**

	<b>Gasoline</b>	<b>Petrodiesel</b>	<b>Biodiesel</b>
Flash Point	_____	_____	_____
Ignition Temperature	536–853°F (280–456°C)	410°F (210°C)	~300°F (~149°C)
Specific Gravity	_____	_____	_____
Vapor Density	_____	_____	_____
Vapor Pressure	_____	_____	_____
Boiling Point	_____	_____	_____
Flammable Range (LEL–UEL)	1.4–7.6	0.6–4.7	Not available
Smoke Character	_____	_____	_____
Toxicity	_____	_____	_____
Solubility	_____	_____	_____

## **Biodiesel-Blended Fuels**

Biodiesel can be used alone or as a blended solution when mixed with traditional diesel fuel (petrodiesel). As was mentioned in previously, biodiesel blends are categorized by the percent of biodiesel in the mix. The system, called “B factor” works as follows:

- B20: contains 20 percent biodiesel
- B99: contains 99 percent biodiesel
- B100: is pure biodiesel

The mixing of biodiesel-blended fuels can take place at a plant (before the mixture is loaded into tanker trucks), splash mixed in the tanker trucks (by adding first one type of fuel then the other into the truck), or line-mixed (loading given percentages of each type of fuel into the tank at the same time).

## **Summary**

Biodiesel is a fuel that is plentiful and nonflammable in its natural state. It is important to know the percentage of biodiesel in any biodiesel-blended product because, although the inherent dangers associated with fire and spills will be present, there is a converse relationship between biodiesel level and flammability.

# Module 2 Production and Manufacturing

## Terminal Objective

Upon the successful completion of this module, participants will be able to describe the process involved in the production of biodiesel.

## Enabling Objectives

1. Describe the production process for biodiesel fuel.
2. Identify common components found in biodiesel fixed facilities.
3. Identify hazards associated with biodiesel production.

## Introduction

Biodiesel is a product that is on the front lines of the war against high fuel prices and global warming. The interest in biodiesel has led to the development of many biodiesel production plants across the country. The awareness of biodiesel has also led to biodiesel enthusiasts making biodiesel for their own use. What is this process?

## Transesterification

Although the production of biodiesel is something that can be done at home, it is made possible by a process with an impossible name—transesterification.<sup>1</sup> What this complicated name means, essentially, is that plant oils will have their chemical structure altered through the use of alcohol and a chemical catalyst (a substance that increases the rate of a chemical reaction). This will thin and clarify the oil enough to be usable in engines. To accomplish this, plant oils are heated (to a given temperature) and then the alcohol and the catalyst are added. At this point, the mixture is mixed for a time and then allowed to settle. When the product settles, there will be two or three layers. The top layer will be biodiesel (chemically called an *ester*), the middle layer will usually be a soap compound, and the bottom layer will be glycerin (which coincidentally is used in soap). The bottom layer(s) are drained off and finally the biodiesel is washed to get rid of any impurities and then dried to get rid of any remaining water.

## Components

### ***Feedstock***

A variety of animal fats and plant oils can be used in the production of biodiesel. Some of these fats and oils include:

- soybean oil,
- canola oil,
- 1. For a more technical definition of transesterification, see Appendix C.
- rapeseed oil,
- palm oil,
- recycled cooking oil,
- beef tallow,
- poultry fat,
- cottonseed oil,
- coconut oil,

- algal oil,
- and jatropha oil.

## **Alcohol**

The major reasons why methanol is the current alcohol of choice are: • Methanol is less expensive than ethanol.

- Ethanol is a larger molecule than methanol and it is incrementally more difficult to get the reaction to go to completion, requiring longer reaction times or higher temperatures.
- It is more difficult to recycle the excess ethanol due to its azeotrope with water at the 95 percent concentration.

## **Catalysts**

In a transesterification reaction, acids are used to neutralize the reaction and not as a catalyst. In an esterification reaction, acids are used as a catalyst while the bases are used to neutralize the reaction.

## **Co-Products**

The primary co-product of biodiesel production is glycerin (glycerol). The glycerin also generally contains impurities like water, salts, and methanol and will require additional refining to bring it up to pharmaceutical grade. Glycerin has over 1,500 known end uses, including many applications as an ingredient or processing aid in cosmetics, toiletries, personal care, drugs, and food products.

**Biodiesel and Glycerin** Due to their high flash points, biodiesel and glycerin are not classified as flammable liquids by the U.S. Department of Transportation (DOT) or the National Fire Protection Association (NFPA). However, both will ignite and burn at sufficiently high temperatures. Class B flammable liquids tactics with foam will be required to extinguish both of these materials. The best recommendation is to stock quantities of Alcohol-Resistant Aqueous Film-Forming Foam (AR-AFFF) foam since it will work on both polar solvents and hydrocarbons.

## **Production Facilities**

The biodiesel production process is simple enough that home brewing has become something of a cottage industry in the United States. Instructions for brewing small amounts of biodiesel at home are found all over the Internet and there are no guidelines aside from local codes and ordinances that must be followed by the home brewer. Large commercial biodiesel production facilities, by contrast, are generally regarded as refineries and must meet all of the safety regulations associated with commercial properties.

These will include:

- special permits for the installation of above-ground storage tanks,
- maintenance of a supply of AR-AFFF foam,
- special permits for the storage of non-miscible oils,
- inspection of boilers and pressure vessels used in production,
- sprinkler system designed for use with methanol,
- methanol leak detection system, and
- containment systems.

## **Hazards of Biodiesel Production**

Interestingly, the greatest hazard associated with biodiesel production comes, not from the biodiesel, but from the chemicals required to produce it. Methanol can cause liver damage, eye damage, brain damage, and several other symptoms. It is flammable, burns explosively, and can be absorbed through the skin. Sodium hydroxide is also known as caustic lye. It is corrosive and can cause severe burn damage via inhalation and skin contact. Although not flammable on its own, contact with metals such as aluminum, magnesium, tin, and zinc cause formation of flammable hydrogen gas. Sodium hydroxide in contact with acids and organic halogen compounds may cause violent chemical reactions. Potassium hydroxide is also known as caustic potash. It is extremely corrosive and can cause severe burn damage via inhalation and skin contact and is destructive to all body tissues. It is fatal if swallowed. Although it is not combustible on its own, potassium hydroxide can mix with water or moisture and cause enough heat to ignite combustibles.

## **Summary**

The transesterification process of producing biodiesel involves taking organic oil and altering its chemical structure through the use of an alcohol and a catalyst. The end product is thin and clear enough to be safely used in diesel engines. Biodiesel is a product that is safe to use but dangerous to manufacture. The chemicals that are used in the transesterification process are more hazardous than the final product. The process is simple enough that many individuals across the United States have established small home breweries.

# Module 3 Planning and Response

## Terminal Objective

Upon the successful completion of this module, participants will be able to develop strategies for preplanning at biodiesel facilities and develop strategies for controlling/fighting fires and spills associated with biodiesel fuels.

## Enabling Objectives

1. State the components of preplanning.
2. Discuss the requirements for assessing a facility's emergency response capabilities.
3. State the effectiveness of foam types in fighting biodiesel fuel fires.
4. List the ways in which foam applications suppress fire.
5. Compare the effectiveness of the different type of foam application techniques.
6. Discuss containment techniques for biodiesel fuels.
7. Discuss fire fighting strategies and techniques for incidents involving biodiesel fuels.
8. Determine effective strategies for biodiesel fuel emergencies.

## Introduction

Plant/Facility personnel must be brought into planning sessions. Developing a strong relationship with these key players is critical for a safe and competent response to their facility. They will provide important information for your preplan and during responses. Having meetings early and often to discuss your department's role in planning and during emergencies, along with the facility's expectations and capabilities, will be of the most assistance as you complete this assessment. Small "mom and pop" or even smaller, home-based biodiesel facilities are common. They may have smaller quantities of the same materials used in production but they may present a greater hazard. These smaller operations are not likely to follow the same safety design as large, commercial biodiesel facilities. They will also be difficult to preplan. You will need to understand your local and state fire codes as they pertain to the use and storage of flammable and corrosive materials.

## Preplanning for the Facility

Preplanning is a vital factor in the strategy of controlling an emergency situation. The level of success obtained in resolving an emergency can, in most cases, be determined by the amount of advance preparation made by fire fighting personnel. The purpose of pre-incident planning is to enable attack preparations and fire-fighting operations to be carried out at the scene of an emergency as efficiently and effectively as possible. The incident management attack operation can begin more quickly if details about the incident site are known prior to the arrival of the firefighters and if positions of equipment and possible hose layouts have been predetermined. When effective pre-incident plans have been made, less time needs to be spent on making decisions concerning the incident site during and after the size-up process. Steps involved in the preplanning process include:

- *Information gathering:* This step includes collecting pertinent information at the selected site that might affect incident management operations, such as construction features, exposures,

utility disconnects, fire hydrant location, water main sizes, suppression systems, foam capabilities, the amount of foam on hand (if any), and anything else that would affect response operations if an emergency should occur.

- *Information analysis:* The information gathered must be analyzed in terms of what is pertinent and vital to incident suppression operations. An operable pre-incident plan must then be formulated and put into a usable format that can be used at the incident site.

- *Information distribution:* All parties that will help to solve the problem should receive copies of the plan so that they become familiar with both the plan and pertinent factors relating to it.

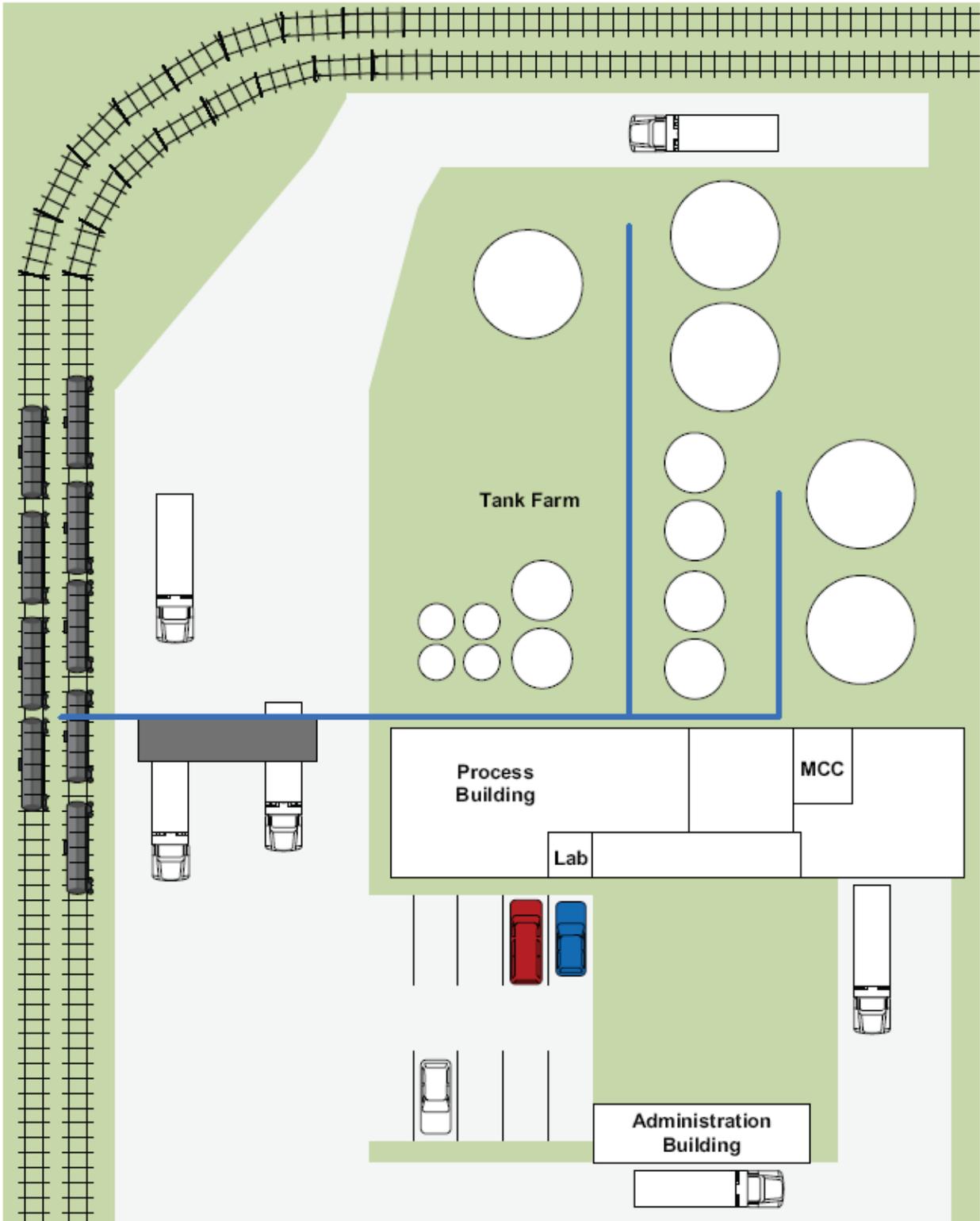
A risk-based response planned on facts, science, and potential circumstances gathered through preplanning with facility personnel will prove to be invaluable as you consider:

- fire,
- hazardous materials,
- medical needs, and
- establishing a unified Incident Command System (ICS) with the facility personnel.

## **Common Plant Layout**

Although there are many bio-refinery design and construction firms, all commercial plants share these common facilities areas (see Figure 3.1). Each area will have unique hazards. Responding to these hazards will be part of your consideration as you assess your jurisdiction's abilities.

**Figure 3.1: Typical Biodiesel Plant Layout**



- Administration building:

- The common construction will be a lightweight wood frame construction with a truss roof. If this building has a basement, the floors will likely contain trusses. This building may have an alarm and/or a sprinkler system.

- Occupancy is administrative and office support employees. The building is commonly occupied Monday through Friday during normal office hours.

- Process building:

- This is the area of the facility where the process of taking the selected feed stock and converting it into biodiesel occurs. This area of the facility will have the greatest potential for fire or other events associated with the storage and use of hazardous materials.

- The construction of these building would be classified as Type II Non Combustible.

- Some areas may be five stories in height.

- Occupancy by employees will be 24 hours each day. The number of employees, contractors and visitors will generally be much greater Monday through Friday 7 a.m. to 7 p.m.

- Some facilities will have these buildings fully protected by automatic and deluge sprinkler systems capable of delivering 2,500 gallons per minute (gpm). The fire protection system will likely have a building that houses the fire pump and backup generator for power failure.

- The process area may have standpipe systems located throughout.

- The process building will contain numerous hazardous materials, some in large quantity. Common hazardous materials found in this area will be organic oil, corrosives such as methanol, hydrochloric acid, phosphoric acid, sodium or potassium hydroxide, and sodium methylate (a mixture of 30 percent sodium hydroxide and 70 percent methanol).

- It is critical that you identify what hazardous materials, storage container types, and quantities are located at the facility in your jurisdiction. This information will be used in your assessment and preplans for a release.

- Physical hazards may include high-temperature liquids and steam, electrical, heights, mechanical, and permit-required confined spaces.

- Some facilities may use nitrogen to blanket flammable process involving methanol creating a potential low oxygen hazard.

- Non-sparking and intrinsically safe equipment is required.

- *Note:* A more detailed layout of a commercial biodiesel facility can be found in Appendix D.

- Motor Control Center (MCC) rooms:

- The MCC is the location of the main electrical control for process functions such as mixer, pump, and conveyor motors in a facility. A typical facility commonly will have two to four MCC rooms. The MCC room is not meant for continuous employee occupancy.

- The MCC rooms will contain several banks of high voltage 480 volt motor controls.

- Hazards of the MCC rooms would be typical hazards of high voltage: electrical shock and arc flash potentials.

- It is common to have high voltage transformers (600 volt) adjacent to or in the MCC rooms.

- The MCC room is the location for the application of locks in the event of controlling energy in a lock out/tag out situation.

- MCC rooms may have halogen, carbon dioxide, or an alternative fire extinguishing system.

- Tank farm/bulk storage:

- The tank farm area of a typical facility will contain six tanks that range in capacity from 500 gallons to 1 million gallons. The fire department must become familiar with types of storage

tanks, products involved, capacity of storage tanks, and any spill or fire protection systems. The tank farm area is Hazard Class I rated. Use of intrinsically safe equipment in this area is required.

— It is common to have the following tank contents:

- Methanol (methyl alcohol): United Nations (UN) 1230
- Hydrochloric acid: UN 1789
- Phosphoric acid: UN 1805
- Sodium hydroxide solution or potassium hydroxide solution: UN 1824/1814
- Sodium methylate, solution in alcohol: UN 1289
- Biodiesel
- Glycerin

— The tank farm will be surrounded by containment berms.

— Piping may have fusible links isolation of piping in the event of a fire.

— The tank farm may have fixed protection foam application piping into the tanks for the delivery of foam in the event of a fire.

— The tank farm may have semi-fixed protection devices in the form of monitor nozzles with foam eductor tubes applied to fire hydrants located around the tank farm for the application of foam.

— The tank farm may employ detection and monitoring systems.

• Product load out (rail and highway):

— Biodiesel load out is the area in which rail tank cars and highway cargo tanks are loaded with biodiesel and glycerin for shipment.

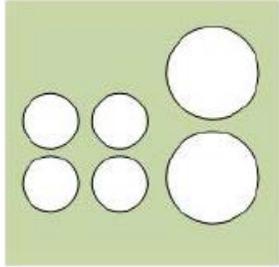
— This area is also the area for delivery of flammable and corrosive chemicals used in the biodiesel production process.

— Hazards in the load out area would include flammable atmospheres and corrosive hazards.

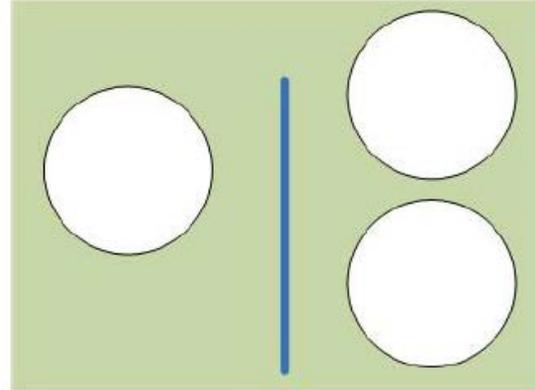
— This area may be classified Hazard Class I. Use of intrinsically safe equipment and tools is required in these areas where methanol and sodium methylate are being unloaded.

## Typical Storage in Tank Farm

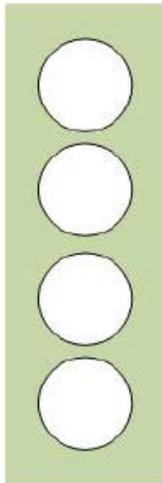
Corrosives  
and  
Catalysts



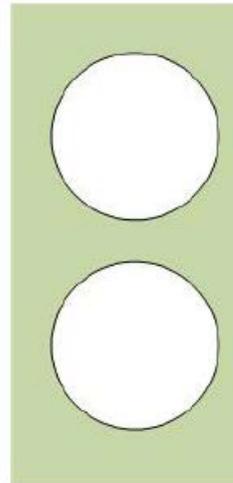
Finished  
Product



Water



Feedstock



## Safety Design Built Into Facilities

The facility should have many safety designs and features built in according to local codes. Your local jurisdiction and/or state may have specific codes and regulations for hazardous materials, fire, and life safety. The facility will typically be engineered and designed following nationally recognized codes and standards along with insurance carrier requirements even if the jurisdiction has not adopted codes or standards. The following is a list of some of the common features built into many facilities. You should become aware of the specific systems in the facility in your jurisdiction.

- Sprinkler system
- Standpipe system
- Hydrant system
- Water supply system
- Backup generators for power failure
- Alarm system

- Containment systems
- Container relief devices
- Emergency showers
- Foam suppression systems

## **Preplan Items**

- Site maps and drawings
- Hazardous materials list and Material Safety Data Sheet (MSDS)
- Tier II reports
- Risk Management Plans (RMP)
- Emergency contact numbers (24 hours)
- Any special training by employees in emergency response
- Any previous incidents
- Fire suppression systems
- Water supply system

## **Sample Preplan Forms**

There are many ways to design preplan forms. The important aspects are that they include all of the information that will be necessary to improve an emergency response at a given facility. Example 3.1 is a sample of a preplan form.

### Example 3.1: Sample Preplan Form

Location:		
Building/Site Name:		
Type of Business:		
Building Size—Frontage:	x Depth:	= Area:
Owner:		
Owner's Address:		
Owner's Telephone:		
Owner's Agent:		
Agent's Address:		
Agent's Telephone:		
Emergency Contact:		
Emergency Telephone:		
Cleanup Contractor:		
Prepared by:		
Remarks/Special Information (number of shifts, security on premises, special orders, other contacts not listed above, etc.):		
Specific Property Use:		
Number of Stories:		
Age of Building		
<i>Construction Type</i>		
1. Fire Resistive	5. Heavy Timber	
2. Protective Non-Combustible	6. Unprotected	
3. Protected Ordinary	7. Unprotected Ordinary	
4. Protected Wood Frame	8. Unprotected Wood Frame	
1st Type:                    %	2nd Type:                    %	
Relevant Features:		
Type of Roof Construction:		

<i>Standpipes</i>			
Exterior Connections:		Locations:	
<i>Interior Connections—Wet:</i>		Dry:	
Location:		Type:	
<i>Sprinkler Systems</i>			
Exterior Connection Location:			
% Coverage—Wet:		Dry:	Both:
Shut-Off Location			
Valves—Open (Y/N):		Supervised (Y/N):	Zoned Areas (Y/N):
<i>Other Extinguishing Systems (halon, CO<sub>2</sub>, dry powder, etc.)—</i>			
Type:		Location:	
<i>Warning System</i>			
Detection Type (heat, smoke, both):			
Alarm Company:		Telephone:	
Access and Entrances:			
<i>Material Information</i>			
Shipping Name:		UN #:	Class #
Chemical Name:		CAS #:	
<input type="checkbox"/> Explosive	<input type="checkbox"/> Poison	<input type="checkbox"/> Gas	<input type="checkbox"/> Color:
<input type="checkbox"/> Flammable	<input type="checkbox"/> Radioactive	<input type="checkbox"/> Liquid	<input type="checkbox"/> Odor:
<input type="checkbox"/> Oxidizer	<input type="checkbox"/> Corrosive	<input type="checkbox"/> Solid	<input type="checkbox"/> Chemical Formula
Average amount stored on site:			
<i>Properties &amp; Hazards</i>			
Boiling Point:	Flash Point:	Specific Gravity:	
Vapor Pressure:	Melting Point:	Ignition Temperature:	
UEL:	LEL:	Vapor Density:	Soluble:

<i>Health Hazards</i>	
Routes of Entry: <input type="checkbox"/> Inhalation <input type="checkbox"/> Dermal <input type="checkbox"/> Ingestion	Target Organs:
<i>Container Information</i>	
Container Type:	Capacity:
Container Material:	
Container Used: <input type="checkbox"/> Fixed <input type="checkbox"/> Portable <input type="checkbox"/> Mobile	Features: <input type="checkbox"/> Insulated <input type="checkbox"/> Pressurized <input type="checkbox"/> Armored Connection to Alarm (local, central, master auxiliary):

## Activity 3.1—Preplanning

### ***Purpose***

To allow participants to practice preplanning for a biodiesel incident.

### ***Participant Directions***

1. Working in your group and using the Worksheet 3.1 and Figure 3.1, consider the hazards associated with your area of the commercial biodiesel facility.
2. Complete the preplanning form.
3. Be prepared to discuss results with class.

### Worksheet 3.1: Sample Preplan Form

Location:		
Building/Site Name:		
Type of Business:		
Building Size—Frontage:	x Depth:	= Area:
Owner:		
Owner's Address:		
Owner's Telephone:		
Owner's Agent:		
Agent's Address:		
Agent's Telephone:		
Emergency Contact:		
Emergency Telephone:		
Cleanup Contractor:		
Prepared by:		
Remarks/Special Information (number of shifts, security on premises, special orders, other contacts not listed above, etc.):		
Specific Property Use:		
Number of Stories:		
Age of Building		
<i>Construction Type</i>		
1. Fire Resistive	5. Heavy Timber	
2. Protective Non-Combustible	6. Unprotected	
3. Protected Ordinary	7. Unprotected Ordinary	
4. Protected Wood Frame	8. Unprotected Wood Frame	
1st Type:                    %	2nd Type:                    %	
Relevant Features:		
Type of Roof Construction:		

<i>Standpipes</i>			
Exterior Connections:		Locations:	
<i>Interior Connections—Wet:</i>		Dry:	
Location:		Type:	
<i>Sprinkler Systems</i>			
Exterior Connection Location:			
% Coverage—Wet:		Dry:	Both:
Shut-Off Location			
Valves—Open (Y/N):		Supervised (Y/N):	Zoned Areas (Y/N):
<i>Other Extinguishing Systems (halon, CO<sub>2</sub>, dry powder, etc.)—</i>			
Type:		Location:	
<i>Warning System</i>			
Detection Type (heat, smoke, both):			
Alarm Company:		Telephone:	
Access and Entrances:			
<i>Material Information</i>			
Shipping Name:		UN #:	Class #
Chemical Name:		CAS #:	
<input type="checkbox"/> Explosive	<input type="checkbox"/> Poison	<input type="checkbox"/> Gas	<input type="checkbox"/> Color:
<input type="checkbox"/> Flammable	<input type="checkbox"/> Radioactive	<input type="checkbox"/> Liquid	<input type="checkbox"/> Odor:
<input type="checkbox"/> Oxidizer	<input type="checkbox"/> Corrosive	<input type="checkbox"/> Solid	<input type="checkbox"/> Chemical Formula
Average amount stored on site:			
<i>Properties &amp; Hazards</i>			
Boiling Point:	Flash Point:	Specific Gravity:	
Vapor Pressure:	Melting Point:	Ignition Temperature:	
UEL:	LEL:	Vapor Density:	Soluble:

<i>Health Hazards</i>	
Routes of Entry: <input type="checkbox"/> Inhalation <input type="checkbox"/> Dermal <input type="checkbox"/> Ingestion	Target Organs:
<i>Container Information</i>	
Container Type:	Capacity:
Container Material:	
Container Used: <input type="checkbox"/> Fixed <input type="checkbox"/> Portable <input type="checkbox"/> Mobile	Features: <input type="checkbox"/> Insulated <input type="checkbox"/> Pressurized <input type="checkbox"/> Armored Connection to Alarm (local, central, master auxiliary):

## Responding to Facility Incidents

Responding to incidents at biodiesel facilities will range from emergency medical and technical rescue to hazardous materials incidents. Fires involving products such as methanol must be viewed as hazardous materials responses. At a minimum all members should be trained to the National Fire Protection Association (NFPA) 472 first responder operations level. Your agency may have members trained to a higher level of response at the technician level that would allow for offensive control and containment techniques. Following the Analyze-Plan-Implement-Evaluate (APIE) process to form a risk-based response will lead to a safe and competent response (see Table 3.1).

**Table 3.1: Analyze-Plan-Implement-Evaluate (APIE) Process**

APIE Process	First Responder Actions
<i>Analyze the problem</i>	<ul style="list-style-type: none"> <li>• Consider dispatch information</li> <li>• Initiate an Incident Management System (IMS); designate a safety officer</li> <li>• Survey the scene: utilize a pre-incident plan; consider occupancy/location, container shapes/sizes, placards, and shipping papers/facility documents; take weather conditions into account</li> <li>• Collect and interpret information: determine the hazards; use the <i>Emergency Response Guidebook (ERG)</i>, <i>National Institute for Occupational Safety and Health (NIOSH) Pocket Guide to Chemical Hazards (Pocket Guide)</i>, and MSDSs; contact shipper, manufacturer, and the CHEMical TRansportation Emergency Center (CHEMTREC)</li> <li>• Conduct risk-benefit analysis</li> </ul>
<i>Plan the response</i>	<ul style="list-style-type: none"> <li>• Determine response objectives and defensive options</li> <li>• Determine the appropriate Personal Protective Equipment (PPE)</li> <li>• Identify emergency decontamination procedures</li> <li>• Assess vulnerable populations; consider evacuation versus shelter in-place</li> </ul>
<i>Implement the plan</i>	<ul style="list-style-type: none"> <li>• Establish and enforce scene control procedures</li> <li>• Implement the response plan</li> <li>• Perform defensive control functions: extinguishment, vapor suppression, defensive spill control, vapor dispersion, remote valve shut-off</li> <li>• Perform decontamination</li> <li>• Conduct rescue/recovery</li> <li>• Don, work in, and doff the appropriate PPE</li> </ul>
<i>Evaluate the progress</i>	<ul style="list-style-type: none"> <li>• Evaluate the status of the implemented plan</li> <li>• Communicate the status of the planned response</li> </ul>

## **Corrosives**

Corrosives, acids, and bases have chemical and thermal hazards associated with them to cause tissue damage and the recognition that chemical reactions generate heat. Corrosives can also have the potential to cause mechanical damage when contacting certain metals.

## **Flammables**

Flammable liquids (methanol) can burn freely and disseminate heat resulting in thermal damage. Containers with flammables may also be at risk of forceful explosions due to the stress caused by exposure to heat.

*Plan* the response • Determine response objectives and defensive options

- Determine the appropriate Personal Protective Equipment (PPE)
- Identify emergency decontamination procedures
- Assess vulnerable populations; consider evacuation versus shelter in-place

*Implement* the plan • Establish and enforce scene control procedures

- Implement the response plan
- Perform defensive control functions: extinguishment, vapor suppression, defensive spill control, vapor dispersion, remote valve shut-off
- Perform decontamination
- Conduct rescue/recovery
- Don, work in, and doff the appropriate PPE

*Evaluate* the progress

- Evaluate the status of the implemented plan
- Communicate the status of the planned response

## **Activity 3.2—Response**

### **Purpose**

To allow participants to practice making decisions during a biodiesel incident.

### **Participant Directions**

1. Working in your group, read your assigned scenario and respond to the associated questions.
2. Be prepared to discuss your results with the class.

### **Scenario 1**

Your department is dispatched to a garage fire in a residential neighborhood. Upon arrival you find a two-car garage with a large volume of fire. The owner advises he has a home biodiesel processing system operating in the garage. The owner advises that the following items are in the garage: 600 gallons of biodiesel, glycerin, sodium hydroxide, sulfuric acid, phosphoric acid, and six 55-gallon drums of methanol.

- What will you select for a strategy: offensive or defensive? \_\_\_\_\_

\_\_\_\_\_

\_\_\_\_\_

- With the information provided on the hazardous materials present, identify potential hazards and their associated outcomes. \_\_\_\_\_

\_\_\_\_\_

\_\_\_\_\_

- 
- 
- Using the current version of the ERG, what would you establish as an isolation distance? \_\_\_\_\_
- 
- 
- 

### **Scenario 2**

You are dispatched to a biodiesel facility for a worker trapped in a tank. Upon arrival facility personnel inform you a contractor has collapsed inside a 100,000-gallon tank. The tank was being repaired and a contractor entered it after returning from lunch. The worker collapsed and has not responded for about 10 minutes. Facility personnel inform you they found that a nitrogen line into the tank had been opened while the site was left unattended for lunch. The valve on that line has been closed prior to your arrival. The facility personnel put a monitor in the tank and got a 5 percent oxygen level.

- What steps would be taken to identify potential hazards to rescuers? \_\_\_\_\_
- 
- 
- 

- Is this a rescue or recovery? \_\_\_\_\_
- 
- 
- 

- What tactics would be used to remove the contractor from the confined space? \_\_\_\_\_
- 
- 
- 

### **Scenario 3**

You are dispatched to a tanker fire at a local biodiesel facility where a highway cargo tank Motor Carrier (MC)/Department of Transportation (DOT) 307/407 was unloading product. The hose came loose, spilling about 500 gallons of product and igniting. Upon arrival you find a pool of fire 100 x 30 feet. The truck has a hazard Class 3 placard with UN # 1230.

- What is the product 1230? What is the current version of the ERG guide page? \_\_\_\_\_
- 
- 
- 

- What is the primary hazard of 1230? What is the secondary hazard? \_\_\_\_\_
- 
- 
- 

- What is the evacuation and isolation distance listed in the current version of the ERG? \_\_\_\_\_
- 
- 
-

- What is the ERG recommendation for protective clothing? \_\_\_\_\_  
\_\_\_\_\_  
\_\_\_\_\_

## Summary

There is no substitute for preplanning a potential incident. Knowing what hazards you will likely encounter will enable you to prepare to face them, enhancing safety for everyone involved. Time spent developing relationships with the agencies and individuals who will be of the most help during an incident is time well spent. While it is less likely that you will be able to fully preplan for home-brew incidents, at the very least, you will want to become familiar with your local and state fire codes as they pertain to the use and storage of flammable and corrosive materials.

# Module 4 Fire Fighting Foam Principles and Biodiesel Fuel

## Terminal Objective

Upon the successful completion of this module, participants will be able to develop foam use strategies for controlling/fighting fires associated with biodiesel-blended fuels.

## Enabling Objectives

1. Describe the manner in which foam applications can be used to fight fuel fires.
2. List the ways in which foam applications suppress fire.
3. Predict when to fight fuel fires and when to simply protect surrounding areas.
4. State the generally accepted “rule of thumb” for the use of foam applications on biodiesel/biodiesel-blended fuel fires.

## Introduction

As discussed previously, we have seen that the commercial production of biodiesel is quite large and likely to continue to increase. The predominate danger from biodiesel emergencies is not from the biodiesel itself, but instead from tanker trucks and rail cars carrying large amounts of chemicals used in the production of biodiesel. Responders need to be prepared for large-scale emergencies and prepared with the most effective techniques and extinguishing media. This module will focus on foam basics and then foam applied specifically to biodiesel-related emergencies.

**Note:** This content refers to Class B foam application and does not include a discussion on Class A foam or compressed air foam systems.

## Basic Foam Principles

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### **What is Foam?**

As defined in National Fire Protection Association (NFPA) 11, low-expansion foam is: “...an aggregate of air-filled bubbles formed from aqueous solutions which is lower in density than flammable liquids. It is used principally to form a cohesive floating blanket on flammable and combustible liquids, and prevents or extinguishes fire by excluding air and cooling the fuel. It also prevents reignition by suppressing formation of flammable vapors. It has the property of adhering to surfaces, which provides a degree of exposure protection from adjacent fires.”

### **Why Use Foam?**

Many extinguishing agents are effective on flammable liquids. However, foam is the only agent capable of suppressing vapors and providing visible proof of security. Reasons to use foam include:

- A foam blanket on an unignited spill can prevent a fire.
- The suppression of vapors prevents them from finding an ignition source.
- Foam can provide post-fire security by protecting the hazard until it can be secured or removed.
- Foam can provide protection from flammable liquids for fire and rescue personnel during emergency operations.

### ***How Foam Works***

Foam can control and extinguish flammable liquid fires in a number of ways. Foam can:

- exclude oxygen from the fuel vapors and thus prevent a flammable mixture,
- cool the fuel surface with the water content of the foam,
- prevent the release of flammable vapors from the fuel surface, and
- emulsify the fuel (some environmental foams).

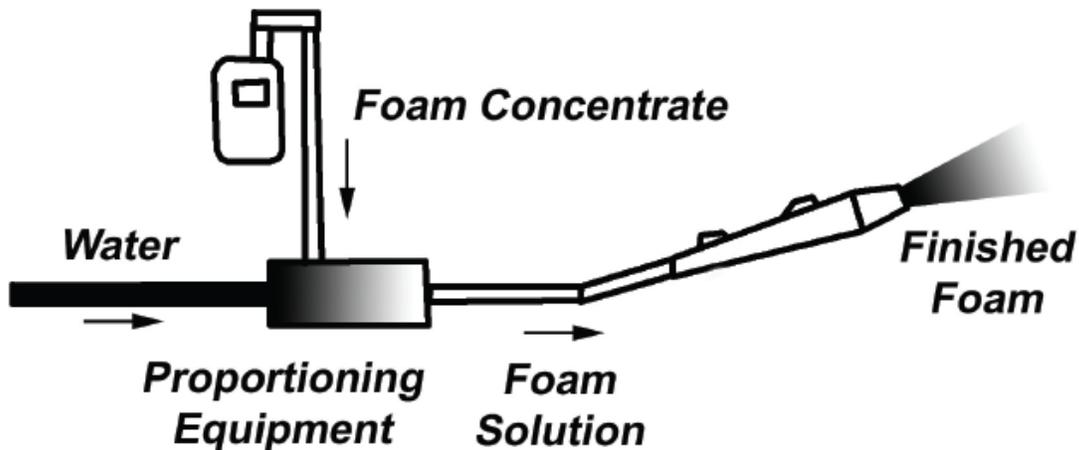
### **Foam Tetrahedron**

Foams used today are primarily of the mechanical type. This means that before being used, they must be proportioned (mixed with water) and aerated (mixed with air). Four elements are necessary to produce a quality foam blanket. These elements include:

- foam concentrate,
- water,
- air, and
- aeration (mechanical agitation).

All of these elements must be combined properly to produce a quality foam blanket (see Figure 4.1).

Figure 4.1: Foam Production



If any of these elements are missing or are not properly proportioned, the result is a poor-quality foam or no foam at all.

### ***What is Foam Not Effective On?***

Foam is *not* effective on all types of fires. It is important to know the type of fire and the fuel involved. Foam is not effective on:

- Class C fires,
- three-dimensional fires,
- pressurized gases, and
- Class D fires.

### **Foam is Not Effective on Class C Electrical Fires**

Class C fires involve energized electrical equipment; water conducts electricity. Since foam contains 94–97 percent water, it is not safe for use on this type of fire. In some cases, foam concentrate is even more conductive than water. Class C fires can be extinguished using nonconductive extinguishing agents such as a dry chemical, carbon dioxide (CO<sub>2</sub>), or halon. The safest procedure for this type of situation is to de-energize the equipment if possible and treat it as a Class A or Class B fire.

### **Foam is Not Effective on Three-Dimensional Fires**

A three-dimensional fire is a liquid-fuel fire in which the fuel is being discharged from an elevated or pressurized source, creating a pool of fuel on a lower surface. Foam is not effective at controlling three-dimensional flowing fires. It is recommended that firefighters control a three-dimensional flowing fire by first controlling the spill fire; then they may extinguish the flowing fire using a dry chemical agent.

### **Foam is Not Effective on Pressurized Gases**

Foam is not effective on fires involving pressurized gases. These materials are usually stored as liquids, but are normally vapor at ambient temperature. The vapor pressure of these types of fuels is too high for foam to be effective. To be effective, foam must set up as a two-dimensional blanket on top of a pooled liquid. Examples of pressurized gases include:

- propane,

- butane,
- vinyl chloride, and
- butadiene.

### **Foam is Not Effective on Combustible Metals**

Class D fires involve combustible metals such as aluminum, magnesium, titanium, sodium, and potassium. Combustible metals usually react with water; therefore, foam is not an effective extinguishing agent. Fires involving combustible metals require specialized techniques and extinguishing agents that have been developed to deal with these types of fires. A Class D extinguisher or a Class D powder is the recommended choice for fires involving combustible metals.

### ***What is Foam Effective On?***

Foam is effective at suppressing vapors and extinguishing Class B fires. Class B fires are defined as fires involving flammable or combustible liquids. For the purposes of this discussion, Class B products are divided into two categories: hydrocarbons and polar solvents.

For our purposes today, we will focus on polar solvents.

### **Polar Solvents**

Polar solvents are products of distillation or products that have been synthetically produced. Polar solvent fuels are miscible, that is they will mix with water. Polar fuels have a varying attraction for water. For example, acetone has a stronger affinity for water than does rubbing alcohol. Polar solvent fuels are usually destructive to foams designed for use on hydrocarbons. Specially formulated foams have been developed for use on polar solvents. Some examples of polar solvent fuels include:

- ketones,
- esters (biodiesel),
- alcohol including ethyl-alcohol (ethanol),
- amine,
- methyl tertiary-butyl ether (MTBE), and
- acetone.

### ***Foam Terminology***

Before discussing the types of foam and the foam making process, it is important to understand the following terms: • *Foam concentrate* is the liquid substance purchased from a manufacturer in a container, pail, drum, or tote.

• *Foam solution* is the mixture obtained when foam concentrate is proportioned (mixed) with water prior to the addition of air.

• *Finished foam* is obtained by adding air to foam solution through either entrainment or mechanical agitation.

### ***Types of Foam***

Several foam types have been developed over the years, each with particular qualities:

• *Protein foam*, one of the earliest foams, is produced by the hydrolysis of protein material such as animal hoof and horn. Stabilizers and inhibitors are added to prevent corrosion, resist bacterial decomposition, and control viscosity.

- *Fluoroprotein foams* are formed by the addition to protein foam of special fluorochemical surfactants that reduce the surface tension of the protein-based concentrate and allow more fluid movement.
- *Aqueous Film-Forming Foam (AFFF)* replaces protein-based foamers with synthetic foaming agents added to fluorochemical surfactants. Designed for rapid knockdown, AFFFs sacrifice heat resistance and long-term stability.
- *Film-Forming Fluoroprotein Foam (FFFP)* is a protein-based foam with the more advanced fluorochemical surfactants of AFFF. FFFPs combine the burnback resistance of fluoroprotein foam with the knockdown power of AFFF.
- *Alcohol-Resistant (AR) foam* is a combination of synthetic stabilizers, foaming agents, fluorochemicals, and synthetic polymers designed for use on polar solvents. The chemical makeup of these foams prevents the polar solvents from destroying them. Today's more modern AR foams can be used on both polar solvents and hydrocarbons.

## **Foam Characteristics**

No single foam product performs the same for all classes of fires. Each foam type excels at different functions; however, performance in other areas is often diminished. Knockdown, heat resistance, fuel tolerance, vapor suppression, and alcohol tolerance are all characteristics of various foam types. Each property is explained in the text that follows.

### **Knockdown**

Knockdown is the speed at which foam spreads across the surface of a fuel. Quick knockdown is achieved by allowing the solution contained in the bubbles to spread rapidly across the fuel surface. Extremely quick knockdown sacrifices good post-fire security, which is required for a stable, long-lasting foam blanket.

### **Heat Resistance**

Heat resistance is the ability of a foam bubble to withstand direct flame impingement or contact with elevated temperature surfaces, with little or no destruction to the foam bubble. The heat resistance of a foam blanket is often called "burnback resistance."

### **Fuel Tolerance**

Fuel tolerance is the ability of the foam to enter the fuel and resurface with little or no pick up of fuel within the structure of the bubble. A foam bubble which picks up fuel while submerged would simply carry the fuel to the surface and feed the fire.

### **Vapor Suppression**

Vapor suppression is the ability of the foam blanket to suppress flammable vapors and prevent their release. Vapor suppression is necessary to extinguish fires involving flammable liquids and to prevent ignition of unignited flammable liquid spills.

### **Alcohol Tolerance**

Alcohol tolerance is the ability of the foam blanket to create a polymeric barrier between the fuel and the foam, thus preventing the absorption of the water from the foam bubbles. This absorption would result in the destruction of the foam blanket.

## Foam Proportioning and Delivery Systems

The effectiveness of foam depends on proper proportioning and the ability to deliver finished foam to the spill or fire.

**Table 4.1: Various Types of Foam Rated by Their Properties**

Property	Protein	Fluoroprotein	AFFF	FFFP	AR-AFFF
Knockdown	Fair	Good	Excellent	Good	Excellent
Heat Resistance	Excellent	Excellent	Fair	Good	Good
Fuel Tolerance	Fair	Excellent	Moderate	Good	Good
Vapor Suppression	Excellent	Excellent	Good	Good	Good
Alcohol Tolerance	None	None	None	None	Excellent

**Source: National Foam**

### Concentration Levels

Foams are applied at various concentration levels depending on the fuel involved and the concentrate being used. Typically for *hydrocarbons*, foam is proportioned at 3 percent: that is three parts foam concentrate to ninety-seven parts water. For *polar solvents*, foam is usually proportioned at 6 percent: that is six parts foam concentrate to ninety-four parts water. Some concentrates allow for proportioning at 1 percent on hydrocarbons.

### Foam Proportioning Systems

A number of ways exist to proportion foam. These include:

- line eductors,
- self-educing nozzles,
- pressure systems, and
- pump proportioning systems.

This section will discuss the most common proportioning systems: line eductors and foam nozzle proportioners (foam nozzles with pickup tubes).

### Eductors

Eductors use the *venturi* principle to pull foam into the water stream. The flow of water past the venturi opening creates a vacuum that draws the concentrate through the metering valve. The *metering valve* controls the amount of concentrate allowed to flow into the water stream.

The *ball check valve* prevents water from flowing back into the pickup tube and the concentrate container. Major elements of the eductor setup include foam concentrate supply, water supply, eductor arrangement, metering valve, pickup tube, and foam solution discharge.

Two common types of eductors are *in-line eductors* and *bypass eductors*.

### In-Line Eductors

In-line eductors are some of the least expensive and simplest pieces of proportioning equipment available (see Figures 4.2 and 4.3). For this reason, they are perhaps the most common type of foam proportioner used in the fire service. Some advantages include:

- low cost,
- minimal maintenance, and
- simple operation.

**Figure 4.2: In-Line Eductor**



**Figure 4.3: In-Line Indicator**



### **Bypass Eductors**

Bypass eductors (see Figures 4.4 and 4.5) differ in that they have a ball valve to divert flow from foam to just water, allowing time for cooling without wasting foam and with less flow restriction.

**Figure 4.4: Bypass Eductor**



**Figure 4.5: Bypass Indicator**



**Common Eductor Failures**

The most common causes for eductor failure include:

- mismatched eductor and nozzle,
- air leaks in the pickup tube,
- improper flushing after use,
- kinked discharge hoseline,
- improper nozzle elevation,
- too much hose between eductor and nozzle, and
- incorrectly set nozzle flow.

These may be eliminated by careful preparation, inspection, and use of the eductor, nozzle, and hose.

Other eductor failures may be caused by:

- incorrect inlet pressure to eductor,
- partially closed nozzle shutoff,
- collapsed or obstructed pickup tube, and
- a pickup tube which is too long.

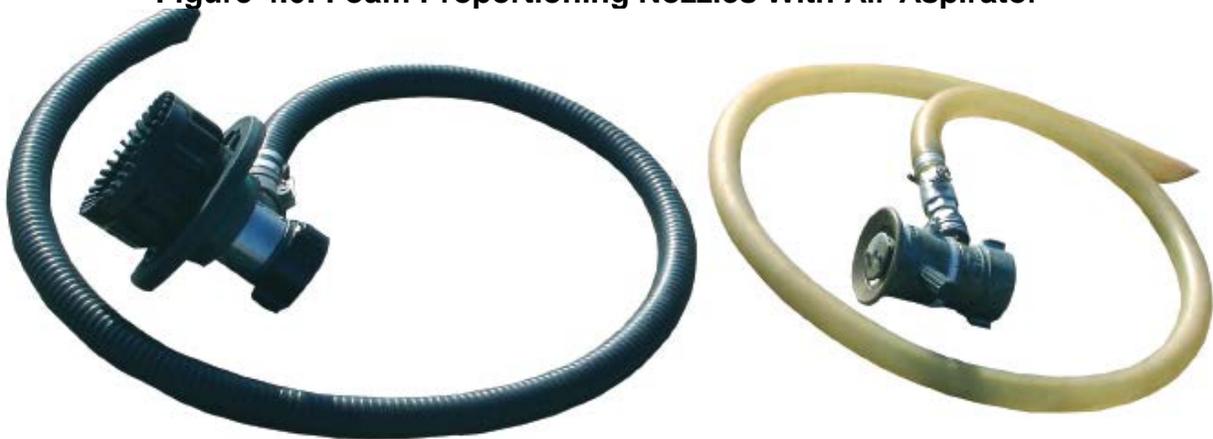
### **Foam Nozzles**

Foam nozzles are either foam proportioning, air aspirating, or non-air aspirating.

### **Foam Proportioning Nozzles**

Foam proportioning nozzles (see Figure 4.6) have built-in orifice plates and utilize the venturi principle of operation, producing a very effective foam. These monitor nozzles have the ability to deliver significant volumes of finished foam. Due to the insignificant pressure drop across the eductor, they are able to project foam over long distances.

**Figure 4.6: Foam Proportioning Nozzles With Air-Aspirator**



Advantages of foam proportioning nozzles include:

- they are easy to operate,
- they are easy to clean,
- there are no moving parts, and
- there is no additional foam equipment needed.

### **Air Aspirating Nozzles**

Air aspirating nozzles are foam generating nozzles that mix air and atmospheric pressure with foam solution (see Figure 4.7). These nozzles produce an expansion ratio of between 8:1 and 10:1 and produce a good-quality, low-expansion foam.

**Figure 4.7: Air Aspirating Nozzles**



***Non-Air Aspirating Nozzles***

Fog nozzles are an example of non-air aspirating nozzles (see Figure 4.8). Non-air aspirating nozzles produce an expansion ratio of between 3:1 and 5:1. This expansion ratio is not as good as that of air aspirating nozzles, but these nozzles often add some versatility which can be beneficial in various fire attack situations. Versatility includes the ability to switch from a foam solution to water in order to protect personnel and provide area cooling. Air aspirating nozzles do not offer this advantage.

**Figure 4.8: Non-Air Aspirating Nozzles**



A disadvantage of aspirating and non-air aspirating nozzles is that you must have additional equipment in order to generate foam. In addition, the gallonage setting on the nozzle must match the set flow for the eductor. It is important to understand the benefits of both types of nozzles in order to select the most appropriate one.

***Application Techniques***

Proper application is critical for foam. The key to foam application is to apply the foam as gently as possible to minimize agitation of the fuel and creation of additional vapors. The most important thing to remember is to *never plunge the foam directly into the fuel*. This will agitate the fuel and create additional vapors.

## **Bounce-Off**

The bounce-off method is effective if there is an object in or behind the spill area. The foam stream can be directed at the object, which will break the force of the stream, allowing the foam to gently flow onto the fuel surface.

## **Bank-In**

When no obstacles exist to bounce the foam off, firefighters should attempt to roll the foam onto the fire. By hitting the ground in front of the fire, the foam will pile up and roll into the spill area. This technique is particularly effective with non-air aspirating fog nozzles. The mechanical agitation of the foam hitting the ground will help to aerate the foam.

## **Rain-Down**

An alternative application technique is the rain-down method. The nozzle is elevated and the foam is allowed to fall over the spill as gently as possible. Warning! *Never* plunge a stream of foam *directly* into fuel! *This is the end of the section that is the property of TEEEX.*

## **Foam and Biodiesel and Biodiesel-Fuel Blends**

Some of the foams mentioned in the previous sections have been around for over fifty years and have proven to be very effective on hydrocarbon fuels. However, these foams that were not developed for application on alcohol fuels are simply ineffective on fuels containing alcohols including methanol and methylate. This is because the alcohol or alcohol content of the blended fuel literally attacks the foam solution, absorbing the foam solution into the alcohol fuel. Foam that is designed to be alcohol resistant forms a tough polymer membrane between the foam blanket and the alcohol-type fuel. It is crucial that these AR foams are used in combating alcohol fuel fires, including methylate. This is an important point. Additionally, to be effective, these foams must be applied gently to the surface of the alcohol fuels. Otherwise, the foam is absorbed into the fuel and will not resurface to form an encapsulating blanket.

## ***Lessons Learned From Ethanol (Ethyl Alcohol)***

Extensive testing done at the Ansil Fire Technology Center indicated that even at low-level blends of ethanol with gasoline, as low as E-10, there is a major effect on foam performance. The testing also indicated that with high-level blends of ethanol with gasoline, even AR foams required careful application methodology and techniques to control fires. AR-type foams must be applied to ethyl alcohol fires using Type II gentle application techniques. For responding emergency services, this will mean directing the foam stream onto a vertical surface and allowing it to run down onto the fuel. Direct application to the fuel surface will likely be ineffective unless the fuel depth is very shallow (i.e., 0.25 inches or less). Type III application (fixed and handline nozzle application) is prone to failure in ethanol-blended fuels of any substantial depth. The only time it is effective is when it is deflected off surfaces, such as tank walls, to create a gentle style application. It has also been found that even with indirect application off surfaces, it may require substantial increases in flow rate to accomplish extinguishments. Therefore, in situations where AR foam cannot be applied indirectly by deflection of the foam off tank walls or other surfaces or there is no built-in application device to provide gentle application, the best option may be to protect surrounding exposures. Another property of alcohol- or ethanol-type fuel fires is that they require a higher flow rate (application rate) of foam to extinguish fires. AFFF-type foams require approximately 1 gallon per minute

(gpm) foam solution flow for every 10 square feet of burning surface on a hydrocarbon-type fuel. Ethanol-blended fuels require approximately double that flow (2 gpm/10 square feet) of an AR-type foam solution. As with all types of foam, mixing percentage is dependent upon the type and design of the foam concentrate.

## **Foam Recommendations for Fire Departments**

Departments that are subject to incidents involving the various blends of fuels found on highway incidents or at storage facilities should strongly consider converting to AR foam concentrates or develop a means of having a cache of AR foam readily available. If a department has a specific hazard that only involves nonalcohol or nonethanol blended fuels, they may want to consider non-AR foam for that specific hazard. However, for over-the-road incidents they should have AR foam readily available. Keep in mind that AR foams are effective on both alcohol fires and hydrocarbon fires. As a matter of fact, some of the AR foams have quicker knockdown abilities and longer foam retention times than some of the traditional protein-based hydrocarbon foams. Since AR foams are universally effective on both polar solvents and hydrocarbons, they would be the foam of choice. When uncertain as to whether the fire encountered is an alcohol-, ethanol-, or biodiesel-blended fuel, fire departments may want to consider doubling their application rate (gpm).

## **Summary**

Foam is accepted as the best fire suppression/fire fighting agent for use in incidents involving hydrocarbons and polar solvents. Because of its ability to maintain a protective layer on these chemicals, AR foam is the best choice for incidents involving these types of products. Because AR foam also works well on gasoline fires, it is the recommended choice for all fuel fires involving either gasoline- or alcohol-blended fuels. AR foam does perform on hydrocarbon fires as well, so if it is unclear the nature of the burning fuel, AR is the preferred choice from a response standpoint.

# Module 5 Personal Protective Equipment (PPE) and Decontamination

## Terminal Objective

Upon the successful completion of this module, participants will be able to select the appropriate Personal Protective Equipment (PPE) for use in incidents related to biodiesel production. Participants will also be able to effectively conduct decontamination efforts on PPE after an incident.

## Enabling Objectives

1. Distinguish between types A, B, C, and D protection.
2. Determine appropriate PPE in various circumstances.
3. List emergency decontamination procedures.

## Introduction

When approaching an incident involving biodiesel or chemicals used in its manufacture, you need to be aware of the need for Personal Protective Equipment (PPE). Sometimes you will find that your structural fire fighting gear will serve your needs; other times you will need to don Chemical-Protective Clothing (CPC).

## Personal Protective Equipment (PPE)

Responses to incidents at biodiesel facilities will present multiple chemical, thermal, and physical hazards to which you will want to limit your exposure. As covered in previous modules, the common hazardous materials at these facilities include corrosives, flammables, and toxins. Emergency personnel can be endangered through exposure by contact and inhalation, as well as fire. Selection of PPE is based on the hazard to the responders. At a minimum, all responders must be trained to the operations level of National Fire Protection Association (NFPA) 472. It is important to define your agency's mission (fire fighting, hazardous materials, or technical rescue) and identify the potential hazards through preplanning the facilities in your jurisdiction. This hazard assessment will also be driven by your level of response: operations or technician. NFPA 472 Job Performance Requirement (JPR) 6.2 requires that responders who will be involved in product control must be trained in the selection, use, and maintenance of the PPE assigned to them. Also, any responder who uses PPE must be trained in technical decontamination (NFPA 472 6.4). The purpose of PPE is to shield or isolate responders from the chemical, physical, and biological hazards encountered during most routine calls. The set of PPE normally available to first responders consists of Structural Fire Fighting Protective Clothing (SFPC) with a Self-Contained Breathing Apparatus (SCBA). This combination of equipment generally provides some protection against flame, heat, and smoke, and offers limited protection from chemicals and biological agents. SFPC should be inspected for damage upon initial delivery and after each use. Cleaning and repairs should be performed according to manufacturer specifications. For SFPC to provide its intended level of protection, it must be:

- well-fitting,
- regularly cleaned and maintained, and
- donned and worn appropriately.

## Structural Firefighter Protective Clothing (SFPC)

In order to make sound decisions regarding personal safety during emergency situations, it is imperative that first responders understand the appropriate use and limitations of SFPC. When determining which level of protection is best for a given situation, the degree of hazard (or risk) and life-saving potential are important considerations. SFPC is designed to provide personnel with limited thermal protection and protection from the toxic by-products of combustion. SFPC is not designed to withstand direct flame impingement (contact).

It is only capable of providing thermal protection from heat and toxic smoke situations routinely encountered by firefighters (see Figure 5.1).

**Figure 5.1: SFPC**



*SFPC is constructed to provide limited protection from heat, but is not designed to provide adequate protection from harmful vapors and liquids that can be produced during hazardous materials incidents. No layers or components of SFPC are designed to protect against chemicals.*

In cases where SFPC can be expected to reliably provide limited protection, the responder who is wearing SFPC along with SCBA may be able to perform a quick “in-and-out” operation (to

attempt an immediate rescue or turn off a remote valve to control a leak, for example). The Incident Commander (IC) makes the decision for a unit(s) to approach the hazard area if, and only if, potential benefits outweigh predicted risks.

### ***Limitations of Structural Firefighter Protective Clothing (SFPC)***

In most cases, SFPC is the only protection available to firefighters even though they respond to various kinds of incidents. SFPC may not be sufficiently protective for either initial or extended use at many emergency scenes. Safe and successful use of SFPC depends on heeding known limitations, gaining proper training, and using safe work habits.

Known limitations include:

- SFPC is easily permeated or penetrated by most hazardous chemicals which may enter through closures, rips, or tears or get trapped under overlapped clothing.
- Direct contact with sunlight and chemicals, including splashes or soaking, may result in serious exposure by way of direct skin contact.
- SFPC is not tested against chemicals, so it cannot be expected to provide reliable protection from chemical exposure.
- It is virtually impossible to ensure adequate decontamination and subsequent integrity of garments without sophisticated laboratory testing.
- Hardware and closure systems may fail or malfunction.
- Repeated chemical and heat exposure may lessen material strength, cause component failure, and reduce the usable lifetime and protective qualities of a garment.
- Repeated use of contaminated SFPC results in chronic exposure to the user.
- Decontamination of SFPC should be based on the manufacturer's recommendations.

## **Respiratory Protection**

Inhalation is a major route of chemical exposure. Firefighters require protection from toxic products of combustion as well as from other hazardous materials that may be present at the emergency incident. Protection of the respiratory system is critical to the survival of firefighters when operating in a hazardous atmosphere. Therefore, respirator use, care, and maintenance are strictly regulated by government and industry standards. There are two types of respirators typically available for use:

- An *SCBA* consists of a facepiece connected by a hose to a regulator carrying air. The apparatus provides positive pressure to the user and offers protection against many types and levels of airborne contaminants.
- *Supplied Air Respirator (SAR)* provide positive pressure and full facepiece protection without a supply cylinder and harness assembly. These respirators reduce or eliminate some of the constraints and physiological stress sometimes associated with conventional SCBA. A high-pressure hoseline from a remote source provides an almost limitless, uninterrupted supply of breathing air. The unit can be resupplied by gradually switching to full bottles while others are being refilled. These units also have additional considerations for use in an emergency situation. A more in-depth study of this type of respiratory protection is needed prior to use.

## Appropriate Personal Protective Equipment (PPE) Selection Planning Tip

As you plan your response and choose the appropriate PPE, whether to go with SFPC for thermal protection or a coverall to protect from product contamination may be a difficult decision. You do not want responders exposed to thermal burns if a fire occurs, but you may not want to contaminate a set of SFPC with a potentially hazardous material when no fire hazard exists. The following can be used to determine an *action level of flammable concern* and aid in the selection of the appropriate PPE. You will need the use of an infrared temperature device or a thermal imaging camera to establish the temperature of the material and/or the surface it is spilled on. Using just the ambient temperature may not always be a good idea. If the spill is on a dark surface such as asphalt, its temperature will likely be much greater than the ambient temperature due to the radiant heat of the sun. Anytime the ambient temperature at an incident is below the flash point of the material in question, you should take this extra step to be certain that you are equipped with appropriate PPE.

*If the temperature of the material and/or surface is greater than your final calculation, then you should be in some type of PPE for thermal protection, such as SFPC.*

Examples:

You have: <ul style="list-style-type: none"><li>• A material with a flash point of 266°F (like biodiesel)</li><li>• A material temperature of 100°F</li></ul>
The math: $266 - 100 = 166$ $166 \div 2 = 88$ $88 + 100 = 188$
Your action level of concern for choosing thermal protection is 188°F.
Because this result is greater than the material temperature of 100°F, there is no need to worry about thermal protection.

A material temperature in excess of the action level result indicates that you should wear sufficient thermal protection.

## Inspecting Personal Protective Equipment (PPE)

An effective PPE inspection program should include five different inspections. All five types of inspections should be conducted as a matter of routine. You must also conduct any SCBA inspections mandated by law: for example, periodic cylinder testing according to Department of Transportation (DOT) regulations. Each inspection covers different areas with varying degrees of

depth. Personnel responsible for PPE inspection should follow inspection procedures suggested by the manufacturer. Damaged or deteriorated PPE must be assessed for either replacement or repair.

### ***Chemical-Protective Clothing (CPC)***

First responders often arrive at an incident scene, ready to fight a fire, only to discover that the incident requires more protection than they generally carry with them. First responders seldom have immediate access to chemical protection at levels A, B, C, and D. Rather, firefighters often arrive with only their bunker gear. If you arrive at an incident without the necessary level of protection, work toward controlling the incident until appropriate protective clothing arrives on scene. The purpose of CPC is to shield responders against chemical, biological, or physical hazards that they may encounter. There are four levels of protection available and the situation in which responders find themselves will dictate which level is appropriate for use at any given incident. Generally, responders will want to ensure that they are adequately protected against exposure when participating in the following activities:

- site survey,
- rescue,
- spill mitigation,
- emergency monitoring, and
- decontamination.

### **Level A Protection**

Level A protection affords the highest level of both respiratory and skin protection (see Figure 5.2). The NFPA standard for Level A protective garments is NFPA 1991, *Standard on Vapor-Protective Ensembles for Hazardous Materials Emergencies*. Suits meeting this standard will include, in addition to the vapor-protective suit, a pressure-demand, full-face SCBA, inner chemical-resistant gloves, chemical-resistant safety boots, and two-way radio communication. Compliant garments will have a label on the inside of the suit stating that it is compliant.

**Figure 5.2: Level A CPC**



The suit will also come with a chart that lists the chemicals the garment protects against and how quickly it will be weakened. As with other types of PPE, remember that there is no single garment style or material that can protect against all types of chemicals.

***Indicators for Use of Level A Protection***

- Highest level of respiratory protection is needed (SCBA or SAR with escape pack)
- Highest level of skin protection is required (skin-absorbable materials)
- Highest level of eye protection is required (obtained by wearing SCBA facepiece)
- Constant high-concentration exposure (offensive work activities such as plugging/patching)
- Suspected or confirmed carcinogens
- Vapor hazard is present

***Level A Advantages***

- Can virtually eliminate possibility of contact with environmental hazards (provides its own environment)
- Best protection known at this time

***Level A Limitations***

- Bulky—requires manpower to don and doff

- Physically stressful; no cooling or heating
- Psychologically stressful (confinement)
- Work duration limited due to heat
- Reduced mobility and dexterity (increases response time)
- Communication may be difficult
- Will not survive fire conditions
- Air supply may be limited

### **Level B Protection**

Level B protection affords the user the same level of respiratory protection as Level A but less skin protection (see Figure 5.3). It protects the skin from contact with product from spills and splashes, but offers no protection against chemical vapors or gases. This level of protection should *never* be used when there is a possibility of contact with a dangerous vapor/gas. The NFPA standard for Levels B and C protective garments is NFPA 1992, *Standard on Liquid Splash-Protective Ensembles and Clothing for Hazardous Materials Emergencies*. The standard was written to stipulate construction for **Personal Protective Equipment (PPE) and Decontamination** splash resistance in order to guard against liquid leaks through seams, closures, and attachments (rather than through the clothing material itself).

**Figure 5.3: Level B CPC**



Suits meeting this standard will include, in addition to the liquid splash-protective suit (meeting NFPA 1992 requirements), a pressure-demand, full-face SCBA, inner chemical-resistant gloves, chemical-resistant safety boots, two-way radio communication, and a hard hat. Compliant garments will have a label on the inside of the suit stating that it is compliant.

### ***Indicators for Use of Level B Protection***

- The highest level of respiratory protection is necessary, but a lesser level of skin protection is needed
- Probable exposure to low concentrations (incidental splash)
- Chemical is mainly a respiratory hazard

### **Level C Protection**

Level C protection illustrates the difference between NFPA and the Environmental Protection Agency (EPA) requirements for protection (see Figure 5.4). The EPA stipulation is the same with respect to splash protection for both Level C and B suits. However, EPA's requirement for Level C respiratory protection is less stringent than that for Level B. Compliance with EPA standards for Level C only requires Air-Purifying Respirators (APR). By contrast, NFPA's Level C requirements include the use of APRs but add garment specifications not required by EPA.

**Figure 5.4: Level C CPC**



Suits meeting this standard will include, in addition to a support function protective garment (meeting NFPA 1993), a full-facepiece, air-purifying, canister-equipped respirator; chemical-resistant gloves and safety boots; two-way communications system; and a hard hat.

***Indicators for Use of Level C Protection***

- Reduced level of respiratory protection needed
- Well characterized and measured products
- Splashes or incidental contact with product will not cause harm to skin or be absorbed

**Level D Protection**

EPA regulations for Level D protection and NFPA guidelines for station uniforms address normal workplace protections. Level D protection is much more commonly used in routine industrial operations than in the fire service. Different workplace environments and varying work activities require different protective clothing/equipment. There is no NFPA standard for Level D garment construction.

***Features of Level D Protection***

- Safety goggles or chemical splash goggles

- Coveralls
- Safety boots/shoes that are steel-toed and steel-shanked
- Hard hat
- Gloves

### ***Indicators for Use of Level D Protection***

- Atmosphere contains no known hazard
- Work activities preclude splashes, immersion, or the potential for unexpected inhalation or contact with hazardous materials

## **Emergency Decontamination Procedures**

NFPA 472 defines decontamination as the physical process of immediately reducing contamination of individuals in potentially life-threatening situations. Decontamination procedures provide an organized process, a series of sequential steps, to reduce contamination. Decontamination activities should accomplish one or more of the following:

- physically remove contaminants,
- deactivate contaminants by chemical detoxification or disinfection/sterilization, and/or
- remove contaminants by a combination of both physical and chemical means.

Decontamination strategies need to be applicable to a wide variety of environments and should be modifiable during inclement weather. Local Standard Operating Procedures (SOP) for decontamination, including alternative options, should be developed and practiced in cooperation with other affected organizations, such as the biodiesel facility and hospital emergency departments. Large biodiesel facilities will have emergency showers that can be used for decontamination in all locations of corrosive materials. Firefighters routinely perform decontamination of their own clothing and equipment from fires and medical calls.

Decontamination of civilians, facility employees, and unprotected responders can become warranted for a variety of reasons in emergency situations, such as preventing severe injury or loss of life and eliminating the possibility of transferring contamination between people, equipment, and vehicles. To further guard against secondary contamination, clothing that has been contaminated and has undergone emergency decontamination should be placed in plastic bags for further decontamination and/or disposal at a later time. It is also for protective purposes that a decontamination staging area must be set up some distance away from the scene, away from potential exposure, as soon as possible. Nobody (including Emergency Medical Services [EMS] transport patients) should be allowed to leave a scene that is suspected of being contaminated until they are decontaminated.

### ***Decontamination Guidelines***

Generally speaking, outer, more heavily contaminated items (such as outer boots and gloves) should be decontaminated and removed first, followed by decontamination and removal of inner, less contaminated items (such as jackets and pants). All equipment used for decontamination must also be decontaminated and/or disposed of properly. Buckets, brushes, clothing, tools, and other contaminated equipment should be collected, placed in containers, and labeled. An attempt should be made to collect and dispose of spent solutions and wash water. Important things to remember about decontamination include:

- Visible, dry contaminants should be removed with a brush, rags, or gauze.

- Removal of clothing, in many cases, will reduce a large portion of contaminants from coming into contact with the body; however, privacy must be ensured.
- Affected skin and mucous membranes (including the eyes) should be flushed with water.
- When multiple areas of the body are affected, priority should be given to particularly vulnerable areas, such as the eyes.
- Large amounts of water must be used when corrosives are involved.
- Start at the top, have victims remain standing, but bent over for hair washing, then proceed downward.

**Note:** In some instances, it might be most appropriate to remove clothing before rather than after flushing. The extent and type of contaminant determines the proper sequence for decontamination steps.

*Decontamination tip:* To check for the effective removal of corrosives responders can use pH paper to test areas of contamination. It takes all guess work out of deciding if responders have completed decontamination of the corrosive. If the pH paper turns red, acid is still present; if the pH paper turns blue the caustic/base is still present. This simple test can be used on facility personnel or responders who may have been exposed to a corrosive. Biodiesel has multiple corrosives in large quantity.

## Activity 5.1—Selection of Personal Protective Equipment (PPE)

### *Purpose*

To enable participants to demonstrate their understanding of the need for CPC at biodiesel incidents.

### *Participant Directions*

Use the *Emergency Response Guidebook* (ERG) to determine the protective clothing recommendations for the list of common hazardous substances found in the biodiesel industry and complete Worksheet 5.1.

### **Worksheet 5.1: Selection of PPE**

For each chemical listed below, use the ERG to determine which type of PPE should be employed when working an incident.

1. Sulfuric acid: UN 1830 \_\_\_\_\_
2. Methanol: UN 1230 \_\_\_\_\_
3. Hydrochloric acid: UN 1789 \_\_\_\_\_
4. Sodium hydroxide: UN 1823 \_\_\_\_\_
5. Biodiesel blends: UN 1993 \_\_\_\_\_

## **Summary**

While biodiesel (as a finished product) is generally considered nontoxic, the ingredients for making it are extremely toxic. Firefighters will usually arrive on scene with only bunker gear for protection. Since you will need to send for additional protective clothing, you will need to have an idea of what kinds of CPC to don. The ERG is a useful tool for determining the level of need. Finally, effective decontamination is required following a toxic incident.

# Appendix A History of Biodiesel

## A Brief History of Biodiesel

Biodiesel is one of a variety of biofuels and has been around for more than a century. To be considered “biodiesel” (as opposed to simply “biofuel”) plant oils (or animals fats or recycled restaurant grease) must undergo a process called transesterification. This process was conducted as early as 1853 by scientists E. Duffy and J. Patrick, many years before the first diesel engine became functional. Developed in the 1890s by inventor Rudolph Diesel, the diesel engine has become the engine of choice for power, reliability, and high fuel economy, worldwide. When Dr. Diesel demonstrated his innovative engine at the 1900 World’s Fair in Paris it operated on peanut oil, a biofuel. His statement at the time was “the diesel engine can be fed with plant oils and would help considerably in the development of agriculture of the countries which use it.” This statement is as true today as it was at the outset of the last century. Early experimenters on plant oil fuels included the French government and Dr. Diesel himself, who envisioned that pure plant oils could power early diesel engines for agriculture in remote areas of the world, where petroleum was not available at the time. Modern biodiesel fuel, which is made by converting plant oils into compounds called fatty methyl esters, has roots in research conducted in the 1930s in Belgium. As petroleum refining went beyond kerosene for lighting, the by-products such as gasoline and gasoil/diesel became significantly more available and cheaper than plant oil, thus dominated the motor fuels market. Despite the widespread use of fossil petroleum-derived fuels, interest in plant oils as fuels in internal combustion engines is reported in several countries during the 1920s and 1930s and later during World War II. Belgium, France, Italy, the United Kingdom, Portugal, Germany, Brazil, Argentina, Japan, and China have been reported to have tested and used plant oils as diesel fuels during this time.

## Appendix B Material Safety Data Sheets (MSDS)

The MSDSs in this appendix are reprinted with permission:

- Renewable Energy Group (REG). (2007). *Crude Glycerin MSDS*. Retrieved September 24, 2008, from <http://www.renewable-energy-group.com/>
- National Biodeisel Board. *Biodiesel MSDS*. Retrieved September 24, 2008, from [http://www.biodiesel.org/pdf\\_files/fuelfactsheets/MSDS.PDF](http://www.biodiesel.org/pdf_files/fuelfactsheets/MSDS.PDF)
- Methanex. (2005). Methanol MSDS. Retrieved September 24, 2008, from [http://www.methanex.com/products/documents/MSDS\\_USenglish.pdf](http://www.methanex.com/products/documents/MSDS_USenglish.pdf)

In the very near future responders may notice a change in MSDSs including terminology, presentation, and contents. This change is due to the establishment of a globally accepted hazard classification and communication provision known as the Globally Harmonized System of Classification and Labeling of Chemicals (GHS). The GHS is a system for standardizing and harmonizing the classification and labeling of chemicals. It is a logical and comprehensive approach to:

- defining health, physical, and environmental hazards of chemicals;

- creating classification processes that use available data on chemicals for comparison with the defined hazard criteria; and
- communicating hazard information, as well as protective measures, on labels and Safety Data Sheets (SDS).

For more information on this system see the following Web sites:

- <http://www.osha.gov/dsg/hazcom/ghs.html>
- [http://www.unece.org/trans/danger/publi/ghs/ghs\\_welcome\\_e.html](http://www.unece.org/trans/danger/publi/ghs/ghs_welcome_e.html)



# Material Safety Data Sheet

NFPA	HMIS	PPE	Transport Symbol						
	<table border="1"> <tr> <td>Health Hazard</td> <td>1</td> </tr> <tr> <td>Fire Hazard</td> <td>1</td> </tr> <tr> <td>Reactivity</td> <td>0</td> </tr> </table>	Health Hazard	1	Fire Hazard	1	Reactivity	0		
Health Hazard	1								
Fire Hazard	1								
Reactivity	0								

Issuing Date 22-Aug-2007

Revision Date

Revision Number 0

## 1. PRODUCT AND COMPANY IDENTIFICATION

Product Name Crude Glycerin

Recommended Use Cosmetic agent, Food additive, Pharmaceutical excipient, Lubricant, Antifreeze.

**Supplier Address**

Renewable Energy Group, Inc.  
416 S. Bell Ave.  
Ames, IA 50010  
TEL: 1-888-734-8686

Company Emergency Phone Number 1-800-633-8253

Emergency Telephone Number CHEMTREC: +1-703-527-3887 (INTERNATIONAL)  
1-800-424-9300 (NORTH AMERICA)

## 2. HAZARDS IDENTIFICATION

**CAUTION!**

**Emergency Overview**

May cause skin and eye irritation  
May cause irritation of respiratory tract  
May cause adverse kidney effects

Appearance Colorless to brown

Physical State Liquid

Odor Musty

**Potential Health Effects**

**Principle Routes of Exposure**

Inhalation, Skin contact, Eye contact.

**Acute Toxicity**

Eyes  
Skin  
Inhalation  
Ingestion

May cause slight irritation.  
Substance may cause slight skin irritation.  
Inhalation of vapors in high concentration may cause irritation of respiratory system.  
Ingestion may cause gastrointestinal irritation, nausea, vomiting and diarrhea.

**Chronic Effects**

No known effect based on information supplied.

## Material Safety Data Sheets (MSDS)

WPS-REG-001 - Crude Glycerin

Revision Date

**Aggravated Medical Conditions** Preexisting eye disorders. Kidney disorders. Skin disorders.

**Environmental Hazard** See Section 12 for additional Ecological Information.

### 3. COMPOSITION/INFORMATION ON INGREDIENTS

**Common Name** Crude Glycerin.  
**Chemical Family** Glycerin, containing water, salt and residual methanol.  
**Formula** C<sub>3</sub>H<sub>8</sub>O<sub>3</sub>

Chemical Name	CAS-No	Weight %
Glycerol	56-81-5	75-90
Water	7732-18-5	6-15
Sodium chloride (NaCl)	7647-14-5	4-10
Methyl alcohol	67-56-1	0-0.2

### 4. FIRST AID MEASURES

**Eye Contact** Rinse thoroughly with plenty of water for at least 15 minutes and consult a physician.

**Skin Contact** Wash skin with soap and water. In the case of skin irritation or allergic reactions see a physician.

**Inhalation** Move to fresh air. If symptoms persist, call a physician.

**Ingestion** Do NOT induce vomiting. Rinse mouth. Drink 1 or 2 glasses of water. Never give anything by mouth to an unconscious person. If symptoms persist, call a physician.

**Notes to Physician** Treat symptomatically.

### 5. FIRE-FIGHTING MEASURES

**Flammable Properties** Combustible material: may burn but does not ignite readily.

**Flash Point** 160°C / 320°F

**Suitable Extinguishing Media** Water spray. Carbon dioxide (CO<sub>2</sub>). Dry chemical. Dry powder. Alcohol-resistant foam.

**Hazardous Combustion Products** Carbon monoxide, Carbon dioxide (CO<sub>2</sub>), Formaldehyde.

**Explosion Data**

**Sensitivity to Mechanical Impact** None

**Sensitivity to Static Discharge** None

**Specific Hazards Arising from the Chemical** Keep product and empty container away from heat and sources of ignition.

**Protective Equipment and Precautions for Firefighters** Wear self-contained breathing apparatus and protective suit.

**NFPA** Health Hazard 1 Flammability 1 Stability 0 Physical and Chemical Hazards -

**HMIS** Health Hazard 1 Flammability 1 Stability 0 Personal Precautions B

## 6. ACCIDENTAL RELEASE MEASURES

<b>Personal Precautions</b>	Use personal protective equipment. Ensure adequate ventilation.
<b>Methods for Containment</b>	Dike to collect large liquid spills. Cover with dry sand/earth. Prevent further leakage or spillage if safe to do so.
<b>Methods for Cleaning Up</b>	Dam up. Cover liquid spill with sand, earth or other noncombustible absorbent material. Take up mechanically and collect in suitable container for disposal. Clean contaminated surface thoroughly. After cleaning, flush away traces with water.
<b>Other Information</b>	Refer to protective measures listed in Sections 7 and 8.

## 7. HANDLING AND STORAGE

<b>Handling</b>	Wear personal protective equipment. Ensure adequate ventilation. Avoid contact with skin and eyes.
<b>Storage</b>	Keep tightly closed in a dry and cool place.

## 8. EXPOSURE CONTROLS / PERSONAL PROTECTION

### Exposure Guidelines

Chemical Name	ACGIH TLV	OSHA PEL	NIOSH IDLH
Glycerol 56-81-5	TWA: 10 mg/m <sup>3</sup>	TWA: 15 mg/m <sup>3</sup> TWA: 5 mg/m <sup>3</sup> (vacated) TWA: 10 mg/m <sup>3</sup> (vacated) TWA: 5 mg/m <sup>3</sup>	
Methyl alcohol 67-56-1	= 250 ppm STEL TWA: 200 ppm Skin	TWA: 200 ppm TWA: 260 mg/m <sup>3</sup> (vacated) TWA: 200 ppm (vacated) TWA: 260 mg/m <sup>3</sup> (vacated) STEL: 250 ppm (vacated) STEL: 325 mg/m <sup>3</sup> Skin	IDLH: 6000 ppm TWA: 200 ppm TWA: 260 mg/m <sup>3</sup> STEL: 325 mg/m <sup>3</sup> STEL: 250 ppm

<b>Engineering Measures</b>	Showers, eyewash stations, and ventilation systems.
<b>Personal Protective Equipment</b>	
<u>Eye/Face Protection</u>	Safety glasses with side-shields.
<u>Skin and Body Protection</u>	Protective gloves.
<u>Respiratory Protection</u>	If exposure limits are exceeded or irritation is experienced, NIOSH/MSHA approved respiratory protection should be worn. Positive-pressure supplied air respirators may be required for high airborne contaminant concentrations. Respiratory protection must be provided in accordance with current local regulations
<b>Hygiene Measures</b>	Handle in accordance with good industrial hygiene and safety practice. Provide regular cleaning of equipment, work area and clothing.

## 9. PHYSICAL AND CHEMICAL PROPERTIES

Appearance	Colorless to brown	Odor	Musty
Odor Threshold	No information available	Physical State	Liquid
pH	5-7.5		
Flash Point	160°C / 320°F	Autoignition Temperature	No information available
Decomposition Temperature	280 °C	Boiling Point/Range	290°C / 554°F (at 1 atm)
Melting Point/Range	0-20°C / 32-68°F		
Flammability Limits in Air	No information available	Explosion Limits	No information available
Specific Gravity	1.26 @ 20°C	Water Solubility	Soluble in water
Solubility	No information available	Evaporation Rate	No information available
Vapor Pressure	No data available	Vapor Density	No data available
VOC Content	Not applicable	Viscosity	21 cP @ 40°C

## 10. STABILITY AND REACTIVITY

Stability	Stable under recommended storage conditions.
Incompatible Products	Strong oxidizing agents. Strong acids.
Conditions to Avoid	Exposure to air or moisture over prolonged periods.
Hazardous Decomposition Products	Carbon monoxide (CO). Carbon dioxide (CO <sub>2</sub> ). Formaldehyde. Acrolein.
Hazardous Polymerization	Hazardous polymerization does not occur.

## 11. TOXICOLOGICAL INFORMATION

### Acute Toxicity

#### Product Information

##### Irritation

May cause skin and eye irritation. May cause irritation to mucous membranes and respiratory tract.

#### Component Information

### Chronic Toxicity

#### Chronic Toxicity

No known effect based on information supplied.

#### Target Organ Effects

Eyes, Respiratory system, Skin, Kidney.

## 12. ECOLOGICAL INFORMATION

### Ecotoxicity

Ecotoxicity effects of component substances.

Chemical Name	Toxicity to Algae	Toxicity to Fish	Microtox	Daphnia Magna (Water Flea)
Glycerol		LC50 51000 - 57000 mg/L Oncoerhynchus mykiss 96 h		EC50 > 500 mg/L 24 h

Chemical Name	Toxicity to Algae	Toxicity to Fish	Microtox	Daphnia Magna (Water Flea)
Sodium chloride (NaCl)	N/A	LC50= 12946 mg/L Lepomis macrochirus 96 h LC50= 7650 mg/L Pimephales promelas 96 h LC50= 9675 mg/L Lepomis macrochirus 96 h	N/A	EC50 = 1000 mg/L 48 h
Methyl alcohol		LC50= 13200 mg/L Onchorhynchus mykiss 96 h LC50= 28100 mg/L Pimephales promelas 96 h	EC50 = 39000 mg/L 25 min EC50 = 40000 mg/L 15 min EC50 = 43000 mg/L 5 min	

**Persistence and Degradability** Product is biodegradable.

**Bioaccumulation/Accumulation** Does not bioaccumulate.

**Mobility** Will likely be mobile in the environment due to its water solubility but will likely degrade over time.

Chemical Name	Log Pow
Glycerol	= -1.76
Methyl alcohol	= -0.77

### 13. DISPOSAL CONSIDERATIONS

**Waste Disposal Method** This material, as supplied, is not a hazardous waste according to Federal regulations (40 CFR 261). This material could become a hazardous waste if it is mixed with or otherwise comes in contact with a hazardous waste, if chemical additions are made to this material, or if the material is processed or otherwise altered. Consult 40 CFR 261 to determine whether the altered material is a hazardous waste. Consult the appropriate state, regional, or local regulations for additional requirements.

**Contaminated Packaging** Dispose of in accordance with local regulations.

Chemical Name	RCRA	RCRA - Basis for Listing	RCRA - D Series Wastes	RCRA - U Series Wastes
Methyl alcohol - 67-56-1		Included in waste stream: F039		U154

This product contains one or more substances that are listed with the State of California as a hazardous waste.

Chemical Name	California Hazardous Waste Status
Methyl alcohol	Toxic; Ignitable

### 14. TRANSPORT INFORMATION

**DOT** Not regulated

**TDG** Not regulated

**MEX** Not regulated

**ICAO** Not regulated

**IATA** Not regulated

**IMDG/IMO** Not regulated

**RID** Not regulated

<b>14. TRANSPORT INFORMATION</b>
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ADR Not regulated

ADN Not regulated

<b>15. REGULATORY INFORMATION</b>
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International Inventories

TSCA	Complies
DSL	Complies
NDSL	Complies
EINECS	Complies
ELINCS	Does not Comply
ENCS	Complies
IECSC	Complies
KECL	Complies
PICCS	Complies
AICS	Complies

U.S. Federal RegulationsSARA 313

Section 313 of Title III of the Superfund Amendments and Reauthorization Act of 1986 (SARA). This product contains a chemical or chemicals which are subject to the reporting requirements of the Act and Title 40 of the Code of Federal Regulations, Part 372:

Chemical Name	CAS-No	Weight %	SARA 313 - Threshold Values %
Methyl alcohol	67-56-1	0.01-0.3	1.0

SARA 311/312 Hazard Categories

Acute Health Hazard	No
Chronic Health Hazard	No
Fire Hazard	No
Sudden Release of Pressure Hazard	No
Reactive Hazard	No

Clean Water Act

This product does not contain any substances regulated as pollutants pursuant to the Clean Water Act (40 CFR 122.21 and 40 CFR 122.42).

CERCLA

This material, as supplied, does not contain any substances regulated as hazardous substances under the Comprehensive Environmental Response Compensation and Liability Act (CERCLA) (40 CFR 302) or the Superfund Amendments and Reauthorization Act (SARA) (40 CFR 355). There may be specific reporting requirements at the local, regional, or state level pertaining to releases of this material.

U.S. State RegulationsCalifornia Proposition 65

This product does not contain any Proposition 65 chemicals.

U.S. State Right-to-Know Regulations

Chemical Name	Massachusetts	New Jersey	Pennsylvania	Illinois	Rhode Island
Glycerol	X		X		X

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**International Regulations**

Mexico - Grade                      Slight risk, Grade 1

Chemical Name	Carcinogen Status	Exposure Limits
Glycerol		Mexico: TWA= 10 mg/m <sup>3</sup>

Canada

This product has been classified in accordance with the hazard criteria of the Controlled Products Regulations (CPR) and the MSDS contains all the information required by the CPR.

WHMIS Hazard Class

Non-controlled

**16. OTHER INFORMATION**

Issuing Date                      22-Aug-2007  
Revision Date  
Revision Note                      No information available

**Disclaimer**

The information provided on this MSDS is correct to the best of our knowledge, information and belief at the date of its publication. The information given is designed only as a guide for safe handling, use, processing, storage, transportation, disposal and release and is not to be considered as a warranty or quality specification. The information relates only to the specific material designated and may not be valid for such material used in combination with any other material or in any process, unless specified in the text.

**End of MSDS**



## SAMPLE MATERIAL SAFETY DATA SHEET



### 1. CHEMICAL PRODUCT

General Product Name: **Biodiesel (B100)**  
Synonyms: Methyl Soyate, Rapeseed Methyl Ester (RME)  
Product Description: Methyl esters from lipid sources  
CAS Number: Methyl Soyate: 67784-80-9; RME: 73891-99-3;

### 2. COMPOSITION/INFORMATION ON INGREDIENTS

This product contains no hazardous materials.

### 3. HAZARDS IDENTIFICATION

#### Potential Health Effects:

##### INHALATION:

Negligible unless heated to produce vapors. Vapors or finely misted materials may irritate the mucous membranes and cause irritation, dizziness, and nausea. Remove to fresh air.

##### EYE CONTACT:

May cause irritation. Irrigate eye with water for at least 15 to 20 minutes. Seek medical attention if symptoms persist.

##### SKIN CONTACT:

Prolonged or repeated contact is not likely to cause significant skin irritation. Material is sometimes encountered at elevated temperatures. Thermal burns are possible.

##### INGESTION:

No hazards anticipated from ingestion incidental to industrial exposure.

### 4. FIRST AID MEASURES

##### EYES:

Irrigate eyes with a heavy stream of water for at least 15 to 20 minutes.

##### SKIN:

Wash exposed areas of the body with soap and water.

##### INHALATION:

Remove from area of exposure; seek medical attention if symptoms persist.

##### INGESTION:

Give one or two glasses of water to drink. If gastro-intestinal symptoms develop, consult medical personnel. (Never give anything by mouth to an unconscious person.)

### 5. FIRE FIGHTING MEASURES

Flash Point (Method Used): 130.0 C or 266.0 F min (ASTM 93)

Flammability Limits: None known

##### EXTINGUISHING MEDIA:

Dry chemical, foam, halon (may not be permissible in some countries), CO<sub>2</sub>, water spray (fog). Water stream may splash the burning liquid and spread fire.

##### SPECIAL FIRE FIGHTING PROCEDURES:

Use water spray to cool drums exposed to fire.

##### UNUSUAL FIRE AND EXPLOSION HAZARDS:

Biodiesel soaked rags or spill absorbents (i.e. oil dry, polypropylene socks, sand, etc.) can cause spontaneous combustion if stored near combustibles and not handled properly. Store biodiesel soaked rags or spill absorbents in approved safety containers and dispose of properly. Oil soaked rags may be washed with soap and water and allowed to dry in

well ventilated area. Firefighters should use self-contained breathing apparatus to avoid exposure to smoke and vapor.

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## 6. ACCIDENTAL RELEASE MEASURES SPILL CLEAN-UP PROCEDURES

Remove sources of ignition, contain spill to smallest area possible. Stop leak if possible. Pick up small spills with absorbent materials and dispose of properly to avoid spontaneous combustion (see unusual fire and explosion hazards above).

Recover large spills for salvage or disposal. Wash hard surfaces with safety solvent or detergent to remove remaining oil film. Greasy nature will result in a slippery surface.

---

## 7. HANDLING AND STORAGE

Store in closed containers between 50°F and 120°F.

Keep away from oxidizing agents, excessive heat, and ignition sources.

Store and use in well ventilated areas.

Do not store or use near heat, spark, or flame, store out of sun.

Do not puncture, drag, or slide this container.

Drum is not a pressure vessel; never use pressure to empty.

---

## 8. EXPOSURE CONTROL /PERSONAL PROTECTION

### RESPIRATORY PROTECTION:

If vapors or mists are generated, wear a NIOSH approved organic vapor/mist respirator.

### PROTECTIVE CLOTHING:

Safety glasses, goggles, or face shield recommended to protect eyes from mists or splashing. PVC coated gloves recommended to prevent skin contact.

### OTHER PROTECTIVE MEASURES:

Employees must practice good personal hygiene, washing exposed areas of skin several times daily and laundering contaminated clothing before re-use.

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## 9. PHYSICAL AND CHEMICAL PROPERTIES

Boiling Point, 760 mm Hg:>200°C

Volatiles, % by Volume: <2

Specific Gravity (H<sub>2</sub>O=1): 0.88

Solubility in H<sub>2</sub>O, % by Volume: insoluble

Vapor Pressure, mm Hg: <2

Evaporation Rate, Butyl Acetate=1: <1

Vapor Density, Air=1:>1

Appearance and Odor: pale yellow liquid, mild odor

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## 10. STABILITY AND REACTIVITY

### GENERAL:

This product is stable and hazardous polymerization will not occur.

### INCOMPATIBLE MATERIALS AND CONDITIONS TO AVOID:

Strong oxidizing agents

### HAZARDOUS DECOMPOSITION PRODUCTS:

Combustion produces carbon monoxide, carbon dioxide along with thick smoke.

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## 11. DISPOSAL CONSIDERATIONS

### WASTE DISPOSAL:

Waste may be disposed of by a licensed waste disposal company. Contaminated absorbent material may be disposed of in an approved landfill. Follow local, state and federal disposal regulations.

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## 12. TRANSPORT INFORMATION

UN HAZARD CLASS: N/A

NMFC (National Motor Freight Classification):

PROPER SHIPPING NAME: Fatty acid ester

IDENTIFICATION NUMBER: 144920

SHIPPING CLASSIFICATION: 65

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## 13. REGULATORY INFORMATION:

### OSHA STATUS:

This product is not hazardous under the criteria of the Federal OSHA Hazard Communication Standard 29 CFR 1910.1200. However, thermal processing and decomposition fumes from this product may be hazardous as noted in Sections 2 and 3.

### TSCA STATUS:

This product is listed on TSCA.

CERCLA (Comprehensive Response Compensation and Liability Act):

NOT reportable.

SARA TITLE III (Superfund Amendments and Reauthorization Act):

Section 312 Extremely Hazardous Substances:

None

Section 311/312 Hazard Categories:

Non-hazardous under Section 311/312

Section 313 Toxic Chemicals:

None

### RCRA STATUS:

If discarded in its purchased form, this product would not be a hazardous waste either by listing or by characteristic. However, under RCRA, it is the responsibility of the product user to determine at the time of disposal, whether a material containing the product or derived from the product should be classified as a hazardous waste, (40 CFR 261.20-24)

### CALIFORNIA PROPOSITION 65:

The following statement is made in order to comply with the California Safe Drinking Water and Toxic Enforcement Act of 1986. This product contains no chemicals known to the state of California to cause cancer.

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## 14. OTHER INFORMATION:

This information relates only to the specific material designated and may not be valid for such material used in combination with any other materials or in any other process. Such information is to the best of the company's knowledge and believed accurate and reliable as of the date indicated. However, no representation, warranty or guarantee of any kind, express or implied, is made as to its accuracy, reliability or completeness and we assume no responsibility for any loss, damage or expense, direct or consequential, arising out of use. It is the user's responsibility to satisfy himself as to the suitability and completeness of such information for his own particular use.

# MATERIAL SAFETY DATA SHEET

*This Material Safety Data Sheet complies with the Canadian Controlled Product Regulations and the United States Occupational Safety and Health Administration (OSHA) hazard communication standard.*

## 1. Product and Supplier Identification

**Product:** Methanol (CH<sub>3</sub>OH)      **Non-Emergency Tel. #:** (604) 661-2600

**Synonyms:** Methyl alcohol, methyl hydrate, wood spirit, methyl hydroxide      **Emergency Tel. #:** 1-800-424-9300  
(CHEMTREC) (Canada and US)

**Product Use:** Solvent, fuel, feedstock

**Company Identification:** Methanex Corporation,  
1800 Waterfront Centre,  
200 Burrard Street,  
Vancouver, B.C.  
V6C 3M1

**Note:** CHEMTREC number to be used only in the event of chemical emergencies involving a spill, leak, fire, exposure or accident involving chemicals.

**Importer:** Methanex Methanol Company  
Suite 1150 – 15301 Dallas Parkway  
Addison, Texas 75001  
Telephone: (972) 702-0909

## 2. Composition

Component	% (w/w)	Exposure Limits*	LD <sub>50</sub>	LC <sub>50</sub>
Methanol (CAS 67-56-1)	99-100	ACGIH TLV-TWA: 200 ppm, skin STEL: 250 ppm, skin notation OSHA PEL: 200 ppm  TLV Basis, critical effects: neuropathy, vision, central nervous system	5628 mg/kg (oral/rat)  20 ml/kg (dermal/ rabbit)	64000 ppm (inhalation/rat)

\* Exposure limits may vary from time to time and from one jurisdiction to another. Check with local regulatory agency for the exposure limits in your area.

### 3. Hazards Identification

**Routes of Entry:**

Skin Contact: Moderate Eye Contact: Moderate Ingestion: Major Inhalation: Major

**Effects of Short-Term (Acute) Exposure:**

**Inhalation:** Inhalation of high airborne concentrations can also irritate mucous membranes, cause headaches, sleepiness, nausea, confusion, loss of consciousness, digestive and visual disturbances and even death. NOTE: Odour threshold of methanol is several times higher than the TLV-TWA. Depending upon severity of poisoning and the promptness of treatment, survivors may recover completely or may have permanent blindness, vision disturbances and/or nervous system effects. Concentrations in air exceeding 1000 ppm may cause irritation of the mucous membranes.

**Skin Contact:** Methanol is moderately irritating to the skin. Methanol can be absorbed through the skin and harmful effects have been reported by this route of entry. Effects are similar to those described in "Inhalation"

**Eye Contact:** Methanol is a mild to moderate eye irritant. High vapour concentration or liquid contact with eyes causes irritation, tearing and burning.

**Ingestion:** Swallowing even small amounts of methanol could potentially cause blindness or death. Effects of sub lethal doses may be nausea, headache, abdominal pain, vomiting and visual disturbances ranging from blurred vision to light sensitivity.

**Effects of Long-Term (Chronic) Exposure:** Repeated exposure by inhalation or absorption may cause systemic poisoning, brain disorders, impaired vision and blindness. Inhalation may worsen conditions such as emphysema or bronchitis. Repeated skin contact may cause dermal irritation, dryness and cracking.

**Medical Conditions Aggravated By Exposure:** Emphysema or bronchitis.

### 4. First Aid Measures

**Note:** Emergency assistance may also be available from the local poison control centre.

**Eye Contact:** Remove contact lenses if worn. In case of contact, immediately flush eyes with plenty of clean running water for at least 15 minutes, lifting the upper and lower eyelids occasionally. Obtain medical attention.

**Skin Contact:** In case of contact, remove contaminated clothing. In a shower, wash affected areas with soap and water for at least 15 minutes. Seek medical attention if irritation occurs or persists. Wash clothing before reuse.

**Inhalation:** Remove to fresh air, restore or assist breathing if necessary. Obtain medical attention.

**Ingestion:** Swallowing methanol is potentially life threatening. Onset of symptoms may be delayed for 18 to 24 hours after digestion. If conscious and medical aid is not immediately

available, do not induce vomiting. In actual or suspected cases of ingestion, transport to medical facility immediately.

**NOTE TO PHYSICIAN:** Acute exposure to methanol, either through ingestion or breathing high airborne concentrations can result in symptoms appearing between 40 minutes and 72 hours after exposure. Symptoms and signs are usually limited to CNS, eyes and gastrointestinal tract. Because of the initial CNS's effects of headache, vertigo, lethargy and confusion, there may be an impression of ethanol intoxication. Blurred vision, decreased acuity and photophobia are common complaints. Treatment with ipecac or lavage is indicated in any patient presenting within two hours of ingestion. A profound metabolic acidosis occurs in severe poisoning and serum bicarbonate levels are a more accurate measure of severity than serum methanol levels. Treatment protocols are available from most major hospitals and early collaboration with appropriate hospitals is recommended.

## 5. Fire Fighting Measures

<b>Flash point:</b>	11°C (TCC)
<b>Autoignition temperature:</b>	385 °C (NFPA 1978), 470 °C (Kirk-Othmer 1981; Ullmann 1975)
<b>Lower Explosive Limit:</b>	6% (NFPA, 1978)
<b>Upper Explosion Limit:</b>	36% (NFPA, 1978), 36.5% (Ullmann, 1975)
<b>Sensitivity to Impact:</b>	Low
<b>Sensitivity to Static Discharge:</b>	Low
<b>Hazardous Combustion Products:</b>	Toxic gases and vapours; oxides of carbon and formaldehyde.
<b>Extinguishing Media:</b>	Small fires: Dry chemical, CO <sub>2</sub> , water spray Large fires: Water spray, AFFF(R) (Aqueous Film Forming Foam (alcohol resistant)) type with either a 3% or 6% foam proportioning system.

**Fire Fighting Instructions:** Methanol burns with a clean clear flame that is almost invisible in daylight. Stay upwind! Isolate and restrict area access. Concentrations of greater than 25% methanol in water can be ignited. Use fine water spray or fog to control fire spread and cool adjacent structures or containers. Contain fire control water for later disposal. Fire fighters must wear full face, positive pressure, self-contained breathing apparatus or airline and appropriate protective clothing. Protective fire fighting structural clothing is not effective protection from methanol. Do not walk through spilled product.

### NATIONAL FIRE PROTECTION ASSOCIATION (NFPA) HAZARD INDEX:

HEALTH: 1

FLAMMABILITY: 3

REACTIVITY: 0

## 6. Accidental Release Measures

**Overview:** Flammable liquid which can burn without a visible flame. Release can cause an immediate risk of fire and explosion. Eliminate all ignition sources, stop leak and use absorbent materials. If necessary, contain spill by diking. Fluorocarbon alcohol resistant foams may be applied to spill to diminish vapour and fire hazard. Maximize methanol recovery for recycling or re-use. Restrict access to area until completion of cleanup. Ensure cleanup is conducted by

trained personnel only. Wear adequate personal protection and remove all sources of ignition. Notify all governmental agencies as required by law.

**Personal Protection:** Full face, positive pressure self-contained breathing apparatus or airline, and protective clothing must be worn. Protective fire fighting structural clothing is not effective protection from methanol.

**Environmental Precautions:** Biodegrades easily in water. Methanol in fresh or salt water may have serious effects on aquatic life. A study on methanol's toxic effects on sewage sludge bacteria reported little effect on digestion at 0.1% while 0.5% methanol retarded digestion. Methanol will be broken down to carbon dioxide and water.

**Remedial Measures:** Flammable liquid. Release can cause an immediate fire/explosion hazard. Eliminate all sources of ignition, stop leak and use absorbent materials. Collect liquid with explosion proof pumps. Do not walk through spill product as it may be on fire and not visible.

**Large Spills:** If necessary, contain spill by diking. Fluorocarbon alcohol resistant foams may be applied to spill to diminish vapour and fire hazard. Maximize methanol recovery for recycling or reuse. Collect liquid with explosion proof pumps.

**Small Spills:** Soak up spill with non-combustible absorbent material. Recover methanol and dilute with water to reduce fire hazard. Prevent spilled methanol from entering sewers, confined spaces, drains, or waterways. Restrict access to unprotected personnel. Full. Put material in suitable, covered, labeled containers. Flush area with water.

## 7. Handling and Storage

**Handling Procedures:** No smoking or open flame in storage, use or handling areas. Use explosion proof electrical equipment. Ensure proper electrical grounding procedures are in place.

**Storage:** Store in totally enclosed equipment, designed to avoid ignition and human contact. Tanks must be grounded, vented, and should have vapour emission controls. Tanks must be diked. Avoid storage with incompatible materials. Anhydrous methanol is non-corrosive to most metals at ambient temperatures except for lead, nickel, monel, cast iron and high silicon iron. Coatings of copper (or copper alloys), zinc (including galvanized steel), or aluminum are unsuitable for storage. These materials may be attacked slowly by the methanol. Storage tanks of welded construction are normally satisfactory. They should be designed and built in conformance with good engineering practice for the material being stored. While plastics can be used for short term storage, they are generally not recommended for long-term storage due to deterioration effects and the subsequent risk of contamination.

Corrosion rates for several construction materials:

<0.508 mm/year	Cast iron, monel, lead, nickel
<0.051 mm/year	High silicon iron
Some attack	Polyethylene
Satisfactory	Neoprene, phenolic resins, polyesters, natural rubber, butyl rubber
Resistant	Polyvinyl chloride, unplasticized

## 8. Exposure Controls, Personal Protection

**Engineering Controls:** In confined areas, local and general ventilation should be provided to maintain airborne concentrations below permissible exposure limits. Ventilation systems must be designed according to approved engineering standards.

**Respiratory Protection:** NIOSH approved supplied air respirator when airborne concentrations exceed exposure limits.

**Skin protection:** Butyl and nitrile rubbers are recommended for gloves. Check with manufacturer. Wear chemical resistant pants and jackets, preferably of butyl or nitrile rubber. Check with manufacturer.

**Eye and Face Protection:** Face shield and chemical splash goggles when transferring is taking place.

**Footwear:** Chemical resistant, and as specified by the workplace.

**Other:** Eyewash and showers should be located near work areas. NOTE: PPE must not be considered a long-term solution to exposure control. PPE usage must be accompanied by employer programs to properly select, maintain, clean, fit and use. Consult a competent industrial hygiene resource to determine hazard potential and/or the PPE manufacturers to ensure adequate protection.

## 9. Physical and Chemical Properties

**Appearance:** Liquid, clear, colourless  
**Odour:** Mild characteristic alcohol odour  
**Odour Threshold:** detection: 4.2 - 5960 ppm  
(geometric mean) 160 ppm  
recognition: 53 - 8940 ppm  
(geometric mean) 690 ppm

**pH:** Not applicable

**Vapour Pressure:** 12.8 kPa @ 20°C

**Solubility:** Completely soluble

**Vapour Density:** 1.105 @ 15°C

**Freezing Point:** -97.8 °C

**Boiling Point:** 64.7 °C @ 101.3 kPa

**Critical Temperature:** 239.4 °C

**Relative Density:** 0.791

**Evaporation Rate:** 4.1 (n-butyl acetate =1)

**Partition Coefficient:** Log P (oct) = -0.82

**Solubility in other Liquids:** Soluble in all proportions in other alcohols, esters, ketones, ethers and most other organic solvents

## 10. Stability and Reactivity

**Chemical Stability:** Yes

**Incompatibility:** Yes. Avoid contact with strong oxidizers, strong mineral or organic acids, and strong bases. Contact with these materials may cause a violent or explosive reaction. May be corrosive to lead, aluminum, magnesium, and platinum.

**Conditions of Reactivity:** Presence of incompatible materials and ignition sources.

**Hazardous Decomposition Products:** Formaldehyde, carbon dioxide, and carbon monoxide.

**Hazardous Polymerization:** Will not occur.

## 11. Toxicological Information

<b>LD<sub>50</sub>:</b>	5628 mg/kg (oral/rat), 20 ml/kg (dermal/rabbit)
<b>LC<sub>50</sub>:</b>	64000 ppm (rat)
<b>Acute Exposure:</b>	See Section 3
<b>Chronic Exposure:</b>	See Section 3.
<b>Exposure Limits:</b>	See Section 2.
<b>Irritancy:</b>	See Section 3.
<b>Sensitization:</b>	No
<b>Carcinogenicity:</b>	Not listed by IARC, NTP, ACGIH, or OSHA as a carcinogen.
<b>Teratogenicity:</b>	No
<b>Reproductive toxicity:</b>	Reported to cause birth defects in rats exposed to 20,000 ppm
<b>Mutagenicity:</b>	Insufficient data
<b>Synergistic products:</b>	None Known

## 12. Ecological Information

**Environmental toxicity:** Methanol in fresh or salt water may have serious effects on aquatic life. A study on methanol's toxic effects on sewage sludge bacteria reported little effect on digestion at 0.1% while 0.5% methanol retarded digestion. Methanol will be broken down into carbon dioxide and water.

**Biodegradability:** Biodegrades easily in water.

## 13. Disposal Considerations

Review federal, provincial or state, and local government requirements prior to disposal. Store material for disposal as indicated in Section #7, **Handling and Storage**. Disposal by controlled incineration or by secure land fill may be acceptable.

## 14. Transport Information

<b>Transport of Dangerous Goods (TDG and CLR):</b>	Methanol, Class 3(6.1), UN1230, P.G. II Limited Quantity: ≤ 1 litres
<b>United States Department of Transport (49CFR): (Domestic Only)</b>	Methanol, Class 3, UN 1230, P.G. II, (RQ 5000 lbs/2270 kg) Limited Quantity: ≤ 1 litres
<b>International Air Transport Association (IATA):</b>	Methanol, Class 3(6.1), UN1230, P.G. II Packaging Instruction: 305, 1 litre maximum per package,
<b>International Maritime Organization (IMO):</b>	Methanol, Class 3(6.1), UN1230, P.G. II, Flash Point = 12 °C EmS No. F-E, S-D Stowage Category "B", Clear of living quarters

## 15. Regulatory Information

### CANADIAN FEDERAL REGULATIONS:

CEPA, DOMESTIC SUBSTANCES LIST: Listed

WHMIS CLASSIFICATION: B2, D1A

### UNITED STATES REGULATIONS:

29CFR 1910.1200 (OSHA): Hazardous

40CFR 116-117 (EPA): Hazardous

40CFR 355, Appendices A and B: Subject to Emergency Planning and Notification

40CFR 372 (SARA Title III): Listed

40CFR 302 (CERCLA): Listed

## 16. Other Information

**Preparation Date:** October 13, 2005

**Prepared by:** Kel-Ex Agencies Ltd., P.O. Box 52201, Lynnmour RPO, North Vancouver, B.C., V7J 3V5

**Disclaimer:** The information above is believed to be accurate and represents the best information currently available to us. Users should make their own investigations to determine the suitability of the information for their particular purposes. This document is intended as a guide to the appropriate precautionary handling of the material by a properly trained person using this product.

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**Revisions:** None

# Appendix C Transesterification

## Transesterification

The production processes for biodiesel are well known. There are three basic routes to biodiesel from oils and fats:

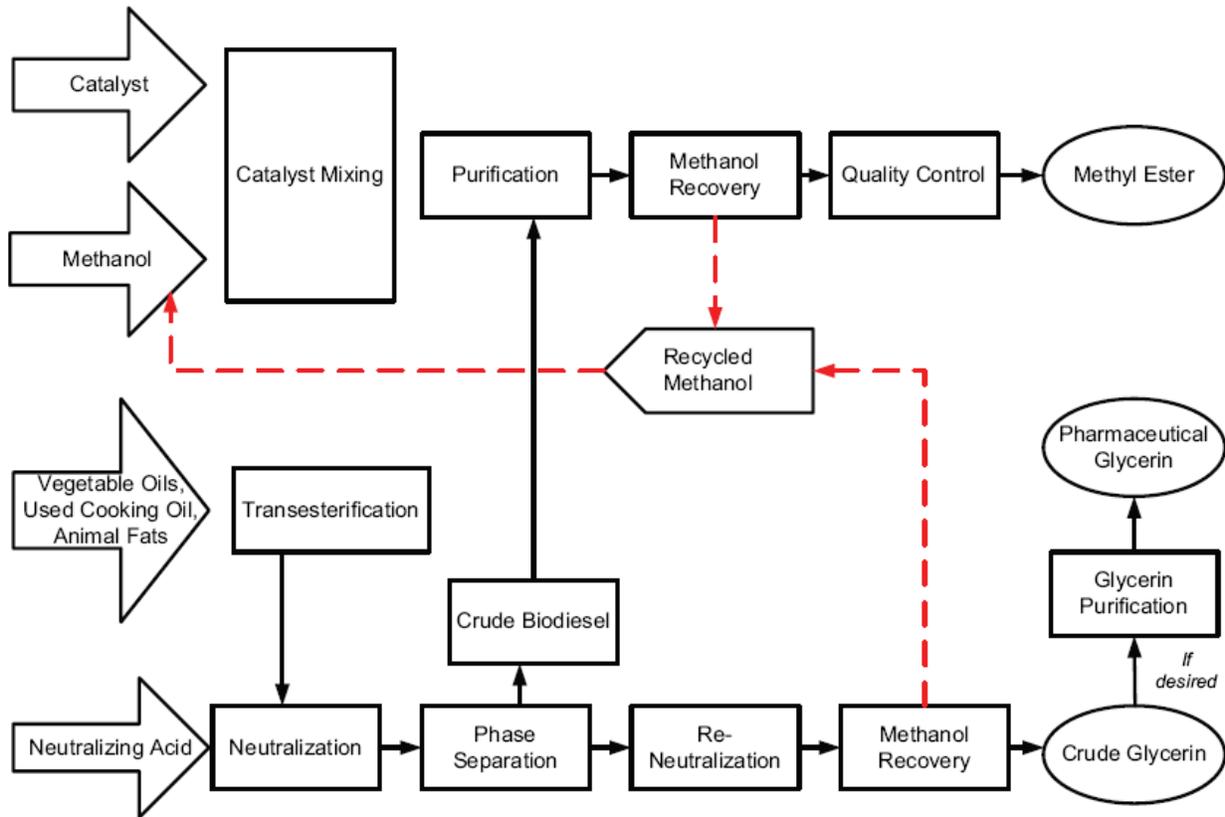
- base catalyzed transesterification of the oil;
- direct acid catalyzed transesterification of the oil; and
- conversion of the oil to its fatty acids and then to biodiesel.

Most of the biodiesel produced today is done with the base catalyzed reaction for several reasons:

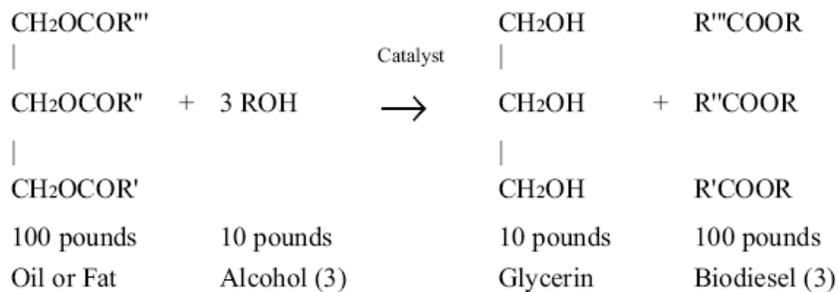
- It is low temperature and pressure.
- It yields high conversion (98 percent) with minimal side reactions and reaction time.
- It is a direct conversion to biodiesel with no immediate compounds.
- No exotic materials of construction are needed.

The chemical reaction for base catalyzed biodiesel production is depicted in Figure C.1. One hundred pounds (45.36 kilograms) of fat or oil (such as soybean oil) are reacted with 10 pounds (4.54 kilograms) of a short chain alcohol in the presence of a catalyst to produce 10 pounds (4.54 kilograms) of glycerin and 100 pounds (45.36 kilograms) of biodiesel. The short chain alcohol, signified by ROH (usually methanol, but sometimes ethanol), is charged in excess to assist in quick conversion. The catalyst is usually sodium or potassium hydroxide that has already been mixed with the methanol. R', R'', and R''' indicate the fatty acid chains associated with the oil or fat which are largely palmitic, stearic, oleic, and linoleic acids for naturally occurring oils and fats (see Figure C.2).

**Figure C.1: The Biodiesel Production Process**



**Figure C.2: The Biodiesel Reaction**



## ***The Biodiesel Production Process***

The base catalyzed production of biodiesel generally occurs using the following steps:

### **Mixing of Alcohol and Catalyst**

The catalyst is typically sodium hydroxide (caustic soda) or potassium hydroxide (potash). It is dissolved in the alcohol using a standard agitator or mixer.

### **Reaction**

The alcohol/catalyst mix is then charged into a closed reaction vessel and the oil or fat is added. The system from here on is totally closed to the atmosphere to prevent the loss of alcohol. The reaction mix is kept just above the boiling point of the alcohol (around 160°F [71.1°C]) to speed up the reaction and the reaction takes place. Recommended reaction time varies from 1–8 hours, and some systems recommend the reaction take place at room temperature. Excess alcohol

is normally used to ensure total conversion of the fat or oil to its esters. Care must be taken to monitor the amount of water and free fatty acids in the incoming oil or fat. If the free fatty acid level or water level is too high, it may cause problems with soap formation and the separation of the glycerin by-product downstream.

### **Separation**

Once the reaction is complete, two major products exist: glycerin and biodiesel. Each has a substantial amount of the excess methanol that was used in the reaction. The reacted mixture is sometimes neutralized at this step if needed. The glycerin phase is much more dense than the biodiesel phase and the two can be gravity separated with glycerin simply drawn off the bottom of the settling vessel. In some cases, a centrifuge is used to separate the two materials faster.

### **Alcohol Removal**

Once the glycerin and biodiesel phases have been separated, the excess alcohol in each phase is removed with a flash evaporation process or by distillation. In other systems, the alcohol is removed and the mixture neutralized before the glycerin and esters have been separated. In either case, the alcohol is recovered using distillation equipment and is re-used. Care must be taken to ensure no water accumulates in the recovered alcohol stream.

### **Glycerin Neutralization**

The glycerin by-product contains unused catalyst and soaps that are neutralized with an acid and sent to storage as crude glycerin. In some cases the salt formed during this phase is recovered for use as fertilizer. In most cases the salt is left in the glycerin. Water and alcohol are removed to produce 80–88 percent pure glycerin that is ready to be sold as crude glycerin. In more sophisticated operations, the glycerin is distilled to 99 percent or higher purity and sold into the cosmetic and pharmaceutical markets.

### **Methyl Ester Wash**

Once separated from the glycerin, the biodiesel is sometimes purified by washing gently with warm water to remove residual catalyst or soaps, dried, and sent to storage. In some processes this step is unnecessary. This is normally the end of the production process resulting in a clear, amber-yellow liquid with a viscosity similar to petroleum diesel (petrodiesel). In some systems the biodiesel is distilled in an additional step to remove small amounts of color bodies to produce a colorless biodiesel.

# Appendix D Schematic of a Biodiesel Plant

