Biodiesel Manufacturing Facility Response Overview

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I. Purpose

The purpose of this document is to provide useful planning and response information to the Region 5 United States Environmental Protection Agency (U.S. EPA) regarding biodiesel manufacturing facilities. The growing demand for alternative fuels has led to the rapid development of biofuels manufacturing facilities in the U.S., many of which are located or will be sited in Region 5. Therefore, U.S. EPA has identified a need to advise responders on the implications regarding potential material and chemical storage and implications of a release from a biodiesel manufacturing facility. This document contains information specific to biodiesel manufacturing facilities and is meant to provide an overall understanding of the biodiesel manufacturing process including the potential chemicals involved, types of potential releases from biodiesel facilities, response measures for the chemicals involved, and Federal regulations applicable to these facilities.

II. Description of Biodiesel Fuel and the Biodiesel Production Process

The biodiesel production process begins with soybeans (or other feedstock) and ends with the production of biodiesel fuel. There are two major parts to the process. The first part is the extraction of the oil from the soybeans (if the feedstock is an animal fat[1] rather than a vegetable oil, the extraction step is not needed). In the second part of the process the oil or fat is chemically modified through a process called transesterification to substitute a simple alcohol, such as methanol, for the complex alcohol, glycerol.[2] This results in a material with a lower viscosity that is more suitable for fuel.

For soybean-based biodiesel fuel, the production process begins when soybeans are delivered to the biodiesel production plant. The handling of soybeans, grain, and other agricultural products is well-known to have the potential to produce dust, so there may be particulate emissions associated with soybean transfer and handling. In addition to being a nuisance, this dust is flammable and therefore may present an explosion hazard if it becomes suspended in air.

The next step is soybean processing. In this step, the hulls (the soybean fiber coat) are removed from the soybeans and then the soybeans are cracked and flaked. In some plants, the flakes are gathered into a porous pellet form. The porous pellet form allows the solvent to flow freely through the bed (during the extraction process) while still letting the solvent extract the oil; otherwise the flakes may gather in a layer that impedes solvent flow.

After this preparation, the oil is extracted from the soybeans with a solvent (typically this solvent is hexane). The soybean flakes are mixed with an approximately equal weight of hexane. Thus, given the large tonnage of soybeans that are processed, the internal hexane flow rates will be considerable. The hexane is captured for recycling.

After the soybean oil is extracted, the remaining product is the soy meal. Soy meal is mainly used as an animal feed. But, after the extraction process, it is still wet with hexane and before it can be used, the hexane (as well as excess moisture) must be removed. This entails multiple stages of steam-heated evaporators with hexane solvent recovery. This is an energy intensive process and one which involves flammable solvent vapors.

The hexane-soybean oil mixture must be separated so that the soybean oil can be recovered. Multiple steam evaporators are used to evaporate the hexane from the soybean oil. The hexane is then condensed and recovered.

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[1] Fats and oils are the same class of organic compounds, the difference is that fats are solid at room temperature, while oils are liquid at room temperature. Both are chemical compounds, called esters, of two components, a fatty acid and the alcohol glycerol.

[2] Glycerin and glycerol are two names for the same substance.

The soybean oil is then washed with hot water to remove undesirable gums.

The production of biodiesel fuel continues with alkali refining of the soybean oil to remove free fatty acids. During this step, the soybean oil is washed with sodium hydroxide and water to remove any free fatty acids in the oil (these would cause gums to form in the fuel if they remained).

The final part of the process is the transesterification reaction. During this process, the glycerol portion of the soybean oil is replaced with methanol, whereby methanol is an input and glycerol is an output.

Wastewater treatment is necessary as part of the overall plant operation. This treatment is necessary to remove residual soybean oil and hexane, both of which are environmentally undesirable in the waste stream and both of which have economic value if recovered.

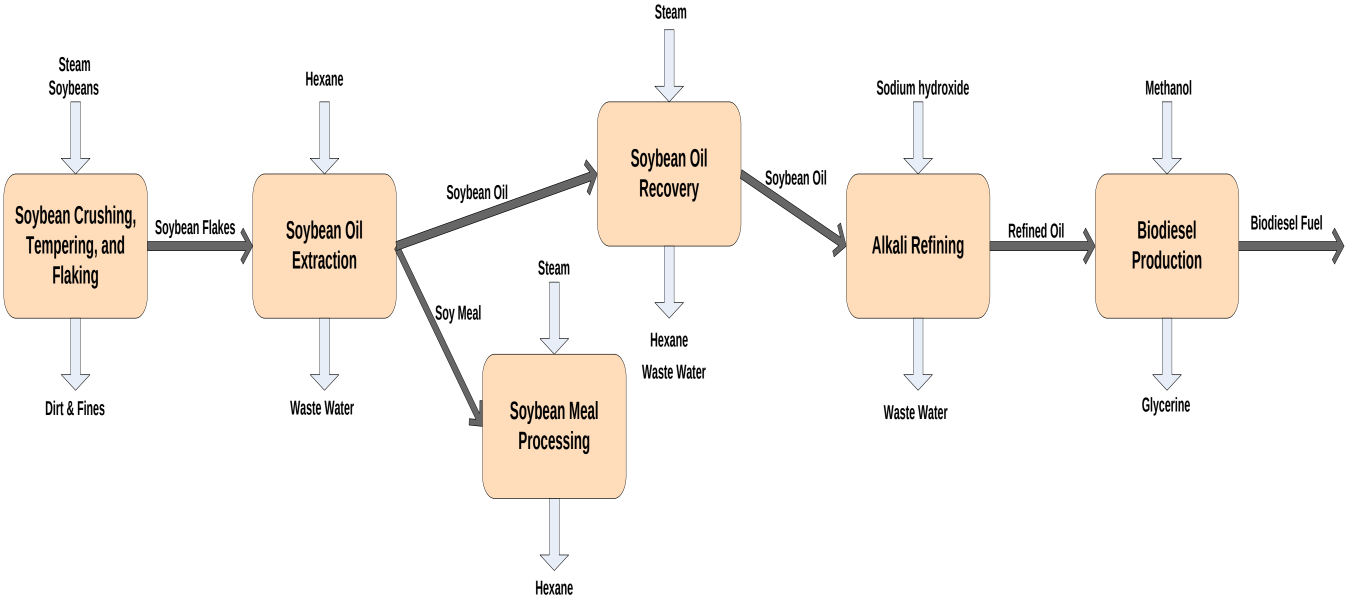

Figure 1. Major Steps in Biodiesel Production

Figure 1 summarizes the major steps in biodiesel production and their associated inputs (shown above the box) and outputs (shown below the box). Although there are other inputs and outputs, these are the most significant when looking at the biodiesel production process. It should be noted again that biodiesel fuel can also be derived from animal fats, such as tallow and yellow grease. In these cases the soybean crushing and extraction steps are omitted, but the balance of the biodiesel production process is similar. **Attachment A** provides a summary of currently-operating industrial-scale biodiesel manufacturing facilities within the Region 5 boundaries.

III. Chemicals Involved in Biodiesel Production

Table 1 summarizes the major components, byproducts, and products of the biodiesel manufacturing process. Quantities produced, stored, or used vary by facility. For instance, a facility producing 5,000,000 gallons of biodiesel annually would likely use between 1,000 and 2,000 gallons of methanol per day. The flammability of materials associated with biodiesel production varies. Hexane and methanol are highly flammable and constitute the principal flammability hazards.

TABLE 1: MAJOR COMPONENTS, BYPRODUCTS, AND PRODUCTS OF THE BIODIESEL MANUFACTURING PROCESS

Chemicals	Used Product, Product or byproduct and purpose	Flammability (National Fire Protection Association)	LEL	UEL	I.P.	S.G.	V.P.	F.P.	pH	Solubility in Water	Color	Odor	IDLH	Comments
Methanol	Used Product – transesterification reaction	3	6%	36%	10.84 eV	0.79	96 mmHg	52 °F	NA	Soluble	Colorless liquid	Pungent odor	6,000 ppm	Incompatibilities & Reactivities: Strong Oxidizers
Sodium Hydroxide	Used Product – washes oil to remove fatty acids.	0	NA	NA	NA	2.13	0 mmHg	NA	13-14	Miscible	Colorless to white,	Odorless solid	10 mg/m3	Non-combustible solid but when in contact with water may generate sufficient heat to ignite combustible materials. Incompatibilities: acids, organics, some metals (i.e. aluminum)
Potassium Hydroxide	Used Product - washes oil to remove fatty acids.	0	NA	NA	NA	2.04	1 mmHg	NA	13	Miscible	White or slightly yellow lumps, rods, flakes, sticks, or pellets.	Odorless	NA	Non-combustible solid but when in contact with water may generate sufficient heat to ignite combustible materials. Incompatibilities: acids, organics
Hexane	Used Product – used for soybean oil extraction	3	1.1%	7.5%	10.18 eV	0.66	124 mmHg	-7 °F	NA	Insoluble	Clear	Mild, gasoline like odor.	1,100 ppm	Incompatibilities & Reactivities: Strong Oxidizers
Glycerol	Byproduct - transesterifiation reaction	1	NA	NA	NA	1.26	0.003 mmHg	320 °F	NA	Miscible	Clear	Odorless	NA	Incompatibilities & Reactivities: Strong Oxidizers

TABLE 1 (CONTINUED): MAJOR COMPONENTS, BYPRODUCTS, AND PRODUCTS OF THE BIODIESEL MANUFACTURING PROCESS														
Chemicals	**Used Product, Product or byproduct and purpose**	**Flammability (National Fire Protection Association)**	**LEL**	**UEL**	**I.P.**	**S.G.**	**V.P.**	**F.P.**	**pH**	**Solubility in Water**	**Color**	**Odor**	**IDLH**	**Comments**
Soybean hulls and fines	Byproduct – soybean process	NA	NA	NA	NA	NA	NA	NA	NA	NA	Tan to Brown	NA	NA	May cause/form explosive mixture if suspended in air.
Fuel for process heat (i.e. natural gas, propane, etc.)	Used Product – Energy Source	2	Varies	Varies	Varies	Varies	Varies	Varies	NA	Slight	Colorless	Foul skunk-like odor (Natural gas, Propane) Diesel-like odor (Fuel oil)	Varies	Keep away from high heat, strong oxidizing agents and sources of ignition.
Biodiesel	Final Product	1	NA	NA	NA	0.88	<2 mmHg	>300 ºF*	NA	Insoluble	Pale yellow	Mild odor	NA	Incompatibilities & Reactivities: Strong Oxidizers

ºF – degrees Fahrenheit
e.V. – electron volts
F.P. – flash point
IDLH - Immediately Dangerous to Life and Health
I.P. – ionization potential
LEL – lower explosive limit
Mg/m3 – milligrams per cubic meter
mmHg – millimeters mercury
NA – not applicable or information not available
% - percent
ppm – parts per million
S.G. – specific gravity
UEL – upper explosive limit
V.P. – vapor pressure
< - less than
> - greater than
* - the flash point provided is for pure biodiesel rather than blended biodiesel.

The sources of process heat, and therefore the chemical properties will vary by facility. Facility-specific information must be obtained to determine source.

Note: Remember to account for correction factors for PID and LEL sensors when using the standard air monitoring device (Multi-RAE)

Note: The National Fire Protection Association ratings are on a 0 to 4 scale with 4 being the most flammable.

IV. Types of Potential Releases

Causes

Chemical releases may result from a variety of causes. Some examples of the causes are:

- **Containment failures**. Possible containment failures range from small, e.g. drips from a leaking fitting to large, e.g. loss of the contents of an entire tank or reactor. The size of containment units will vary by facility depending on the scale of production. For example, if the biodiesel product at a facility is shipped in 30,000 gallon capacity rail cars, there must be tankage at the facility sufficient to fill one or more rail cars. A recent incident in Defiance, Ohio involved a 10,000 gallon glycerin tank. As mentioned above, a facility producing 5,000,000 gallons of biodiesel annually would likely use between 1,000 and 2,000 gallons of methanol per day and require storage of several thousand gallons.
- **Process upsets**. Process upsets are often the result of operator error. If the process design is adequate, safety relief valves will prevent equipment failures and vent streams will be directed to safe locations. The ability of the equipment to function properly or shut down properly in the event of an evacuation or incident depends primarily on the control system (i.e. how automated it is, whether or not it has fail safe design, and how much damage it may have sustained). If the control system is not functional, then process operations and upsets will likely continue until they can be manually shut down. But if the system is well designed, equipment should be automatically shut down in an orderly manner.
- **Equipment malfunctions**. Equipment malfunctions include a wide variety of conditions from inoperable sensors, pumps that fail to pump, valves that fail to close or open, broken or jammed equipment, or clogged pipes.
- **Loss of utilities**. The most obvious utility loss is an electrical power failure, though for some plants, loss of cooling water supply may be a risk. The location of some biodiesel processing plants in rural areas may make them more susceptible to loss of utilities.
- **Unexpected chemical reactions**. While the chemistry of biodiesel production is relatively old and quite well known, there is always the possibility that an unexpected chemical reaction may occur. For processes like biodiesel production that are well-understood, the most common cause of unexpected chemical reactions is mislabeling, mishandling of materials, mistaken delivery of materials, or the use of contaminated materials.

Consequences

Whatever the cause of a release at a biodiesel facility, the seriousness of the release is dependant on the amount of inventory of material on site. This will vary with the scale of the process, and the amount of storage provided. Consequences of a biodiesel facility release could range from relatively minor (small releases contained on site) to very significant (large quantities released affecting off site areas or an explosion or fire). The assessment of the amounts of various materials typically stored at biodiesel production plants is an area where further facility-specific information gathering is needed. Industrial-scale facilities are subject to many of the regulations summarized in Section VIII including hazardous substance storage and reporting requirements. Therefore, local first responders should have industrial-scale facility information on file for those within their response jurisdiction if the proper reporting requirements are being followed. The facilities subject to reporting requirements must have product quantity and storage information on-site to be in compliance with applicable regulations.

V. Response to a Release

The response to releases depends on the size, location, and nature of the release. In general, identification of the material being released is often the first and most essential task. In this respect, labeled tanks or containers (at a minimum with NFPA hazard codes) would be most useful.

An important issue is that partially processed soy products may be quite high in hexane content. For example, soy meal, as it is first produced contains up to 40 percent hexane solvent. This solvent is removed and recovered prior to sale as a final product, but if due to an accident or loss of containment, partially processed soy meal is released, there would be a significant flammability and toxicity hazard from the hexane solvent. The same is true for the partially processed soy oil, and for various other process and waste streams from which hexane is normally recovered prior to re-use or discharge. A similar situation can occur for portions of the process where methanol is used.

For releases, air monitoring must first be used to determine if there are sufficient vapors to cause a health or flammability hazard. For both hexane and methanol the health exposure limit is about 100 times less than the lower explosive limit.

For both hexane and methanol containment strategies similar to those used for gasoline are appropriate. However, because methanol is miscible with water and relatively biodegradable, simple dilution with excess water may be appropriate for small spills.

Both sodium and potassium hydroxides release large amounts of heat when they react with water. Because of the amount of heat released, steam may be formed that can result in the dispersal of the hydroxide through the air.

In the case of fire, the main issue is that accidental fires rarely have an adequate amount of oxygen delivered to the fuel to achieve complete combustion. Thus, in addition to the oxides of nitrogen formed by all types of combustion in air, the partial combustion results in the emissions of carbon monoxide, unburned fuel, partially burned fuel, and soot. The amount of such emissions varies widely depending on the geometry and circumstances of the fire. Data on the amounts of various air pollutants produced by accidental fires in process plants are sparse to non-existent, and in any case, the differences in circumstances are such that data from one incident will not have much applicability.

Table 2 provides a summary of the appropriate monitoring instruments and response measures to be taken in the event of a release of one of the major components, byproducts, or products of the biodiesel manufacturing process. When responding to a biodiesel facility where biodiesel fuel has been released, the situation in general should be treated the same as a diesel fuel spill. Pure biodiesel and/or biodiesel mix (B20 - a mixture of biodiesel and petroleum diesel) response procedures would be the same as response procedures for a diesel release, but biodegradation in the environment would be quicker (for biodiesel), as biodiesel speeds and aids in petroleum diesel degradation.

The U.S. Coast Guard and U.S. EPA do not have different regulations for biodiesel fuel versus diesel fuel releases; both are regulated under the Oil Pollution Act of 1990 (OPA 90). The Region 5 Oil and Hazardous Substances Integrated Contingency Plan (ICP) provides specific action that should be used when responding to an oil or hazardous materials incident. (http://www.great-lakes.net/partners/epa/acp-rcp/).

Glycerin is nonhazardous and when in its solid form, responders or cleanup personnel can use a shovel to place the material into a waste disposal container. Vapors are not a likely hazard at room temperature provided glycerin mists are not present. When glycerin is in its liquid form it can be absorbed with an inert material and placed into a waste disposal container. Water spray can be used to reduce glycerin vapors. However, glycerin does have a flash point of approximately 320 ºF and can therefore present a fire hazard under high heat conditions. Further, the transesterification process results in the glycerin being soaked with methanol until the methanol can be recovered or removed. Therefore, glycerin stored at a biodiesel facility may exhibit the characteristics of methanol and should be treated as such with regards to flammability, cleanup, and respiratory protection considerations. Glycerin released to surface water or storm water can increase the biochemical oxygen demand (BOD) of the aquatic system or wastewater treatment operations. The increased BOD can disrupt aquatic systems and wastewater treatment plant operations by increasing organisms such as macroinvertebrates that are more tolerant of lower dissolved oxygen (i.e. leeches and sludge worms), and organisms that need higher oxygen levels (i.e. caddis fly larvae and mayfly nymphs) will not survive. Equipment at a wastewater treatment plant can also malfunction because of the inability to process the higher BOD concentrations.

TABLE 2: APPROPRIATE MITIGATION MEASURES FOR RELEASES OF MAJOR COMPONENTS, BYPRODUCTS, AND PRODUCTS OF THE BIODIESEL MANUFACTURING PROCESS		
Chemicals	**Proper Air Monitoring Equipment**	**Proper Spill Containment**
Biodiesel Fuel	Biodiesel fuel has a very low volatility at normal ambient temperatures. However, vapors/mists may be generated when heated above ~266 degrees Fahrenheit (°F).	Containment/response should follow typical oil containment procedures; use oil-dry, petroleum-compatible absorbent socks, booms, etc; do not store soaked materials near combustibles; the absorbent material used should be resistant to alcohol in the event methanol has commingled with the biodiesel release. Disposal of biodiesel-contaminated soil or products can be considered non-hazardous provided methanol and/or hexane have not commingled with the release to meet the flammability characteristic for hazardous waste.
Methanol	For health-related assessment of exposure to methanol vapors: non-dispersive infrared analyzer, such as the MIRAN; flameionizing detector (FID); or 11.7 electron volt (eV) photoionizing detector (PID) For fire-hazard assessment: a combustible gas indicator (CGI). Remember to account for correction factors when using air monitoring equipment.	Ventilate the area of leak or spill and remove all sources of ignition; use alcohol-compatible sorbents that are non-combustible. Use non-sparking tools and equipment. For large spills, consider using a vapor suppressant foam or fuels neutralizer to prevent ignition. Waste generated from clean-up may meet the flammability characteristic for hazardous waste; or depending on the nature/source of the release classify as listed hazardous waste (i.e. F003 or U154).
Sodium Hydroxide	Sodium hydroxide is non-volatile; however flakes/particulates may become airborne and particulate monitoring is recommended.	Ventilate area. Pick up spilled contents and containerize using a method to minimize particulate generation. Spill residues can be diluted with water and neutralized with acetic acid, hydrochloric acid, or sulfuric acid and absorbed with inert, corrosive-compatible materials. Color change indicator materials both absorb and neutralize the spills. Waste generated from cleanup may meet the corrosivity characteristic for hazardous waste.
Potassium Hydroxide	Potassium hydroxide is non-volatile; however flakes/particulates may become airborne and particulate monitoring is recommended.	Ventilate area. Pick up spilled contents and containerize using a method to minimize particulate generation. Spill residues can be diluted with water and neutralized with acetic acid, hydrochloric acid, or sulfuric acid and absorbed with inert, corrosive-compatible materials. Color change indicator materials both absorb and neutralize the spills. Waste generated from clean-up may meet the corrosivity characteristic for hazardous waste.
Hexane	For health-related assessment of exposure to hexane vapors: non-dispersive infrared analyzer, such as the MIRAN; FID; or 10.6 eV PID For fire-hazard assessment: a CGI. Remember to account for correction factors when using air monitoring equipment.	Ventilate area of leak or spill. Remove all sources of ignition. Contain and recover liquid when possible. Use non-sparking tools and equipment. Collect liquid in an appropriate container or absorb with an inert material (e. g., vermiculite, dry sand, earth), and place in a chemical waste container. For large spills, consider using a vapor suppressant foam or fuels neutralizer to prevent ignition. Do not use combustible materials, such as saw dust. If a leak or spill has not ignited, use water spray to disperse the vapors, to protect personnel attempting to stop leak, and to flush spills away from exposures. Waste generated from cleanup may meet the flammability characteristic for hazardous waste.
Glycerin	Volatility of glycerin is extremely low at normal ambient temperatures – but monitoring should be similar to methanol as a precautionary measure due to glycerin becoming soaked with methanol during the production process. Flash point is ~320 ºF for glycerin only.	Clean spillage with a compatible absorbent material, booms, pigs, pads etc. and place in a tight container for later disposal. Avoid contamination of sewers, storm drains, surface waters and soils due to possibility of glycerin increasing BOD and potential flammability if soaked with methanol.
Soybean hulls and fines	A filter-based or optical based particulate matter meter.	Non-sparking shovels and brooms, in indoors spill monitor dust concentrations, and use engineering controls to minimize dust generation.
Fuel for process heat	For fire-hazard assessment: a CGI	Ventilate area of leak or spill. Remove all sources of ignition. Do not extinguish fires involving flammable gas cylinders unless the source of ignition can be shut off. Ventilate the area with explosion proof fans to eliminate explosive gas cloud formation. Use petroleum-compatible sorbents to clean up contents on surfaces or deploy booms for surface water releases.

VI. Environmental Receptors and Concerns

Table 3 summarizes the expected fate of the primary biodiesel manufacturing products and byproducts

TABLE 3: EXPECTED FATE OF THE MAJOR COMPONENTS, BYPRODUCTS, AND PRODUCTS OF THE BIODIESEL MANUFACTURING PROCESS

Chemicals	Release in Soil	Release in Water	Release in Air as result of spill/fire	Release to storm/sanitary sewers
Biodiesel Fuel	Biodegradation occurs, with faster rates under aerobic conditions than anaerobic conditions.	Insoluble in water. Degrades rapidly and fairly extensively in aquatic environments. Estimated to degrade at a rate approximately four times faster than petroleum diesel – 85% of pure biodiesel expected to degrade within 28 days.	Combustion produces carbon monoxide, carbon dioxide along with thick smoke.	May be high in free fatty acids and glycerin, and can have a high BOD. These can disrupt wastewater treatment plant operations.
Methanol	Not likely to persist in soil due to its rapid biodegradation. Highly soluble, little potential for adsorption.	Miscible in water and consequently will dissolve quickly and be diluted to low concentrations. Will not volatilize from water but is easily biodegraded.	Liquid is flammable and, at normal room temperatures, it evolves vapors which form explosive mixtures over a wide range of concentrations. Violent reaction with oxidizing agents	Accelerates biodegradation
Sodium Hydroxide	Separates into sodium cations and hydroxide anions when it comes into contact with moisture.	Separates in water to sodium cations and hydroxide anions, which ultimately decrease the acidity of the water. May give off heat with water contact.	Breaks down readily in the atmosphere by reacting with other chemicals. Dangerous gases may accumulate in confined spaces. Incompatible with combustible materials, acids, halo carbons, metals, halogens, oxidizing materials, peroxides, metal salts. Thermal decomposition product is oxides of sodium.	Separates in water to sodium cations and hydroxide anions, can make the water highly basic and corrosive.
Potassium Hydroxide	Contact with moisture or water will generate heat.	Dissolves readily in water, giving off much heat and forming a caustic solution. May steam and splatter.	The substance is a strong base; it reacts violently with acid and is corrosive in moist air to metals such as zinc, aluminum, tin and lead forming a combustible /explosive gas (hydrogen). Reacts with ammonium salts to produce ammonia causing fire hazard. Attacks some forms of plastics, rubber or coatings. No thermal decomposition products.	This material is alkaline and may raise the pH of surface waters with low buffering capacity.

TABLE 3 (CONTINUED): EXPECTED FATE OF THE MAJOR COMPONENTS, BYPRODUCTS, AND PRODUCTS OF THE BIODIESEL MANUFACTURING PROCESS

Chemicals	Release in Soil	Release in Water	Release in Air as result of spill/fire	Release to storm/sanitary sewers
Hexane	Much of it will evaporate into the air before it penetrates the soil. Any *n*-hexane that penetrated the soil would probably be broken down by bacteria. If *n*-hexane leaks from an underground storage tank, it will float on the groundwater, rather than mixing with it since *n*-hexane is lighter than water.	A very small portion will dissolve in the water, but most will float on the surface and then evaporate into the air. The *n*-hexane dissolved in the water can be broken down by certain types of bacteria.	*n*-Hexane evaporates very easily into the air. Once in the air, *n*-hexane can react with oxygen and be broken down in a few days. It is an extremely flammable liquid and vapor; vapor may cause flash fire. Contact with oxidizing materials may cause extremely violent combustion. Explodes when mixed @ 28ºC (degrees Celsius) with dinitrogen tetraoxide. Sensitive to static discharge. May produce acrid smoke and irritating fumes when heated to decomposition.	Evaporates quickly; floats on surface.
Glycerin	No information found.	Miscible in cold water, hot water and alcohol.	Glycerin is incompatible with strong oxidizers such as chromium trioxide, potassium chlorate, or potassium permanganate and may explode on contact with these compounds. Explosive glyceryl nitrate is formed from a mixture of glycerin and nitric and sulfuric acids. Perchloric acid, lead oxide + glycerin form perchloric esters which may be explosive. Glycerin and chlorine may explode if heated and confined. As with any organic compound, this material may produce toxic carbon monoxide and dioxide gases if heated to decomposition.	Can have a high BOD, which can disrupt wastewater treatment plant operations by increasing organisms such as macroinvertebrates that are more tolerant of lower dissolved oxygen (i.e. leeches and sludge worms) Organisms that need higher oxygen levels (i.e. caddisfly larvae and mayfly nymphs) will not survive. Equipment can also malfunction at the plant because it can not handle the higher BOD.
Natural gas	NA	Slightly soluble in water	Dangerous fire and explosion hazard when exposed to heat, sparks or flame. Liquefied Natural Gas (LNG) releases flammable gas at well below ambient temperatures and readily forms a flammable mixture with air. Decomposition products include carbon monoxide, carbon dioxide and non-combusted hydrocarbons (smoke).	NA

TABLE 3 (CONTINUED): EXPECTED FATE OF THE MAJOR COMPONENTS, BYPRODUCTS, AND PRODUCTS OF THE BIODIESEL MANUFACTURING PROCESS

Chemicals	Release in Soil	Release in Water	Release in Air as result of spill/fire	Release to storm/sanitary sewers
Propane	Releases are expected to cause only localized non-persistent environmental damage. The passage of odorized propane through soil because of an underground leak will also diminish or eliminate entirely the smell of odorized propane.	Slightly soluble in water	Normal combustion produces carbon dioxide; incomplete combustion can produce carbon monoxide. Propane vapors will form explosive mixtures with air and will easily ignite by heat, sparks, flames, build-up of static electricity, and other sources of ignition. Note: Ethyl mercaptan might, under certain conditions (when oxygen, water, iron oxide or other oxidizers are present in containers and piping) react with oxidizers which diminish or eliminate entirely its distinct smell, thereby reducing or eliminating the ability of a person to detect a leak. Incompatible with strong alkalines and oxidizers such as chlorine (gas or liquid) and oxygen.	Waste mixtures containing these gases should not be allowed to enter drains or sewers where there is danger of vapors being ignited.
Fuel Oil	Some chemicals in fuel oils evaporate into the air. Other chemicals in the fuel oils dissolve in water. Some may slowly move down through the soil to the groundwater. Others can attach to particles in the soil or water and, in water, may sink down into the sediment. The chemicals that dissolve in water may also be broken down by primarily bacteria and fungi in the soil. However, this may take up to a year to occur, if ever, depending on the environmental conditions. Chemicals that attach to soil may remain in the environment for more than a decade.	Some chemicals in fuel oils evaporate into the air. Other chemicals in the fuel oils dissolve in water. Others may sink down into the sediment. The chemicals in water may be broken down by primarily bacteria and fungi; however, this may take up to a year to occur, if ever, depending on the environmental conditions. Some chemicals may remain up more than a decade.	Avoid high temperatures, open flames, sparks, welding, smoking and other ignition sources. Keep away from strong oxidizers; Viton®; Fluorel®. Decomposition products include carbon monoxide, carbon dioxide and non-combusted hydrocarbons (smoke). The chemicals that evaporate may break down in air by reacting with sunlight, *e.g.*, photooxidation, or other chemicals in the air.	Can have a BOD, which can disrupt wastewater treatment plant operations. Can produce flammable gases.

NA – not applicable or no information found

VII. Overall Health Risks from a Release from a Biodiesel Facility

This section addresses the immediate and long term human health and/or environment hazards associated with a release from a biodiesel fuel facility.

Biodiesel Fuel

- **Human Health Effects**

Inhalation effects are negligible unless heated to produce vapors. Vapors or finely misted materials may irritate the mucous membranes and cause irritation, dizziness, and nausea. May cause eye irritation. Prolonged or repeated contact is not likely to cause significant skin irritation. Material sometimes encountered at elevated temperatures. Thermal burns are possible from material encountered at elevated temperatures. No hazards anticipated from incidental ingestion to industrial exposure.

If biodiesel fuel were to be ingested, enzymes in the body called esterases would break the biodiesel fuel molecules into the component fatty acids and alcohol molecules[i,ii]. The alcohol is usually methanol and methanol is toxic. Thus, methanol toxicity could be a concern for ingestion of biodiesel fuel.

Although methanol is toxic to humans and other primates, methanol is relatively non-toxic to non-primates, such as rodents. Thus, rodent data on biodiesel toxicity is not relevant for assessing the health effects of human exposure to methanol.

Neat biodiesel fuel is approximately 11 percent methanol by weight, so ingestion of 100 grams of biodiesel would release 11 grams, or 14 milliliters (mL),[3] of methanol. For a 70 kilogram (kg) adult, the fatal dose of methanol ranges from 60 to 160 mL.

- **Ecological Effects**

A number of studies have found that biodiesel biodegrades much more rapidly than conventional diesel. When biodiesel is present in bulk in the environment, it can coat animals that come in contact with it and may reduce the ability of oxygen to reach aquatic systems. In this respect, its action is similar to petroleum diesel fuel. However, biodiesel does not have the toxicity and the solvent action that diesel fuel has, so its effects on animals are expected to be less severe.

The treatment of oiled birds and animals would be similar to the treatment provided when an oil spill occurs. The fuel can be flushed from its eyes and intestines and those heavily oiled are wiped with absorbent clothes to remove the fuel. Basic personal protection equipment, including gloves, coveralls, and safety glasses should be worn by those individuals cleaning the animals.

Methanol

- **Human Health Effects**

Target organs: central nervous system and retina. Poisoning may occur from ingestion, inhalation, or percutaneous absorption. Acute ingestion of as little as 4 to 10 mL of methanol may cause permanent

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[i] " Esters are broken down in the bloodstream by plasma esterases to the constituent carboxylic acids and alcohols," Industrial Toxicology, Edited by Phillip L. Willimas and James L Burson. Van Nosrand Reinhold, New York, 1985. p. 245

[ii] Mammalian tissues contain nonspecific esterases…that hydrolyze..ester linkages in foreign compounds. This …liberates an alcohol function in the case of esters." Caserett and Duell's Toxicology: The Basic Science of Poisons, Second Edition, John Doull, Curtis D. Klassen, and Mary O. Amdur, Editors, Mcmillan, 1980. p. 59 [3]

blindness. Evidence from the photographic film industry has shown that repeated exposure to air levels in excess of the threshold limit value of 200 ppm does not cause significant discomfort or illness. Persons with any disorder of the central nervous system (CNS) and/or reduced visual acuity should not be exposed to methanol. Methanol is associated with birth defects in rats following both oral and inhalational exposure, but not considered carcinogenic or mutagenic. Methanol: Time-weighted average (TWA) of 200 ppm, 15-minute average short-term exposure limit (STEL) of 250 ppm

- **Ecological Effects**

In primates, methanol causes metabolic acidosis and ocular damage. In non-primate laboratory animals, however, it acts as a CNS-depressant. Methanol has a negligible bioaccumulation potential and is relatively non-toxic to ecological receptors. Many of the effects of short term exposure are temporary and reversible. While methanol is essentially non-toxic to aquatic fish species, a surface water spill of methanol could result in the depletion of oxygen which would prove to be toxic to local aquatic species.

Sodium Hydroxide

- **Human Health Effects**

Sodium hydroxide is very corrosive and can cause severe burns in all tissues that come in contact with it. Inhalation of low levels of sodium hydroxide as dusts, mists or aerosols may cause irritation of the nose, throat, and respiratory airways. Inhalation of higher levels can produce swelling or spasms of the upper airway leading to obstruction and loss of measurable pulse; inflammation of the lungs and accumulation of fluid in the lungs may also occur. Ingestion of solid or liquid sodium hydroxide can cause spontaneous vomiting, chest and abdominal pain, and difficulty swallowing. Corrosive injury to the mouth, throat, esophagus, and stomach is very rapid and may result in perforation, hemorrhage, and narrowing of the gastrointestinal tract. Case reports indicate that death results from shock, infection of the corroded tissues, lung damage, or loss of measurable pulse.

Skin contact with sodium hydroxide can cause severe burns with deep ulcerations. Pain and irritation are evident within 3 minutes, but contact with dilute solutions may not cause symptoms for several hours. Contact with the eye may produce pain and irritation, and in severe cases, clouding of the eye and blindness.

Long-term exposure to sodium hydroxide in the air may lead to ulceration of the nasal passages and chronic skin irritation. Not classified for carcinogenicity or reproductive n humans. We do not know if exposure to sodium hydroxide could affect reproduction in humans. Sodium hydroxide: TWA of 2 milligrams per cubic meter (mg/m3)

- **Ecological Effects**

Highly toxic to aquatic life. As a contaminant in surface water, the primary effect of sodium hydroxide would be to raise the pH. Not bioaccumulated.

Potassium Hydroxide

- **Human Health Effects**

Inhalation causes irritation (possibly severe), chemical burns, pulmonary edema. Skin contact causes irritation (possibly severe), chemical burns, with long term exposure causing dermatitis. Eye exposure causes irritation (possibly severe), chemical burns, eye damage, blindness; long-term exposure causes visual disturbances. Short term ingestion exposure causes irritation (possibly severe), chemical burns, nausea, and vomiting. Not carcinogenic

- **Ecological Effects**

Potassium hydroxide has exhibited moderate toxicity to aquatic organisms. Potassium hydroxide is inorganic and not subject to biodegradation. This material is believed not to bioaccumulate. This material has exhibited slight toxicity to terrestrial organisms.

Hexane

- **Human Health Effects**

Contact will cause irritation, redness and a burning sensation of eyes. Hexane is an irritant to the skin and can be absorbed through the skin in harmful amounts. Ingestion may cause gastrointestinal irritation, nausea, vomiting and headache. Inhalation of the vapors may depress the central nervous system causing dizziness, difficulty in walking, respiratory tract irritation, numbness of the extremities and may result in eventual respiratory paralysis high concentrations. There is no evidence that exposure to *n*-hexane increases the risk of cancer in people. Some evidence indicates hexane may cause mutagenic, teratogenic, and/or reproductive effects. Hexane: TWA of 50 ppm

- **Ecological Effects**

n-Hexane is not concentrated by plants, fish, or animals.

Glycerin

- **Human Health Effects**

May cause skin irritation. May be absorbed through skin. May cause eye irritation with stinging, redness, burning sensation, and tearing, but no eye injury. Low toxicity by ingestion except with very large doses. When large doses are ingested, it can cause gastrointestinal tract irritation with thirst (dehydration), nausea, vomiting, and/or diarrhea. It may also affect behavior/central nervous system/nervous system (central nervous system depression, general anesthetic, headache, dizziness, confusion, insomnia, toxic psychosis, muscle weakness, paralysis convulsions), urinary system/kidneys(renal failure, hemoglobinuria), cardiovascular system (cardiac arrhythmias), liver. It may also cause elevated blood sugar. Due to low vapor pressure, inhalation of the vapors at room temperature is unlikely. Inhalation of mist may cause respiratory tract irritation.

Prolonged or repeated ingestion may affect the blood (hemolysis, changes in white blood cell count), endocrine system (changes in adrenal weight), respiratory system, and may cause kidney injury. Information is not available on carcinogenic, teratogenic, mutagenic, reproductive, or developmental effects. Glycerol, mist: 8-hour TWA of 10 mg/m3

- **Ecological Effects**

The products of degradation are less toxic than the product itself. Ecotoxicity in water lethal concentration 50 percent (LC50): 58.5 ppm 96 hours [Trout].

Soybean hulls and fines

- **Human Health Effects**

Soybean has caused occupational asthma in handlers of soybean flour and asthma epidemics in populations living near harbors where it was unloaded. The exposure to hull parts of the plant may cause occupational asthma in the absence of disease related to soy flour.

- **Ecological Effects**

No information found

Natural gas

- **Human Health Effects**

Not irritating. However, contact with pressurized vapor may cause frostbite, freeze burns, and permanent eye damage. This product is considered to be non-toxic by inhalation. Inhalation of high concentrations may cause central nervous system depression such as dizziness, drowsiness, headache, and similar narcotic symptoms, but no long-term effects. Numbness, a "chilly" feeling, and vomiting have been reported from accidental exposures to high concentrations. This product is a simple asphyxiant and may cause death due to lack of oxygen. No evidence of carcinogenicity.

- **Ecological Effects**

This product is expected to exist entirely in the vapor phase in ambient air.

Propane

- **Human Health Effects**

Direct contact with liquid propane can result in skin burns (frostbite). High vapor concentrations may produce a reversible central nervous system depression (anesthesia). Higher concentrations may produce asphyxiation. Ingestion is not likely.

This product is not classified as a carcinogen. Animal studies have shown that inhalation of high vapor levels of the components of this product have produced cardiac sensitization. Laboratory animals exposed to high levels of propylene for prolonged periods of time showed evidence of effects in the liver, kidneys, and nasal cavity.

- **Ecological Effects**

Liquid release is only expected to cause localized, non-persistent environmental damage, such as freezing. Biodegradation of this product may occur in soil and water. Volatilization is expected to be the most important removal process in soil and water. This product is expected to exist entirely in the vapor phase in ambient air.

Fuel oil

- **Human Health Effects**

Little information is available about the health effects that may be caused by fuel oils. People who use kerosene stoves for cooking do not seem to have any health problems related to their exposure.

Breathing some fuel oils for short periods may cause nausea, eye irritation, increased blood pressure, headache, light-headedness, loss of appetite, poor coordination, and difficulty concentrating. Breathing diesel fuel vapors for long periods may cause kidney damage and lower your blood's ability to clot.

Drinking small amounts of kerosene may cause vomiting, diarrhea, coughing, stomach swelling and cramps, drowsiness, restlessness, painful breathing, irritability, and unconsciousness. Drinking large amounts of kerosene may cause convulsions, coma, or death. Skin contact with kerosene for short periods may cause itchy, red, sore, or peeling skin. Some fuel oils (heavy) may possibly cause cancer in humans, but for other fuel oils (light) there is not enough information to make a determination. Occupational exposures to fuel oils during petroleum refining are probably carcinogenic in humans. Some studies with mice have suggested that repeated contact with fuel oils may cause liver or skin cancer.

- **Ecological Effects**

Studies of the accidental and intentional release of fuel oils to the aquatic environment indicate that aquatic organisms are able to bioaccumulate some hydrocarbon fractions, particularly PAHs; however, depuration does occur if the source of the contamination is removed.

VIII. Applicable Regulations

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

TABLE 4: SUMMARY OF APPLICABLE FEDERAL REGULATIONS

Act Establishing Regulation	Regulation	Overview of Regulation	Chemicals/Thresholds where Regulations Apply
Emergency Planning and Community Right Know ACT (EPCRA)	Sections 311-312 – Hazardous chemical reporting	Requires facilities storing hazard chemicals on site to report this to local emergency authorities (annual inventory (Tier II report) required for most facilities)	Methanol, sodium hydroxide, potassium hydroxide, and glycerin are considered hazardous chemicals. The threshold planning quantity (TPQ) is for each chemical, not all chemicals combined.
Emergency Planning and Community Right Know ACT (EPCRA)	Section 304 – Emergency release notification	Facilities are required to report a release or discharge of a regulated chemical if it exceeds the chemical's reportable quantity (RQ) and crosses the facility property line.	- Extremely Hazardous Substances 40 Code of Federal Regulation (CFR); Part 355; Appendix A and B. - Comprehensive Environmental Response and Compensation Liability Act (CERCLA) hazardous substances 40 CFR Part 302; Table 302.4 (including methanol, hexane, sodium hydroxide, potassium hydroxide); and -Oil.
Emergency Planning and Community Right Know ACT (EPCRA)	Section 313 – Toxic Release Inventory	An inventory is required of toxic chemical emissions from certain types of facilities. This inventory is called the Toxic Release Inventory (TRI) or Form R report.	Must report if -More than 10 full time employees -Facility has specific standard industrial code (SIC) -Manufactures/processes or otherwise uses listed toxic chemicals in more than threshold quantities. Methanol is included on the list.
U.S. EPA Oil Pollution Control/Federal Water Pollution Control Act	Spill Prevention Control and Countermeasure (SPCC) Plans	Plan is required for facilities with above-ground aggregate storage capacity for oil or oil products (including vegetable oils) of greater than 1,320 gallons.	Must consider total capacity of tanks, containers, and system piping, not just the actual amount of oil stored. Containers less than 55 gallons in size are not included in this capacity.
Clean Water Act	National Pollution Discharge Elimination System (NPDES) Response Plans	Those regulated must obtain a NPDES storm water permit and develop a storm water pollution prevention plan (SWPPP) that shows the steps taken to reduce or prevent storm water contamination. An oil response plan in the event a release reaches water ways is required for facilities that store large quantities of oil.	Biodiesel production plants fall under the major SIC industrial group 28 (2869). Discharges of process wastewater to storm water would require a permit.

TABLE 4 (CONTINUED): SUMMARY OF APPLICABLE FEDERAL REGULATIONS

Act Establishing Regulation	Regulation	Overview of Regulation	Chemicals/Thresholds where Regulations Apply
Oil Pollution Act of 1990 (OPA 90)	Liability for Releases of Oil to Surface Water	On-shore facilities, deep water ports, and vessels from which oil is discharged or poses a threat of discharge are liable for damages/removal costs. Provides for spill contingency plans and mandates development of response plans for worst case discharge; and provides for requirements for spill removal equipment. States have the authority to impose OPA for navigable waters of the State.	Applies to facilities that store or produce oil – including biodiesel. Facilities with over a one million gallon storage capacity and/or are next to water must submit Facility Response Plans to U.S. EPA. The U.S. Congress has stipulated that the U.S. Coast Guard and U.S. EPA must differentiate between oils in regulating (i.e. petroleum versus plant oils), but currently there is no differentiation.
Resource Conservation and Recovery Act (RCRA)	RCRA Contingency Plan	Contingency Plan is required for Hazardous Waste Large Quantity Generators (LQGs)	LQGs must establish and maintain emergency procedures to mitigate fires, explosions, or other releases. Must provide plan to local and state emergency authorities and make arrangements to familiarize them with the facility. Waste containing methanol or hexane may exhibit the flammability characteristic. Depending on the nature/source of a release, waste containing methanol may classify as a listed hazardous waste. Waste containing sodium or potassium hydroxide may exhibit the corrosivity characteristic.
Clean Air Act (CAA)	Section 112(r)(1) – Chemical Accident Provisions	General Duty Clause	The CAA general duty clause directs owners and operators of stationary sources to identify hazards that may result from accidental releases, to design and maintain a safe facility, and to minimize the consequences of releases when they occur.
DOT Hazardous Materials Regulations (HMR); as amended by Homeland Security Act of 2002	HM-232 – Transportation Security Plan	Facilities must develop and implement a security plan if they offer for transportation or transport regulated types or quantities of hazardous materials under the rule	Applies to hazardous material in an amount that must be placarded in accordance with Subpart F of Part 172 of the HMR; a hazardous material in a bulk packaging having a capacity equal to or greater than 13,248 L (3,500 gallons) for liquids or gases or more than 13.24 cubic meters (468 cubic feet) for solids.

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ATTACHMENT A

CURRENTLY OPERATING INDUSTRIAL-SCALE BIODIESEL MANUFACTURING FACILITIES IN U.S. EPA REGION 5

Current Industrial-Scale Producers in U.S. EPA Region 5

COMPANY	CITY	STATE	ANNUAL PRODUCTION CAPACITY	PRIMARY FEEDSTOCK	OPERATING SINCE	WEBSITE
Incobrasa Industries, Ltd.	Gilman	Illinois	31,000,000	Soy	Jan-07	www.incobrasa.com
Heartland Biodiesel, Inc.	Marion	Illinois	3,000,000	Soy	Dec-07	NA
Stepan Company	Millsdale	Illinois	22,000,000	Soy	Jan-01	www.stepan.com
Midwest Biodiesel Products, Inc.	South Roxanna	Illinois	30,000,000	Multi Feedstocks	May-07	www.midwestbiodieselproducts.com
Louis Dreyfus Agricultural Industries, LLC	Claypool	Indiana	80,000,000	Soy	Jan-08	www.ldcommoditites.com
Heartland Biofuel	Flora	Indiana	450,000	Multi Feedstock	Apr-06	NA
Evergreen Renewables	Hammond	Indiana	5,000,000	Soy	May-06	NA
e-biofuels, LLC	Middletown	Indiana	25,000,000	Multi Feedstock	Jun-07	www.e-biofuels.com
Integrity Biofuels	Morristown	Indiana	10,000,000	Soy	Aug-06	www.integritybiofuels.com
NextDiesel	Adrian	Michigan	20,000,000	Multi Feedstock	Aug-07	www.nextdiesel.net
Michigan Biodiesel, LLC	Bangor	Michigan	10,000,000	Multi Feedstock	Jan-07	www.mibiodiesel.com
Ag Solutions, Inc.	Gladstone	Michigan	5,000,000	Multi Feedstock	Jan-07	NA
Soymor	Albert Lea	Minnesota	30,000,000	Soy	Aug-05	www.soymor.com
Minnesota Soybean Processors	Brewster	Minnesota	30,000,000	Soy	Aug-06	www.mnsoy.com
Green Range Renewable Energy	Ironton	Minnesota	150,000	Recycled Cooking Oil	Jul-06	NA
FUMPA BioFuels	Redwood Falls	Minnesota	3,000,000	Multi Feedstock	Dec-04	www.biopup.com
Agrifuels, LLC	Bremen	Ohio	1,000,000	Multi Feedstock	Mar-07	www.ohioagrifuel.com
American Made Fuels, Inc.	Canton	Ohio	5,000,000	Soy	Jan-08	www.americanmadefuels.com
Peter Cremer	Cincinnati	Ohio	30,000,000	Soy	Oct-02	www.petercremerna.com
Center Alternative Energy Company	Cleveland	Ohio	5,000,000	Soy, Choice White Grease	May-07	www.centeroil.com
American Ag Fuels, LLC	Defiance	Ohio	7,000,000	Multi Feedstock	Jul-05	www.americanagfuels.com
Jatrodiesel Inc.	Miamisburg	Ohio	5,000,000	Multi Feedstock	Jun-07	www.jatrodiesel.com
Best Biodiesel, Inc.	Cashton	Wisconsin	10,000,000	Multi Feedstocks	Jan-08	www.bestenergies.com
Sanimax Energy Inc.	Deforest	Wisconsin	20,000,000	Multi Feedstock	Apr-07	www.sanimax.com
Walsh Bio Diesel, LLC	Mauston	Wisconsin	5,000,000	Soy	May-07	NA

Capacity is in Gallons
NA – not applicable

Source: National Biodiesel Board
Note: Other small, sub-industrial scale producers are operating in addition to the list above