

# Environmental, Health and Safety Guidelines for Oleochemicals Manufacturing

## Introduction

The Environmental, Health, and Safety (EHS) Guidelines are technical reference documents with general and industry-specific examples of Good International Industry Practice (GIIP)<sup>1</sup>. When one or more members of the World Bank Group are involved in a project, these EHS Guidelines are applied as required by their respective policies and standards. These industry sector EHS guidelines are designed to be used together with the **General EHS Guidelines** document, which provides guidance to users on common EHS issues potentially applicable to all industry sectors. For complex projects, use of multiple industry-sector guidelines may be necessary. A complete list of industry-sector guidelines can be found at: [www.ifc.org/ifcext/enviro.nsf/Content/EnvironmentalGuidelines](http://www.ifc.org/ifcext/enviro.nsf/Content/EnvironmentalGuidelines)

The EHS Guidelines contain the performance levels and measures that are generally considered to be achievable in new facilities by existing technology at reasonable costs. Application of the EHS Guidelines to existing facilities may involve the establishment of site-specific targets, with an appropriate timetable for achieving them.

The applicability of the EHS Guidelines should be tailored to the hazards and risks established for each project on the basis of the results of an environmental assessment in which site-specific variables, such as host country context, assimilative

<sup>1</sup> Defined as the exercise of professional skill, diligence, prudence and foresight that would be reasonably expected from skilled and experienced professionals engaged in the same type of undertaking under the same or similar circumstances globally. The circumstances that skilled and experienced professionals may find when evaluating the range of pollution prevention and control techniques available to a project may include, but are not limited to, varying levels of environmental degradation and environmental assimilative capacity as well as varying levels of financial and technical feasibility.

capacity of the environment, and other project factors, are taken into account. The applicability of specific technical recommendations should be based on the professional opinion of qualified and experienced persons.

When host country regulations differ from the levels and measures presented in the EHS Guidelines, projects are expected to achieve whichever is more stringent. If less stringent levels or measures than those provided in these EHS Guidelines are appropriate, in view of specific project circumstances, a full and detailed justification for any proposed alternatives is needed as part of the site-specific environmental assessment. This justification should demonstrate that the choice for any alternate performance levels is protective of human health and the environment.

## Applicability

The EHS Guidelines for Oleochemicals Manufacturing include information relevant to manufacturing facilities that produce fatty acids, glycerin, and biodiesel using fats and oils from vegetable or animal sources. Annex A contains a description of industry activities for this sector.

This document is organized according to the following sections:

- Section 1.0 — Industry-Specific Impacts and Management
- Section 2.0 — Performance Indicators and Monitoring
- Section 3.0 — References and Additional Sources
- Annex A — General Description of Industry Activities

## 1.0 Industry-Specific Impacts and Management

The following section provides a summary of EHS issues associated with oleochemicals manufacturing which occur during the operations phase, along with recommendations for their management. Recommendations for the management of EHS issues common to most large industrial facilities during the construction and decommissioning phases are provided in the **General EHS Guidelines**.

### 1.1 Environment

The main environmental issues related to the oleochemicals manufacturing sector are:

- Air emissions
- Wastewater
- Hazardous materials
- Wastes and by-products
- Noise

Optimizing process conditions (associated with an appropriate selection of good quality raw materials and feedstock) significantly reduces the environmental impact of these manufacturing plants by limiting the production of waste, wastewater, and air emissions.

#### Air Emissions

Oleochemicals manufacturing facilities typically consume large amounts of energy to heat water and produce steam for process applications (e.g., splitting, refining, and distillation processes). Energy consumption is also associated with refrigeration and compressed air systems. Facilities may have captive power plants to supply energy.

Combustion source emissions guidelines associated with steam and power generation from sources with a heat input capacity

equal to or lower than 50 thermal megawatts (MWth) are addressed in the **General EHS Guidelines**. Larger power source emissions are addressed in the **EHS Guidelines for Thermal Power**. Detailed recommendations for energy efficiency are presented in the **General EHS Guidelines**.

#### *Fatty Acids Production*

Air emissions from fatty acids production mainly include fugitive emissions of volatile organic compounds (VOCs), including hexane from solvent fractionation processes; fugitive emissions of hydrogen from hydrogenation units; odor emissions of low molecular fatty acids; and degradation products such as ketones and aldehydes from storage tanks, and pre-treatment, splitting, and distillation units.

Recommended emission prevention and control measures include the following:

- Implement a solvent recovery process via distillation and condensation;
- Monitor and record solvent consumption and implement a maintenance program to detect, monitor, and minimize hexane emissions from the solvent recovery unit and from leaks in piping and vents; and
- Collect and treat fugitive VOC emissions from storage tanks, and pre-treatment, splitting, and distillation units. Activated carbon filters and scrubber systems using oil or alkaline water should be installed to abate solvent and odor emissions. Consider incineration of solvent vapors and / or odor substances as an alternative option.

#### *Glycerin Production*

VOCs may be generated from the pre-treatment of low-quality glyceric solutions or from vacuum generator equipment. VOCs may cause odor emissions due to the presence of low molecular weight decomposition products.

Recommended emission prevention and control measures include the following:

- Consistently monitor the presence of methanol when using glyceric solutions from biodiesel production;
- Maintain pre-treatment temperatures as low as practical and install efficient condensers to minimize VOC emissions; and
- Use scrubbers to abate air emissions at plants using low-quality raw materials.

### *Biodiesel Production*

Air emissions from biodiesel production include: VOCs, mainly methanol, from the distillation and condensation of excess methanol at the end of the transesterification process; fugitive VOC emissions from reactors, methanol storage, or pipe leaks; methanol from the rectification of the aqueous methanol produced by the esterification process; and VOC and odor emissions associated with vacuum generation equipment during the distillation process.

Recommended emission prevention and control measures include the following:

- If possible, remove excess methanol used in the transesterification reaction before the wash step to prevent the presence of methanol in wastewater effluents and avoid the need for further rectification of the methanol aqueous solution and emission of methanol to air; and
- Install activated carbon filters and wet scrubbers, or vapor incineration, to abate VOC and odor emissions collected from different plant units, including storage tanks.

## **Wastewater**

### *Industrial Process Wastewater*

#### **Fatty Acids Production**

Fatty acids production plants generate a significant amount of wastewater containing suspended fatty acids and fats, with high biochemical oxygen demand (BOD) and chemical oxygen demand (COD) levels. Wastewater sources include fatty acids vapor condensation from water sprays; release of high-pressure fatty acids streams at the exit of splitting towers; vapor condensation from deodorizing operations; and vacuum generators using steam.

Recommended pollution control and abatement measures include the following:

- Consider installing indirect condensers and dry vacuum pumps where water is not in contact with fatty acid process streams to reduce the volume of wastewater generated by the process;
- Maximize water reuse and install cooling towers, as needed;
- Design and install a floating / settling unit to process water streams from both routine operations (including cleaning procedures) and non-routine circumstances (accidental release of fats and oils). Further biological treatment should be conducted prior to discharge, depending on influent concentrations and applicable discharge standards; and
- Where practical, recover and reprocess sludge from the treatment unit in the production process.

#### **Glycerin Production**

Condensation water from glyceric solution evaporation and distillation, and water from vacuum generation systems, are typically generated during glycerin production. Condensation water produced by the distillation process may contain up to 30 percent glycerin and residues of fatty esters and acids.

Condensation water produced by a multistage evaporation process may contain small amounts of glycerin and is characterized by high COD and BOD levels. Water from vacuum generation systems may contain traces of glycerin.

Recommended pollution prevention and control measures include the following:

- Recycle condensation water produced by the distillation process to the production process via lime and acid treatment, filtration, and evaporation;
- Where glycerin production plants are integrated with fatty acid production plants, reuse condensation water produced by the evaporation process as feed in the fat and oil splitting process;
- As an alternative to biological treatment and discharge, consider reusing condensation water as washing water for recovering glycerin from spent activated carbon panels;
- Neutralize acid and caustic solutions collected from reactivation of resins in ion-exchange processes used to treat glyceric solutions before disposal;
- Use of dry pumps as vacuum generators and indirect condensers, where water has not been in direct contact with vapors, is preferred to reduce wastewater volumes; and
- Recycle water from vacuum generation systems as process water, where needed.

### **Biodiesel Production**

Ester wash water is the main liquid effluent from biodiesel production units. It contains organic residues (esters, fatty acids, soaps, glycerin, and traces of methanol) and inorganic acids and salts produced by neutralization of residual catalyst with acids (usually hydrochloric acid and sodium chloride). The use of phosphoric acid is a challenge during wastewater treatment due to the associated high levels of phosphate in the stream, although it generates salts that can be recycled as fertilizers.

Water produced from scrubbers and rectification process contains organic impurities and traces of methanol. The aggregate process wastewater typically has a high organic and diluted acid load, resulting in high COD and BOD levels.

Recommended pollution prevention and control measures include the following:

- Remove excess methanol used in the transesterification reaction before the wash step if possible, or otherwise recover it from wastewater streams;
- Treat methanol-free wastewater via a settling / floating unit to collect floating residues, followed by neutralization and biological treatment prior to discharge; and
- When phosphoric acid is used, monitor phosphate concentrations in wastewater and adjust or modify wastewater treatment systems as necessary to meet applicable discharge standards.

### *Process Wastewater Treatment*

Techniques for treating industrial process wastewater in this sector include grease traps, skimmers, dissolved air floatation, or oil water separators for separation of oils and floatable solids; filtration for separation of filterable solids; flow and load equalization; sedimentation for suspended solids reduction using clarifiers; biological treatment, anaerobic (if wastewater BOD is high) followed by aerobic treatment for reduction of soluble organic matter (BOD); chemical or biological nutrient removal for reduction in nitrogen and phosphorus; chlorination of effluent when disinfection is required; dewatering and disposal of residuals in designated hazardous waste landfills. Additional engineering controls may be required for (i) containment and treatment of volatile organics stripped from various unit operations in the wastewater treatment system, (ii) removal of recalcitrant organics using activated carbon or advanced chemical oxidation, (iii) reduction in effluent toxicity using appropriate technology (such as reverse osmosis, ion

exchange, activated carbon, etc.), and (v) containment and neutralization of nuisance odors.

Management of industrial wastewater and examples of treatment approaches are discussed in the **General EHS Guidelines**. Through use of these technologies and good practice techniques for wastewater management, facilities should meet the Guideline Values for wastewater discharge as indicated in the relevant table of Section 2 of this industry sector document.

### *Other Wastewater Streams & Water Consumption*

Guidance on the management of non-contaminated wastewater from utility operations, non-contaminated stormwater, and sanitary sewage is provided in the **General EHS Guidelines**. Contaminated streams should be routed to the treatment system for industrial process wastewater. Recommendations to reduce water consumption, especially where it may be a limited natural resource, are provided in the **General EHS Guidelines**.

### **Hazardous Materials**

Oleochemicals manufacturing facilities use significant amounts of hazardous materials, including raw materials and intermediate / final products. The handling, storage, and transportation of these materials should to be managed properly to avoid or minimize the potential for environmental impacts. Recommended practices for hazardous material management are presented in the **General EHS Guidelines**.

### **Wastes and By-products**

#### *Fatty Acids Production*

The principal waste streams generated from fatty acid production are spent bleaching earths, pitches, and spent catalyst filter cakes. Spent bleaching earths represent the main solid waste stream, accounting for between 0.5 percent and 2 percent by weight of treated oils and fats. The spent bleaching earths contain up to 40 percent fat material, and include

impurities such as coloring pigments, mucilaginous matters, fibers, protein degradation products, ashes, and soaps. Pitches are generated as residues of fatty acid distillation. Spent catalyst filter cakes are produced from fat hydrogenation. Both spent bleaching earths and spent catalyst filter cakes have pyrophoric properties.

Recommended waste management strategies include the following:

- Adoption of an efficient filtration technology may play a relevant role in the reduction of the amount of fat material present in spent filtration panels, minimizing both solid waste and fat loss;
- Fat-rich waste, such as spent bleaching earths, should be considered for recycling and energy recovery through combustion. Other recycling alternatives include its reuse as feedstock for the building industry, fertilizer, and land spreading. Contamination levels should be ascertained before reuse;
- When a continuous distillation process is used, pitches should be re-hydrolyzed and redistilled in a second batch distillation process to reduce the amount of waste generated;
- Reuse of pitches should be explored, including their use in road construction due to their water-repellent properties, and energy recovery through combustion in boilers;
- Spent nickel catalyst filter cakes are pyrophoric and should be dried with nitrogen before storage and disposal. Appropriate on-site management of spent catalysis includes submerging pyrophoric spent catalysts in water during temporary storage and transport until they can reach the final point of treatment to avoid uncontrolled exothermic reactions;
- Spent catalysis should be returned to the manufacturer for regeneration or sent to specialized contractors for metals

recovery. Off-site management of spent catalysts by specialized companies includes recovery of the heavy or precious metals, through recovery and recycling processes whenever possible, or handling and disposal according to hazardous and non-hazardous waste management recommendations presented in the **General EHS**

**Guidelines**. Catalysts that contain platinum or palladium should be sent to a noble metals recovery facility; and

- Use of low-impact palladium-based catalyst instead of nickel catalyst should be considered for new plant installations.

### *Glycerin Production*

Waste and by-products generated in glycerin production include heavy fractions from distillation and residues from filtration and / or bleaching, consisting of spent activated carbons, activated clays, and filtering aids containing fat material, soaps, lime, coagulating salts (such as aluminum sulfate or ferric chloride), and coloring pigments.

Recommended waste management strategies include the following:

- Spent filter panels that are not contaminated by heavy metals and solvents should be considered for recycling as animal feed or fertilizer, especially if they contain salts produced by the neutralization of potassium hydroxide with phosphoric acid;
- Contaminated filter panels should be segregated and managed according to the waste management guidance present in the **General EHS Guidelines**; and
- Use distillation heavy ends as low grade glycerin, or use as fuel for energy production following a concentration step.

### *Biodiesel Production*

Industry-specific solid wastes and by-products from oleochemicals manufacturing include spent catalyst salt

precipitates from glyceric phase neutralization; fatty acids and fatty soaps; spent bleaching earth or filtering aid panels produced from purification of low-quality raw material; and heavy and light-end boiling esters from distillation process.

Recommended waste management strategies include the following:

- Consider recycling spent catalyst salts as fertilizers if potassium hydroxide is used as catalyst and phosphoric acid as neutralizer;
- Manage spent bleaching and filtering panel treatment and disposal as described for the same waste streams from fatty acids production;
- Fatty soaps should be neutralized, and fatty acids produced should be recovered and esterified to methyl esters by means of acid-catalyzed esterification;
- Reuse heavy and light-end boiling esters in different oleochemical manufacturing sectors where quality requirements are lower; and
- Consider use of very low-quality pitches as fuel for energy production.

### **Noise**

Typically sources of noise emissions include compressors and turbines, pumps, electric motors, air coolers, rotating drums, spherodizers, conveyors belts, cranes, fired heaters, and from emergency depressurization. Guidance on noise control and minimization is provided in the **General EHS Guidelines**.

## **1.2 Occupational Health and Safety**

Facility-specific occupational health and safety hazards should be identified based on a job safety analysis or comprehensive hazard and risk assessment using established methodologies such as a hazard identification study [HAZID], hazard and operability study [HAZOP], or a quantitative risk assessment

[QRA]. As a general approach, health and safety management planning should include the adoption of a systematic and structured approach for prevention and control of physical, chemical, biological, and radiological health and safety hazards described in the **General EHS Guidelines**.

Occupational health and safety issues for specific consideration in oleochemicals manufacturing plants include:

- Process Safety
- Chemicals hazards
- Fire and explosions
- Other occupational hazards

### *Process Safety*

Process safety programs should be implemented due to industry-specific characteristics, including complex chemical reactions, use of hazardous materials (e.g., toxic, reactive, flammable, or explosive compounds), and multi-step organic synthesis reactions.

Process safety management includes the following actions:

- Physical hazard testing of materials and reactions;
- Hazard analysis studies to review the process chemistry and engineering practices, including thermodynamics and kinetics;
- Examination of preventive maintenance and mechanical integrity of the process equipment and utilities;
- Worker training; and
- Development of operating instructions and emergency response procedures.

### *Chemical Hazards*

Oleochemicals manufacturing activities may present a risk of exposure to hazardous chemicals, such as inhalation of hexane, methanol, or other solvents used for extraction; inhalation and

dermal exposure to toxic chemicals including acids or bases; inhalation of dust from transportation of raw materials; and inhalation of dust from bleaching earth, filter aid, and catalysts. Guidance on the management of chemical hazards in the workplace is presented in the **General EHS Guidelines**.

Additional industry-related recommendations include the following:

- Train employees in chemical handling, for example, the correct interpretation of material safety data sheets, international chemical safety cards, and first aid procedures (seasonal and other temporary workers should be fully trained before they work with chemicals);
- Provide employees with the necessary personal protective clothing (PPE) and equipment when specified as part of the job safety analysis and safety data;
- Ensure there is adequate air circulation to reduce the concentration of solvents in oil extraction areas;
- Provide adequate ventilation, especially at workstations related to raw-material handling, milling, handling of bleaching earth, and use of solvents;
- Ensure proper distillation of oil after extraction for effective solvent removal;
- Apply preventive maintenance to reduce the risk of burns from all pipes carrying steam and all hot surfaces; and
- When feasible, use hot water rather than solvents for cleaning.

### *Fire and Explosions*

Oleochemicals manufacturing may present a risk of explosions resulting from volatilization of solvents (e.g., hexane), and fire from spent bleaching earth with high iodine-value oil, spent catalysts, and high ambient temperatures. Recommendations to prevent and control fire and explosion hazards include the following:

- Maintain air concentrations of VOCs below 10 percent of lower explosive limits;<sup>2</sup>
- Prevent leaks and spills of oils in the extraction plant;
- Control the flash-point temperature of the incoming extracted oils and use temperature control for all facilities receiving solvent extracted oils;
- Implement fire and auto-ignition prevention and control measures where storage and handling of spent catalyst and spent bleaching earths is conducted;
- Dry pyrophoric spent catalyst filter panels with nitrogen, and store in sealed containers preventing any contact with air;
- Use non-combustible materials in methanol or hydrogen handling equipment;
- Locate the hydrogen storage area at a safe distance from other plant facilities;
- Design storage tanks, pipelines, and equipment using hydrogen to avoid any possible accumulation of hydrogen;
- Install hydrogen leak detectors in locations selected as part of a risk analysis;
- Equip hydrogen handling systems with automatic valve shut-off devices;
- Prevent accumulation of methanol and other VOC vapors in all plant locations. For example, the reactor design should ensure that methanol remains in a liquid state even under low pressure conditions; and
- Install adequate systems to cool tanks, pipelines, and reactors to prevent methanol auto-ignition in case of plant upset conditions and equipment failure.

### Other Occupational Hazards

Physical hazards in oleochemicals manufacturing facilities are similar to those present in other industry sectors and include the potential for falls caused by slippery floors and stairs, potential

collisions with internal transport such as trucks, and accidental contact with conveyor systems, such as those used in the crushing plants and for the removal of spent earth. Operators in may also be exposed to noise from internal transport, conveyors, boilers, pumps, fans, various steam and air leaks, and so on. Guidance on general workplace conditions are presented in the **General EHS Guidelines**.

### 1.3 Community Health and Safety

The most significant community health and safety hazards associated with oleochemicals manufacturing facilities occur during the operation phase and include the threat from major accidents related to potential fires and explosions or accidental releases of raw materials or finished products during transportation outside the processing facility. Guidance for the management of these issues is presented below and in relevant sections of the **General EHS Guidelines** including: Traffic Safety, Transport of Hazardous Materials, and Emergency Preparedness and Response.

Additional relevant guidance applicable to transport by sea and rail as well as shore-based facilities can be found in the EHS Guidelines for Shipping, Railways, Ports and Harbors, and Crude Oil and Petroleum Products Terminals.

<sup>2</sup> For example, the lower explosive limit for hexane is 1.1 percent (volume per volume [v/v]) and the upper explosive limit is 7.5 percent (v/v);

## 2.0 Performance Indicators Monitoring

### 2.1 Environment

#### Emissions and Effluent Guidelines

Tables 1 and 2 present emission and effluent guidelines for this industry sector. Guideline values for process emissions and effluents in this sector are indicative of good international industry practice as reflected in relevant standards of countries with recognized regulatory frameworks. These guidelines are achievable under normal operating conditions in appropriately designed and operated facilities through the application of pollution prevention and control techniques discussed in the preceding sections of this document.

Emissions guidelines are applicable to process emissions. Combustion source emissions guidelines associated with steam and power generation activities from sources with a heat input capacity equal to or lower than 50 megawatt thermals are addressed in the **General EHS Guidelines** with larger power source emissions addressed in the **Thermal Power EHS Guidelines**. Guidance on ambient considerations based on the total load of emissions is provided in the **General EHS Guidelines**.

Effluent guidelines are applicable for direct discharges of treated effluents to surface waters for general use. Site-specific discharge levels may be established based on the availability and conditions in the use of publicly operated sewage collection and treatment systems or, if discharged directly to surface waters, on the receiving water use classification as described in the **General EHS Guidelines**. These levels should be achieved, without dilution, at least 95 percent of the time that the plant or unit is operating, to be calculated as a proportion of annual operating hours. Deviation from these levels in consideration of

specific, local project conditions should be justified in the environmental assessment.

**Table 1. Air Emissions Levels for Oleochemicals Manufacturing Plants**

Pollutant	Units	Guideline Value
VOCs	mg/Nm <sup>3</sup>	100 <sup>a</sup>

a. At 273 K (0 °C) and 101.3 kPa (1 atmosphere).

**Table 2. Effluents Levels for Oleochemicals Manufacturing Plants**

Pollutant	Units	Guideline Value
pH	S.U.	6-9
BOD <sub>5</sub>	mg/L	40
COD	mg/L	150
Total Nitrogen	mg/L	30
Total Phosphorous	mg/L	5
Oil and Grease	mg/L	10
Total Suspended Solids	mg/L	50

#### Resource Use, Energy Consumption, Emission and Waste Generation

Table 3 provides examples of resource consumption / generation indicators for energy in this sector, whereas Table 4 provides examples of emission and waste generation indicators. Industry benchmark values are provided for comparative purposes only and individual projects should target continual improvement in these areas.

**Table 3. Resource and Energy Consumption**

Input per Unit Product	Unit	Industry Benchmark
<b>Water Use</b>		
Fatty Acid / Glycerin Production	m <sup>3</sup> /t product	0.6 – 0.8
Biodiesel Production	m <sup>3</sup> /t product	1.6 – 2.0
<b>Energy</b>		
Fatty Acid / Glycerin Production	Per ton raw material	550kg(vapor@30 bar) + 200kg (vapor @10 bar) + 45 kWh
Biodiesel Production	Per ton product	600kg(vapor@ 5 bar) + 1.2*106 kJ + 40 kWh

**Table 4. Wastewater and Waste Generation**

Output per Unit Product	Unit	Industry Benchmark
<b>Process Wastewater<sup>(1)</sup></b>		
Fatty Acid / Glycerin Production	m <sup>3</sup> /t raw material	<0.1 <sup>(2)</sup>
Biodiesel Production	m <sup>3</sup> /t product	0.9 – 1.3
<b>Solid Water</b>		
Fatty Acid / Glycerin Production	kg/t raw material	5 (spent catalysts) 10 (distillation residues)
Biodiesel Production	kg/t product	50 (potassium phosphates)
<b>Notes:</b>		
1. Cooling water not included. The 90-95 percent of cooling water should be recycled		
2. Based on one ton raw material consisting of 900 kg of fatty acids and 100 kg of glycerin		

## Environmental Monitoring

Environmental monitoring programs for this sector should be implemented to address all activities that have been identified to have potentially significant impacts on the environment, during normal operations and upset conditions. Environmental monitoring activities should be based on direct or indirect indicators of emissions, effluents, and resource use applicable to the particular project.

Monitoring frequency should be sufficient to provide representative data for the parameter being monitored. Monitoring should be conducted by trained individuals following monitoring and record-keeping procedures and using properly calibrated and maintained equipment. Monitoring data should be analyzed and reviewed at regular intervals and compared with the operating standards so that any necessary corrective actions can be taken. Additional guidance on applicable sampling and analytical methods for emissions and effluents is provided in the **General EHS Guidelines**.

## 2.2 Occupational Health and Safety

### Occupational Health and Safety Guidelines

Occupational health and safety performance should be evaluated against internationally published exposure guidelines, of which examples include the Threshold Limit Value (TLV<sup>®</sup>) occupational exposure guidelines and Biological Exposure Indices (BEIs<sup>®</sup>) published by American Conference of Governmental Industrial Hygienists (ACGIH),<sup>3</sup> the Pocket Guide to Chemical Hazards published by the United States National Institute for Occupational Health and Safety (NIOSH),<sup>4</sup> Permissible Exposure Limits (PELs) published by the Occupational Safety and Health Administration of the United States (OSHA),<sup>5</sup> Indicative Occupational Exposure Limit Values published by European Union member states,<sup>6</sup> or other similar sources.

### Accident and Fatality Rates

Projects should try to reduce the number of accidents among project workers (whether directly employed or subcontracted) to a rate of zero, especially accidents that could result in lost work time, different levels of disability, or even fatalities. Fatality rates may be benchmarked against the performance of facilities in this sector in developed countries through consultation with published sources (e.g. US Bureau of Labor Statistics and UK Health and Safety Executive).<sup>7</sup>

### Occupational Health and Safety Monitoring

The working environment should be monitored for occupational hazards relevant to the specific project. Monitoring should be

<sup>3</sup> Available at: <http://www.acgih.org/TLV/> and <http://www.acgih.org/store/>

<sup>4</sup> Available at: <http://www.cdc.gov/niosh/npg/>

<sup>5</sup> Available at: [http://www.osha.gov/pls/oshaweb/owadisp.show\\_document?p\\_table=STANDARDS&p\\_id=9992](http://www.osha.gov/pls/oshaweb/owadisp.show_document?p_table=STANDARDS&p_id=9992)

<sup>6</sup> Available at: [http://europe.osha.eu.int/good\\_practice/risks/ds/oel/](http://europe.osha.eu.int/good_practice/risks/ds/oel/)

<sup>7</sup> Available at: <http://www.bls.gov/iif/> and <http://www.hse.gov.uk/statistics/index.htm>

designed and implemented by accredited professionals<sup>8</sup> as part of an occupational health and safety monitoring program.

Facilities should also maintain a record of occupational accidents and diseases and dangerous occurrences and accidents. Additional guidance on occupational health and safety monitoring programs is provided in the **General EHS Guidelines**.

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<sup>8</sup> Accredited professionals may include Certified Industrial Hygienists, Registered Occupational Hygienists, or Certified Safety Professionals or their equivalent.

### 3.0 References and Additional Sources

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## Annex A: General Description of Industry Activities

The Oleochemicals Manufacturing industry produces a wide range of substances deriving from physical and chemical modification of natural oils and fats, which include:

- Fatty acids by cleavage (splitting) of the triglycerides molecule into its constituents, (i.e., fatty acids and glycerin);
- Biodiesel, mainly by substitution (transesterification) of glycerin with methanol in the triglycerides molecule; and
- Glycerin by processing glyceric aqueous solutions mainly derived from transesterification and splitting.

### Fatty Acids Production

Fatty acids, obtained from natural oils and fats splitting, are further purified and modified by means of distillation, fractionation, and hydrogenation (Figure A.1). Fatty acids can be directly used in several industrial applications or can be the base of a wide range of oleochemicals, such as esters, amides, and metallic soaps.

### Raw Materials

Raw materials include vegetable oils (mainly soybean oil, palm oil, rapeseed oil, sunflower-seed oil, cotton oil, and olive oil), which represent about 85 percent of the fats production worldwide, with the remaining 15 percent coming from animal origin fats such as tallow, lard, butter, poultry fat, and fish oil<sup>9</sup>.

Although an increasing volume of oleochemicals is produced by high-quality fats, the feedstock of the oleochemicals industry includes low-quality raw materials such as semi-refined or recycled oils, and residues from refining of fats.

### Processing Operations

#### Pretreatment of Fats and Oils

It is essential to remove impurities present in the feedstock, such as protein degradation products, ashes, soaps, mucilaginous matters, and coloring pigments. For the manufacture of high-quality oleochemicals, pretreatment is normally carried out by filtering the feedstock with a variable amount (0.1 – 2.0 %) of activated bleaching earth (diatomaceous earth). The spent filter clay, containing up to 40% of fat material, represents the main solid waste from fatty acids production.

#### Fats and Oils Fractionation

The fractionation process can be applied to oils and fats (widely used for palm oil), but also to fatty acids after splitting (discussed below). Fractionation allows for separating of the feedstock in two fractions: a more liquid fraction (with higher content of unsaturated fats or fatty acids and higher commercial value) and a more solid fraction (with higher content of saturated fats or fatty acids than the feedstock).

Fractionation is based on the partial crystallization of the fat obtained by controlled cooling. Three fractionation technologies are commonly used: dry fractionation or winterization, wet fractionation, and solvent fractionation.

In dry fractionation, crystals are separated from the liquid phase by filtration, while in wet fractionation, a surfactant solution is used as a wetting agent for the crystals that are separated by centrifugation. Solvents (typically hexane or acetone) are used in solvent fractionation as media for crystallization and separation of the solid fraction. Both wetting agents and solvents are recovered and reused in the process. The purity of the fractions obtained, as well as capital and production costs,

<sup>9</sup> Inform, April 2006, Volume 17(4)

increase from dry fractionation to wet fractionation to solvent fractionation<sup>10</sup>.

### Splitting

Fats and oils are hydrolyzed in the splitting process to yield free fatty acids and glycerin. Typical splitting plants can operate as continuous or batch processes at temperatures of 210 – 250 °C and vapor pressures of 20 – 40 bar without catalysts<sup>11</sup>. In order to achieve a high yield of splitting (higher than 97 percent), glyceric water (sweet water) is continuously separated from the fat phase. Raw fatty acids are released to atmospheric pressure and the vapors produced are condensed by water sprays. The resulting water is discharged after separation of the floating fat. Raw fatty acids are then dehydrated and sent to the distillation plant. The sweet waters, containing up to 20% of glycerin, are settled from the remaining fats and can be purified with light lime treatment and filtration before being further processed for glycerin production.

### Hydrogenation

The hydrogenation process can be performed before or after splitting. Hydrogenation is the reaction between hydrogen and the ethylenic double bond of an unsaturated fat in the presence of a catalyst. The saturated (hydrogenated) fat obtained is characterized by better stability properties and higher melting point. The typical hydrogenation process is carried out at a temperature between 180 – 250°C and hydrogen pressure of 10 – 25 bar with the presence of a finely divided nickel catalyst supported on silica gel or diatomaceous earth<sup>12</sup>.

The reaction is exothermic and the heat is recovered for preheating of the fat. The resultant hydrogenated fat is filtered, and the spent catalyst filter cakes (dried with nitrogen due to its pyrophoric properties) collected and sent to the catalyst industry

for reactivation. A further purification step (post-refining) by filtering with activated bleaching earths may be necessary in order to eliminate traces of nickel (nickel soaps).

### Fatty Acids Distillation and Fractional Distillation

Crude fatty acids coming from the splitting units contain 2 – 5 percent of partial glycerides, oligomers, unsaponifiable matter, and oxidation products. Distillation plants, operating normally at 160 – 250°C and 2 – 20 mbar, produce light colored fatty acids, light ends, and residues. Light ends are condensed and collected for further treatment and disposal. Residues of continuous processes still contain a certain percentage of fatty acids and can be either used for low quality productions or re-hydrolyzed and redistilled in batches. The pitches generated are collected for recycling and/or disposal. Fatty acids distillation towers produce several fatty acid fractions based of their different vapor pressures. Fatty acids can also be fractionated by low-temperature partial crystallization.

### Glycerin Production

Animal or vegetable grade glycerin is produced through cleavage of the triglycerides of animal and vegetable fats by splitting, transesterification, or saponification. Glyceric aqueous solutions are purified, concentrated, and distilled (Figure A.2) in order to meet different market specifications and can be used for producing other oleochemicals such as mono and di-glycerides.

### Raw Materials

Modern splitting plants produce glyceric solutions containing up to 20 percent of glycerin in water (“sweet waters”).

Concentrations of glycerin up to 85 – 90 percent and salts up to 5 percent are obtained from transesterification process; recovery of excess methanol from glyceric solution and its recycling in the process are common operations of the biodiesel industry. Spent lye glycerin, obtained from saponification

<sup>10</sup> G. Dieckelmann and H.J. Heinz, 1989. AOCS, Inform, May 2006, Volume 17(5)

<sup>11</sup> G. Dieckelmann and H.J. Heinz, 1989

<sup>12</sup> Bailey's Industrial Oil and Fat Production. 1985

process, has lower content of glycerin (5 – 8 percent) and higher concentration of salts (10 – 15 percent) and impurities.

### *Processing Operations*

#### **Pretreatment of the Glyceric Solutions**

Spent soap lye and glycerol solutions, coming from splitting or transesterification of low grade or recycled fats, are treated with coagulating salts such as aluminum sulfate or ferric chloride, acids, and lime to remove impurities (e.g., soaps, protein degradation products, fatty acids or esters, ashes, and fibers). They are then filtered through activated clay or activated carbon. Typically, sweet waters and transesterification solutions have lower impurities content and need only a light lime treatment followed by pH adjustment and filtration.

Glyceric solutions can be also purified by an ion-exchange process. This process is mainly used for solutions containing low levels of salts and soaps, which after purification can reach concentrations higher than 99.5 percent via evaporation, avoiding the distillation step. The resins are reactivated by acids and caustic solutions that must be neutralized before disposal.

#### **Evaporation**

Spent soap lye and sweet waters are processed under reduced pressure and high temperature in multistage evaporators where glycerin achieves concentrations of up to 90 percent. The distilled water is condensed and discharged. After bleaching with activated carbon, the 90 percent glycerin can be sold as technical grade glycerin or further distilled.

#### **Distillation**

Glyceric solutions from transesterification and from evaporation containing up to 90 percent glycerol are distilled in packed columns where heavy and light boiling impurities are separated and pure glycerin (more than 99.5 percent) is obtained. In the case of glycerin with high salts content (such as spent lye or

biodiesel glycerin), a salt squeezing device allows reduction of the heavy fractions, which, depending on their glycerol content, can be further purified, destined for other uses (e.g., fertilizers), or disposed of. Light fractions, which are water solutions containing some percentage of glycerin (10 – 30 percent) and traces of fatty acids and esters, can be recycled to the production process via lime and acid treatment, filtration, and evaporation. The distilled yellowish glycerin is usually bleached with activated carbon to meet the pharmaceutical requirements.

### **Biodiesel Production**

Biodiesel is defined as mono-alkyl esters of long-chain fatty acids.<sup>13</sup> Biodiesel is mainly obtained by direct reaction (transesterification) of oils and fats of vegetable and animal origin with methanol of fossil origin (Figure A.3), although other alcohols (e.g., ethanol, isopropanol) can also be used. The resulting products are fatty acid methyl esters (FAMES) and glycerin. FAMES are also the base of other important oleochemical products, including fatty alcohols (surfactants industry).

#### *Raw Materials*

Natural oils and fats of vegetable origin are widely used as feedstock. Rape seed oil, soybean oil, palm oil, sunflower seed oil, and cotton seed oil are the most frequently used. Animal origin fats, such as tallow and lard, can also be used. Most of the manufacturing plants use multiple feedstocks and can also accept lower quality oils, such as used frying oils or crude oils. Fatty acids of animal or vegetable origin are used in the esterification process.

The main requirement for methanol is the absence of water that interferes with the transesterification reaction. Ethanol, which can be used in the transesterification process instead of

<sup>13</sup> See for example EU EN 14214, EN 14213, and ASTM 6751-06

methanol, forms an azeotrope with water that may complicate its recovery and recycling during the process.

### *Processing Operations*

#### **Pretreatment**

Transesterification processes normally require feedstocks with a very low content of free fatty acids. Fats and oils are neutralized by chemical or physical refining or by esterification. Used frying oils, animal fats, and high acid level oils are usually esterified with methanol and acid catalyst; the reaction water is removed and the acid catalyst is neutralized with sodium or potassium hydroxide before proceeding with the transesterification. Fatty acids streams coming from physical refining can also be esterified<sup>14</sup>.

#### **Methyl Esters Synthesis by Transesterification**

The transesterification of fats and oils with methanol is typically carried out with basic catalysts (e.g., sodium hydroxide, potassium hydroxide, and sodium methylate) at 60 – 70°C and normal pressure, although higher temperature and pressure are also used. The equilibrium of the reaction is pushed to the ester production by an excess of methanol and by the settling of the glyceric phase in the bottom of the reactor. Once the reaction is complete, the mixture is allowed to settle or is separated by centrifugation.

#### **Methyl Esters and Glycerol Purification**

Excess alcohol is removed from both phases by evaporation and then condensed and recycled. The ester is washed with acidic water to remove traces of catalyst, soaps, and residual methanol and glycerin prior to drying. The wash water can be collected in the glyceric stream. The glyceric phase is then neutralized with mineral acids, normally hydrochloric acid; if potassium hydroxide and phosphoric acid are used, the resulting salt has a value as fertilizer. Fatty acids from soaps

neutralization can be recovered and re-esterified; crude glycerin is then sent to glycerin refining units.

#### **Methyl Esters Synthesis by Esterification**

Fatty acids can be converted into FAMES by esterification with methanol in the presence of an acid catalyst. Process water is purified from the excess methanol used in the reaction before discharge. Continuous counter current plants produce methyl esters streams at yields of 99 percent and above.

#### **Distillation**

Crude methyl esters, especially coming from highly degraded feedstock, can be distilled to remove heavy and light boiling impurities and meet the required standards.

<sup>14</sup> Biorenewable Sources, August 2006, Volume 2

*Figure A.1: Fatty Acid Production*





