

# FEDIOL Guide to good practice on safe operation of Hydrogenation units (applicable as from 01 October 2007) Terminology used: ISO-9001:2000; ILO-OSH 2001.

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# **1** Definitions

- 1. Condensate: any material that has been condensed from the vapor state to the liquid state.
- 2. Condenser: a piece of equipment that lowers the temperature of a vapor to the point where it changes to a liquid.
- 3. Hydrogenation Supervisor: the person in charge of the hydrogenation process
- 5. Hydrogenation Process: The Hydrogenation Process is an exothermic chemical reaction of hydrogen with unsaturated triglycerides under influence of temperature, pressure and a catalyst, typically a nickel compound. It's a batch process taking place in a dead end or loop reactor. The purpose of hydrogenation is to increase the resistance of the oil to rancidity and/or changing the melting behavior of the oil. Physical characteristics will change under the hydrogenation process where viscosity and melting point will increase as the degree of saturation increases.
- 6. Catalyst : A substance that influences the chemical reaction without being used in the reaction. At the end of the reaction the catalyst is still chemically unchanged.
- 7. Flame Arrester : a device that prevents the transmission of a flame through a flammable gas/air mixture by quenching the flame on the surfaces of an array of small passages through which the flame must pass. The emerging gases are sufficiently cooled to prevent ignition on the protected side.
- 8. Heat Exchanger : equipment that transfers heat from one vapor or liquid to another vapor or liquid.
- 9. Hydrocarbon : a chemical substance consisting of only hydrogen and carbon atoms.
- 10. Inert Gas : a gas that is noncombustible and nonreactive.
- 11. Inerting : a technique by which a combustible mixture is rendered non-ignitible by adding an inert gas.
- 12. Lower Flammable Limit (LFL) : that concentration of a combustible material in air below which ignition will not occur.
- 13. Noncombustible Material : a material that, in the form in which it is used and under the conditions anticipated, will not ignite, burn, support combustion, or release flammable vapors when subjected to fire or heat. Materials that are reported as passing ASTM E 136, Standard Test Method for Behavior of Materials in a Vertical Tube Furnace at 750°C and in accordance with European Directive 89/106/EEC (the Construction Product Directive with links to standards for testing and approval), shall be considered noncombustible materials.
- 14. Site Management : the management in charge of all operations of several units on the same site.
- 15. Upper Flammable Limit (UFL) : that concentration of a combustible material in air above which ignition will not occur.

# 2 Scope and Limitations

### **2.1 Intention of this guide**

This guide has been established to give FEDIOL members a code of practice for making safety and health risk assessment for explosive atmospheres in hydrogenation plants required by local legislation through the European Community Directive 1999/92/EC.

### 2.2 Basis for safety

The basis for safety for vapors in hydrogenation as used throughout this document is:

- 1. Prevention of explosive mixtures
- 2. Avoidance of the ignition sources under normal operation conditions.

Normal operation conditions will include start up phase, in production, shutting down phase and while the plant is down under load.

### 2.3 Limits and liability of the codes

- 2.3.1 The following chapters will define normal operating conditions for existing or new hydrogenation plants.
- 2.3.2 This code does not include the hydrogenation generation and/or the use/handling of liquid hydrogen.
- 2.3.3 This code covers the reception of hydrogen through the whole process of hydrogenation as described under 4.3.2.2 and all auxiliary equipment related to these process steps, assuming all hydrogen has been removed before filtration.
- 2.3.4 This guide establishes rules and procedures to be developed around the risk analysis.
- 2.3.5 The requirements of this guide reflect a consensus of what is required to provide an acceptable degree of protection from the hazard of explosions at the time the guide was issued. specified, otherwise technical and constructional Unless requirements should be applied to facilities, equipment, structures or installations that existed or were approved prior to the effective date of this code of practice. Where not possible due to constraints the risk control measures are within the ALARP concept (as low as reasonably possible). Alternative prevention methods may have to be developed to meet this level.
- 2.3.6 However, FEDIOL does not assume any responsibility and/or liability for any site claiming to adhere to the FEDIOL guide to good practice on ATEX for hydrogenation.
- 2.3.7 This guide of practice has been developed in accordance with EU legislation, best practices and currently applied technology. Any additional national requirements are the responsibility of the individual operator.

# **3** Organization of the operations

### 3.1 Responsibility and accountability

### **3.1.1** Allocation of Responsibility and Accountability for :

3.1.1.1 Safe operating practices, including but not limited to documented and detailed operating procedures and procedures for start-up and shutdown and while plant is idle under load, shall be the responsibility of the Site Management for installations put into operation for the first time before 2003. For installations put into service after 2003 the Site Management and the Main Equipment Suppliers will be responsible through the instruction manuals provided.

However, in case of turnkey projects put into service since 2003, the main supplier will be solely responsible until 'handing over' to the Site Management. Deviations from this approach may be agreed in the contract.

- 3.1.1.2 Repair Authorization. When it is necessary to make repairs to the areas covered by this standard, the work shall be authorized by the Site Management or its approved delegate before the work is started. Where hot work is required, this authorization shall be in writing.
  - A hot work/ sparking/ ignition work permits system (only after inerting/venting/vacuum) shall be at least the responsibility of the Site Management.
  - The opening of equipment that contains or is likely to contain hydrogen shall be authorized in writing by the individual in responsible charge of the plant before the work is started.

#### **3.1.2 Procurement**

3.1.2.1 Site Management has put practices in place to ensure that materials and equipment to be used in the zoned areas will comply with the conditions as specified in the explosion risk assessments.

#### 3.1.3 Contracting

3.1.3.1 Site management has put practices in place to ensure that companies and persons supplying services in zoned areas are informed of the risks as documented and appropriate control measures in the risks assessment to avoid or reduce the risks of an explosion.

#### **3.1.4** Monitoring and measurement

- 3.1.4.1 Site Management has allocated responsibilities for planned inspections and maintenance of all equipment identified as critical (4.3.3.4) used in the zoned areas
- 3.1.4.2 Site Management has allocated responsibilities to conduct task observations of employees and others in the zoned area for adherence to the work- and operating instructions as well as using the appropriate control measures.
- 3.1.4.3 Site Management has allocated responsibilities to conduct verification of rules and work permits of activities in zoned areas.

### 3.1.5 Investigation of incidents

3.1.5.1 Site Management ensures that all unplanned events in the zoned areas are investigated and that corrective or preventive measures are taken to avoid re-occurrence.

### 3.1.6 Audit

3.1.6.1 Site management has put a plan in place to ensure that all elements as listed in this document are yearly audited and where required improvements are made.

#### 3.1.7 Management review

3.1.7.1 Site Management yearly conducts a review of the system in place and uses information from investigation of incidents, audits and other sources to develop and initiate actions to improve the system in place.

#### 3.1.8 Action for improvement

- 3.1.8.1 Site management ensures that a plan is present that includes the preventive and corrective actions and monitors the progress of execution.
- 3.1.8.2 Site management has established a system to monitor developments outside their location that will lead to continual improvement of the prevention of explosions.

### 3.2 Competence and training

3.2.1 Operating and maintenance employees shall be instructed in plant operations.

The instruction or training includes, and adheres to, the following:

- identity of dangerous substances that present risks to safety and the area where they are used;
- Extent and type of risks and factors that increase the risks as smoking or other ignition sources (MSDS contain most of this information and employees are to have access to these);
- the significant findings of the risk assessment ;
- the control/ mitigation measures implemented, including work instructions, the reason for them and how to use them properly;
- procedures to deal with accidents, incidents and emergencies;
- includes theory as well as practice;
- the way of supplying information and instruction is appropriate and can be done by: class or group tuition, individual tuition, written instructions as leaflets, courses, etc...;
- the training is appropriate to the knowledge and experience of the employees ;
- is updated when changes or reviews deem this necessary ;
- is refreshed when deemed necessary ;
- is suited for employees not mastering the language.

### 3.3 Records and documents

3.3.1 Proper systems are maintained to keep records and documents such as on training, permits, equipment classification, and risk assessment.

### 3.4 Communication/ Coordination

- 3.4.1 The content of the information that is communicated to all parties that are present in zoned areas meets the requirements as listed in 3.2.
- 3.4.2 When two or more employers share a workplace, management responsible for the workplace is required to coordinate the implementation of measures to protect employees and others from the risks of explosive atmospheres. The aim of the coordination is to :
  - alert other employers, employees and others of the presence of hazardous places or substances;
  - ensure suitable control and mitigation measures are in place;
  - ensure that everybody has had sufficient training
  - facilitate emergency arrangements in case of an incident.

# 4 Planning and implementation

# 4.1 Identify applicable legislation

This guide includes references to or made use of :

89/106/EEC	<b>Construction Product Directive</b>
89/391/EEC	Introduction of measures to encourage improvements in the safety and health of workers at work
94/9/EC	Equipment and protective systems intended for use in explosive atmospheres
97/23/EC	Pressure Equipment Directive
98/37/EC or 2006/42/EC	Machine Directive
1999/92/EC	Protection of workers potentially at risk from explosive atmospheres
СОМ (2003) 515	Non-binding guide of good practice for implementing Directive 1999/92/EC

Also the following standards are referred to :

EN 1127-1 Explosive atmospheres- Explosion prevention and protection -Part 1: Basic concepts and methodology

EN 13463-1 Non-electrical equipment for potentially explosive atmospheres; Basic method and requirements

EN 13563-1 Non-metallic components including sight glasses for ATEX installations

#### EN 14986 Fan and Ventilator for ATEX installations

#### EN 12874-2001 Flame arrestor for ATEX installations

NFPA 55 Standard for the Storage, Use, and Handling of Compressed Gases and Cryogenic Fluids in Portable and Stationary Containers, Cylinders, and Tanks

### 4.2 Identify and assess risks

- 4.2.1 Avoiding process conditions in each step of the batch process or failures resulting in the release of substances that could create an explosive atmosphere. For this several methods are available, such as: hazard and operability study (HAZOP); What if; EN 1050; Fault tree analysis (for an overview of methods see: The RASE Project report Methodology for the risk assessment of Unit operations and Equipment for use in Potentially Explosive Atmospheres.
- 4.2.2 Avoiding hazardous situations due to human interference. Their tasks and activities will have to be risk assessed and where required procedures or instructions have to be developed to avoid loss, as well as injury, damage to health or release of substances that could create an explosive atmosphere. Assessment method for this are: Task risk analysis, Job safety analysis.
- 4.2.3 Areas with a potential for explosive atmospheres have to be identified and documented. This guide provides proposals in Chapter 5 for this as well as requirements.

Explosive atmosphere could form when certain circumstances are present, such as:

\* Outside the equipment (fugitive losses)

- Leakages at connections, vessels or seals

- Disconnecting hoses/ pipes during truck unloading or connecting up to the process.

\* Inside the equipment, whether or not linked to guided emissions - Filling of the process vessel and mixing of hydrogen with air present (when no inert gas is used)

- Damping out of the hydrogen in the standing vessel

- Removing residual hydrogen through the use of a vacuum system
- 4.2.4 Avoidance of occurrence of explosive mixtures (this can be achieved by applying the details as described in this document).

#### 4.2.4.1 Hydrogen

Physical and Chemical properties.	
Molecular weight	2.016
Specific gravity at 0°C and 1 atm	0.06960
Gas density at 21.1°C and 1 atm	0.08342 kg/m <sup>3</sup>
Solubility in water at 15.6°C and 1 atm	0.019
Percent volatiles by volume	100
Boiling point at 1 atm	-252.76°C

Melting point at 1 atm	-259.20°C
Autoignition temperature	500°C
Flammable limits in air, % by volume	
_ower (LFL)	4%
Jpper (UFL)	75%
Minimum Ignition Energy (MIE)	0.01 mJ
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Hydrogen is a flammable gas with a low solubility in oil. It is colorless, odorless, tasteless, and nontoxic. It is the lightest gas known and diffuses rapidly in air and through materials not normally considered porous. It burns in air with a pale blue, almost invisible flame. It remains a gas even at high pressure. It is nontoxic, but is able to cause asphyxiation when it displaces the normal 21 percent oxygen in a confined area without ventilation to maintain an oxygen content exceeding 19.5 percent. Because hydrogen is colorless, odorless, and tasteless, its presence cannot be detected by human senses.

#### 4.2.4.2 **Catalyst**

#### fresh catalyst.

For the hydrogenation of edible oils, nickel catalyst is most commonly used. Nickel catalyst usually consists of Ni-containing substances on an inert carrier material (f.e. silica), incapsuled in pellets of fully hydrogenated edible oil.

To the best of our knowledge, there is no literature or practical experience indicating specific fire/explosion risks associated with this material, other than that the fully hydrogenated oil in the pellets is combustible like any edible oil.

#### spent catalyst.

After the hydrogenation reaction, the catalyst is separated from the hydrogenated product by filtration and subsequently dried. The resulting spent catalyst cake consists of Ni-containing substances, the inert carrier material and residual hydrogenated fat. Spent catalyst may be (partially) re-used or disposed and processed as hazardous waste by a third party. At elevated temperatures, there is a risk of spent catalyst starting to smolder. For this reason precautions, such as cooling or nitrogen blanketing, must be in place.

#### 4.2.4.3 **Oil and fats**:

Vegetable oils and fats are water-insoluble substances composed of triglycerides with a fatty acid composition characteristic for the specific oil type. Generally speaking, oils are liquid at room temperature and fats are solid. The temperature-based distinction between oils and fats is imprecise, since the temperatures of rooms vary, and typically any one substance has a melting range instead of a single melting point.

Triglyceride based vegetable oils and fats can be transformed through partial or complete hydrogenation into oils and fats of higher melting point. The hydrogenation process involves "sparging" the oil at high temperature and pressure with hydrogen in the presence of a catalyst, typically a nickel compound. As a double-bond in the triglyceride is broken, two hydrogen atoms form single bonds. The elimination of double-bonds by adding hydrogen atoms is called saturation; as the degree of saturation increases, the oil progresses towards being fully hydrogenated. An oil may be hydrogenated to increase resistance to

rancidity or to change its physical characteristics. As the degree of saturation increases, the oil's viscosity and melting point increase.

- 4.2.5 Avoidance of ignition sources Sources of ignition are listed below as identified in the standard EN 1127-1, which distinguishes 13 types of ignition sources :
- 4.2.5.1 **Hot surfaces** Explosive atmospheres can be ignited by contact with hot surfaces, if the temperature of a surface reaches the atmosphere's ignition temperature.

If hot surfaces can come in contact with explosive atmospheres, a safety margin should be ensured between the maximum surface temperature and the atmosphere's ignition temperature.

- 4.2.5.2 **Flames and hot gases** Both flames and incandescent solid particles can ignite explosive atmospheres. Even very small flames must generally be eliminated from hazardous places. Flames should occur only if they are safely enclosed. Naked flames from welding or smoking must be prevented by organizational measures.
- 4.2.5.3 **Mechanically generated sparks** Friction, impact and abrasion processes, such as grinding, can give rise to sparking. Ingress of foreign materials, e.g. stones or tramp metals, into equipment must be considered as a cause of sparking.
- 4.2.5.4 **Electrical apparatus** Even at low voltages, electrical sparking and hot surfaces may occur as source of ignition in electrical apparatus (e.g. on making and breaking circuits and as a result of stray electrical currents).
- 4.2.5.5 Stray electrical currents, cathodic corrosion protection
- 4.2.5.6 **Static electricity** Separation processes involving at least one material with a specific electrical resistance or objects with a high surface resistance may under certain conditions give rise to incendive discharges of static electricity capable of igniting most gases or solvent vapors.
- 4.2.5.7 **Lightning** Provisions shall be made for protection against lightning.
- 4.2.5.8 Electromagnetic fields in the frequency range from 9 kHz to 300 GHz
- 4.2.5.9 Electromagnetic radiation in the frequency range from 300 GHz to 3 million GHz or wavelength range from 1000μm to 0.1 μm (optical spectrum)

#### 4.2.5.10 **Ionizing radiation**

- 4.2.5.11 Ultrasonic
- 4.2.5.12 Adiabatic compression, shock waves, gas flows
- 4.2.5.13 **Chemical reactions** which develop heat (exothermic reactions) can cause substances to heat up and thus become a source of ignition. Hydrogenation is known to be an exothermic reaction.

### **4.3 Prevention and control measures**

The control measures which have been listed here are highly recommended in order to use the zone classification as given in Chapter 5.

### 4.3.1 Design and construction requirements

The basis of safety is given in 2.2. In order to avoid explosive mixture or contact of the mixture with ignition sources the following general requirement should be adhered to:

Develop processes and equipment so that the high risks are reduced by engineering to safe design levels, as to allow further risk reduction by means such as:

- 1) Safety distances as mentioned in this section
- 2) Inerting / venting / vacuum
- 3) Safety devices
- 4) Any other solution providing the same level of safeguards, while avoiding ignition sources

#### 4.3.1.1 Bulk hydrogen Unloading Site and storage tanks

- 4.3.1.1.1 General requirements
- 4.3.1.1.1.1 Systems shall be located above ground either at grade or above grade.
- 4.3.1.1.2 Systems within 15 m of above ground storage of all classes of flammable and combustible liquids shall be located on ground higher than such storage, except where dikes, diversion curbs, grading, or separating solid walls are used to prevent accumulation of these flammable and combustible liquids under the system.
- 4.3.1.1.2 Specific requirements
- 4.3.1.1.2.1 The location of hydrogen systems shall be in accordance with the following table:

Quantity of hydrogen					
Location	< (MAQ)	>MAQ to	100m <sup>3</sup> to	400m <sup>3</sup> and	
		<100m <sup>3</sup>	<400 m <sup>3</sup>	above	
Outdoors	А	А	А	А	
In detached building	A	A	A	A	
In a gas room	A	A	A	Detached building required	
Not in a gas room	A	NA	NA	NA	

A: Allowed; NA: Not allowed, MAQ: Maximum Allowable Quantity.

4.3.1.1.2.2 The minimum distance from a hydrogen system of indicated capacity located outdoors to any specific exposure shall be in accordance with the following table:

Total C	Gaseous Hydro	ogen storage	2
	<100m <sup>3</sup>	100m <sup>3</sup> to <400 m <sup>3</sup>	400m <sup>3</sup> + above
Type of Outdoor	Distance in	Distance in	Distance in
Exposure	meter	meter	meter
(1) Building or structure			
(A) Wall(s) adjacent to system	em constructed	of noncombusti	ble or limit-
combustible materials			
1. noncombustible	0	1.5	1.5
contents or sprinklered			
building or structure			
2. unsprinklered building			
or structure with			
combustible content			
(a) Adjacent wall(s) with	0	3.0	7.5
fire resistance rating less			
than 2 hours			
(b) Wall(s) adjacent to	0	1.5	1.5
system constructed of			
combustible content	• •		
(B) Wall(s) adjacent to	3.0	7.5	15.0
system constructed of			
other than			
noncombustible or			
limited-combustible			
materials			
(2) Wall openings	2.0	2.0	2.0
(A) Not above any part of	3.0	3.0	3.0
a system			
(B) Above any part of a	1.5	1.5	1.5
system			
(3) All classes of flammab	le and combus	tible liquids ab	ove ground
(A) 0-3500 liter	3.0	/.5	/.5
(B) in excess of 3500 liter	/.5	15.0	15.0
(4) All classes of flammab	le and combus	tible liquids be	low ground from
0-3500 liter	2.0	2.0	2.0
(A) Tank	3.0	3.0	3.0
(B) Vent or fill opening of	7.5	7.5	7.5
tank			
(5) All classes of			
flammable and			
combustible liquids			
below ground in excess			
of 3500 liter			
(A) Tank	6.0	6.0	6.0
(B) Vent or fill opening of	7.5	7.5	7.5
tank			

(6) Flammable gas storage (other than hydrogen), either high- or low-				
pressure				
(A) $0-400 \text{ m}^3$ capacity	3.0	7.5	7.5	
(B) in excess of $400 \text{m}^3$	7.5	15.0	15.0	
capacity				
(7) Fast-burning solids,	15.0	15.0	15.0	
such as ordinary lumber,				
excelsior, or paper				
(8) Slow-burning solids	7.5	7.5	7.5	
such as heavy timber or				
coal				
(9) Open flames and	7.5	7.5	7.5	
welding				
(10) Air compressor	15.0	15.0	15.0	
intakes or inlets to				
ventilating or air-co				
equipment				
(11) Places of public	7.5	15.0	15.0	
assembly				
(12) Public sidewalks and	4.5	4.5	4.5	
parked vehicles				
(13) Line of adjoining	1.5	1.5	1.5	
property that is able to				
be built upon				
(14) Encroachment by				
overhead utilities				
(A) Horizontal distance	15.0	15.0	15.0	
from the vertical plane				
below the nearest				
overhead wire of an				
electric trolley, train, or				
bus line				
(B) Horizontal distance	1.5	1.5	1.5	
from the vertical plane				
below the nearest				
overhead wire other than				
(A)				
(C) Piping containing	4.5	4.5	4.5	
other hazardous materials				

- 4.3.1.1.2.3 The distances in numbers (1), (3) through (9), and (13) inclusive in the table in 4.3.1.1.2.2 shall not apply where fire barrier walls having a minimum fire resistance rating of 2 hours are located between the system and the exposure.
- 4.3.1.1.2.4 Portions of wall more than 3m (measured horizontally) from any part of a system shall have a fire resistance rating of at least <sup>1</sup>/<sub>2</sub> hour.
- 4.3.1.1.2.5 When determining the minimum distance between the hydrogen system and the adjacent fire-rated walls, windows and doors shall be excluded from the fire rating determination.
- 4.3.1.1.2.6 Portions of wall less than 3m (measured horizontally) from any part of a system shall have a fire resistance rating of at least 1 hour.
- 4.3.1.1.2.7 Unloading connections on delivery equipment shall not be positioned closer to any of the exposures sited in the table under 4.3.1.1.2.2 than the distances given for the storage system

#### 4.3.1.2 Hydrogenation process

- 4.3.1.2.1 The hydrogenation process shall be located in the open or in a building suitable for the purpose. The building shall be a light construction. Existing buildings not meeting this requirement will be provided with areas of light construction.
- 4.3.1.2.2 The zoned areas shall be posted with signs EX (triangular shape yellow with black surround) around the perimeter warning of the possible explosion hazard.
- 4.3.1.2.3 The building or structure housing the hydrogenation process shall be of fire-resistive or noncombustible construction with the ground floor at or above grade.
- 4.3.1.2.4 An hydrogenation building or open process structure over two stories in height shall be provided with at least two remotely located means of egress from each floor, one of which shall be enclosed or separated from the process by a wall that is blank except for doors.
- 4.3.1.2.5 The enclosure or separating wall shall be of masonry or other noncombustible construction.
- 4.3.1.2.6 Self-closing, noncombustible doors, normally kept closed, shall be provided for access to the means of egress.
- 4.3.1.2.7 Indoor Hydrogen System Location.

A separable part of a process containing hydrogen of less than 100 m3 and greater than the MAQ, where located inside buildings, shall be located in the building so that the system will be as follows:

- (1) In a ventilated area
- (2) Separated from incompatible materials
- (3) 7.5 m from open flames and other sources of ignition
- (4) 15 m from intakes of ventilation, air-conditioning equipment, and air compressors

(a) The distance is permitted to be reduced to 3 m where the room or area is protected by a listed detection system that shall shut down the fuel supply in the event of a leak that results in a concentration that exceeds 25 percent of the LFL.

(b) Isolation valves used to isolate the fuel supply shall be of a fail-safe design.

(5) 15 m from other flammable gas storage

#### (6) Protected against damage

More than one system of 100 m3 or less shall be permitted to be installed in the same room or area, provided the systems are separated by at least 15 m or a full-height fire-resistive partition having a minimum fire resistance rating of 2 hours is located between the systems.

The separation distance between multiple systems of 100 m3 or less shall be permitted to be reduced to 7.5 m in buildings where the space between storage areas is free of combustible materials and protected with a sprinkler system.

#### 4.3.1.3 **Inerting**

4.3.1.3.1 Whenever required, the hydrogenation installation (piping, equipment and reactor) shall be either purged a few times with nitrogen and/or purged by vacuum followed by pressure equalization with nitrogen see 4.3.1.5.1

#### 4.3.1.4 **Venting**

- 4.3.1.4.1 The hydrogen gas supply is stopped and excess pressure is vented from the reactor after the hydrogenation reaction and is evacuated to a safe location either outside, vertically vented to the atmosphere above roof level, or to a buffer vessel for re-use of hydrogen.
- 4.3.1.4.2 The hydrogenated oil will be subject to further treatment prior to discharge to the final product tanks.

#### 4.3.1.5 **Vacuum**

4.3.2.1

- 4.3.1.5.1 Vacuum is used to purge the installation from hydrogen while pressure is equalized with nitrogen (see paragraph 4.3.1.3.1).
- 4.3.1.5.2 the risk of residual hydrogen gas in the oil in final storage tanks may be considered to be highly limited.

#### 4.3.1.6 Safety devices

- 4.3.1.6.1 Excessive temperature in the reactor or loss of cooling water will close the safety shutoff valve for the hydrogen supply.
- 4.3.1.6.2 Safety valves shall separate the hydrogenation process from upstream and downstream processes.

#### 4.3.2 Develop flow sheets and P&ID

Short description of the hydrogenation batch process.

In the process vessel an oil fat mixture is present to which a catalyst is added. This mixture is stirred (usually with a mechanical driven stirrer that enters the vessel through a seal) and hydrogen is added. An exothermic process takes place in which the chemical structure of the oil/ fat is changed through which melting points of the oil/fat can be modified. Pressure of the vessel is usually vented to the outside using a stack

The next process step for the product is usually to remove remaining hydrogen by standing or even using a vacuum and blanketing the product with an inert gas. After the process has taken place the oil/fat is transfered to a next process step (outside the ATEX zoned area).





Schematic Hydrogenation process

(In the dashed box are the possible process steps which can occur in different or the same vessels) The box, inclusive of auxiliary equipment, is the scope of this Good practice guide.

### 4.3.3 Develop standard operating procedures

- In this paragraph we distinguish between :
- Operating the equipment under various conditions,
- Good housekeeping standards and
- Maintaining the critical equipment.
- All to ensure avoidance of potential explosive atmospheres

#### 4.3.3.1 **Operating the equipment under various conditions**

4.3.3.1.1 Documented procedures for hydrogenation **start-up** shall be established to minimize the hazards resulting from passing through the flammable range. The instruction manuals of the equipment supplier and their recommendations shall be incorporated in the various procedures. Inerting or vacuum shall be used to reduce the oxygen content and meet this requirement.

The equipment shall be operated in line with suppliers' instructions, such as keeping pumps under liquids.

- 4.3.3.1.2 A similar approach will developed at **shut down of the process**. Isolation from upstream and down stream equipment shall be secured.
- 4.3.3.1.3. Documented procedures for other operating conditions shall be established to minimize the hazards of the flammable hydrogen. The instruction manuals of the equipment supplier and their recommendations are incorporated in the various procedures.

### 4.3.3.2 **Preparing hydrogenation units for maintenance**

- 4.3.3.2.1 The hydrogenation unit is stopped and emptied out completely (no product left in vessels).
- 4.3.3.2.2 Main hydrogen gas supplies are properly isolated.
- 4.3.3.2.3 Excess pressure (if present) is vented from the reactor and the reactor is put under vacuum.
- 4.3.3.2.4 The remaining hydrogen gas is then vented from the reactor by:
  - either continuous flushing with nitrogen gas to the vacuum system
  - or repeatedly putting the reactor under vacuum, then nitrogen pressure for several times.
- 4.3.3.2.5 Connection with vacuum system is closed and isolated.
- 4.3.3.2.6 Nitrogen supply is closed and isolated.
- 4.3.3.2.7 The hydrogenation unit is ready for maintenance work. All the maintenance work that is executed shall be under work permit.

#### 4.3.3.3 Maintaining the critical equipment

4.3.3.3.1 All equipment identified as critical shall be included in a maintenance program. The program indicates frequency, description and criteria for the maintenance to be conducted.

Equipment is critical when one of the criteria below is valid:

- (1) leak tightness is lost more then twice/year and the equipment can't be taken out of service immediately
- (2) the assessment according to EN 13463-1 indicates that a certain periodical replacement or attention is required to avoid an ignition source
- (3) equipment is considered essential for preventing the occurrence or detection of an potentially explosive mixture (such as

detection and or ventilation equipment)

(4) equipment is used to avoid propagation of an explosion or to limit effects.

### 4.3.4 Provide for gas tight hydrogen process equipment

#### 4.3.4.1 **Hydrogen transfer equipment**

4.3.4.1.1 Pumps and Mixers:

Pumps and mixers shall be designed for the hydrogen, the working pressures, and the structural stresses to which they will be subjected.

#### 4.3.4.2 **Piping, Valves and Fittings**

- 4.3.4.2.1 All pressure equipment shall comply with Directive 1997/23/EC when applicable. All piping, valves, fittings shall be designed for the working pressures and structural stresses to which they will be subjected and shall be of steel or other material approved for the service intended.
- 4.3.4.2.2 Pipe Systems. Pipe systems shall be substantially supported and protected against physical damage caused by expansion, contraction, and vibration.
- 4.3.4.2.3 Armored hoses shall be permitted to be used where vibration exists or where frequent movement is necessary.
- 4.3.4.2.4 All piping and equipment shall be coded for identification.
- 4.3.4.2.5 Drain valves shall be provided with plugs to prevent leakage.
- 4.3.4.2.6 Rupture disks and/or pressure relief valves may be used on hydrogen supply lines and the hydrogenation reactor. Excess hydrogen gas is to be evacuated to a safe location.

#### 4.3.4.3 **Pressure Vessels and Tanks.**

- 4.3.4.3.1 Pressure vessels such shall be constructed in accordance with the Pressure Equipment Directive 1997/23/EC.
- 4.3.4.3.2 Where sight glasses are installed, they shall be of the high-pressure type protected against breakage and loss of product and in accordance with EN 13563-1.
- 4.3.4.4 Vacuum Systems
- 4.3.4.4.1 Usually, a vacuum system is consisting of a condenser and a vacuum pump.

### 4.3.5 Hydrogen detection

4.3.5.1 For indoor applications, approved and calibrated combustible gas indicators shall be permanently installed and maintained in good working order and shall be used to start ventilation and/or shutting off equipment, including hydrogen supply. Provisions shall be made for monitoring the atmosphere in areas where bydrogen can present an explosion risk. Monitoring shall be

where hydrogen can present an explosion risk. Monitoring shall be permitted to be accomplished by installing an approved combustible gas detection system with audible and visual alarms and which closes the hydrogen supply. Where such a detection system is used, it shall be tested and maintained in good working order in accordance with the manufacturer's instructions.

4.3.5.2 Entrapment of hydrogen in roof containment Hydrogenation buildings and installations shall be designed and executed to avoid accumulation of hydrogen, by means of sufficient (roof) ventilation. Special attention shall be paid to steel constructions

and sloped roof areas to avoid that hydrogen gets trapped in deadend corners of the roof construction.

If entrapment cannot be avoided, a hydrogen detection system has to be installed to ensure that in case of the formation of explosive mixtures no ignition sources will be active in that area, or other measures have to be implemented to avoid the risk of an explosion.

### 4.3.6 Avoiding ignition sources

#### 4.3.6.1 **General**

To ensure that ignition through equipment is avoided, there are two options :

- 4.3.6.1.1 Equipment made available for the first time before June, 30, 2003 should be assessed using the standard EN 13463-1. The equipment should be assessed for normal operating conditions when installed in an area classified as zone 2, and for normal operating conditions and expected malfunctions when installed in an area classified as zone 1. Equipment installed in an area classified as zone 0 should be assessed for: normal operating conditions and rare malfunctions.
- 4.3.6.1.2 All equipment made available for the first time after June 30, 2003 should meet the appropriate minimum requirements as listed in Directive 94/9/EC. This means a Declaration of Conformity with the minimum requirements of the Directive 94/9/EC should be present for each piece of equipment.

#### 4.3.6.2 Hot surfaces

Hot surface temperatures shall not exceed 500°C.

#### 4.3.6.3 Flames and hot gases

- 4.3.6.3.1 Flares or burners from process vents shall be prohibited within areas classified as zone 0, 1 and 2, but shall be permitted to be installed outside these areas. Such flares or burners shall be equipped with approved devices to prevent flashbacks in the vent piping.
- 4.3.6.3.2 To prevent potential explosions caused by fire in the building a sprinkler/deluge should be considered.

#### 4.3.6.4 Mechanically generated sparks

4.3.6.4.1 In mechanical equipment that has moving parts and where friction, impact or abrasion can occur, the combination of light metal and steel should be avoided. The contents of light metal for category 1 equipment (for use in zone 0,1 and 2) should be not more than 10% in total by mass of aluminum, magnesium, titanium and zirconium or not more than 7.5% in total by mass of magnesium, titanium and zirconium.

For category 2 equipment (for use in zone 1 and 2) not more than 7.5% by mass of magnesium.

For category 3 equipment (for use in zone 2) there are no special requirements for light metal use.

The use of non-sparking tools and equipment is compulsory when the installation is operating or when hydrogen can be present.

4.3.6.4.2 Power transmission belts shall not be used in any area that is classified as a zone 0, 1 and 2.

#### 4.3.6.5 **Electrical apparatus** (see Annex 3)

4.3.6.5.1 Electrical equipment used in hazardous places shall meet the requirements for at least category 2 equipment in accordance with Directive 94/9/EC or equivalent when made available for the first time

before June 30, 2003. Equipment made available for the first time after June 30, 2003 must be selected on the basis of the zoning as per Directive 1999/92/EC Annex I and comply with Directive 94/9/EC. In accordance with the explosion protection document the work equipment, including warning devices, must be designed, operated and maintained with due regard to safety.

- 4.3.6.6 **Stray electrical currents, cathodic corrosion protection** 
  - 4.3.6.1.1.1.1 In line with risk assessment conducted.

#### 4.3.6.7 Static electricity

- 4.3.6.7.1 Transfer or storage tanks, unloading structures, tank cars, and tank trucks shall be electrically interconnected with supply piping or containers during the transfer of hydrogen.
- 4.3.6.7.2 Static protection shall be installed in accordance with accepted good practice and tested periodically by a competent person.
- 4.3.6.7.3 All tanks, vessels, motors, pipes, conduit, grating, and building frames within the process shall be electrically bonded together.
- 4.3.6.7.4 Building frames and metal structures shall be grounded and tested periodically to determine electrical continuity.
- 4.3.6.7.5 All hose, except hose used in water service, shall be electrically bonded to the supply line and to the tank or vessel where discharge takes place.
- 4.3.6.7.6 All clothing consists of materials which don't give rise to electrostatic discharges that can ignite explosive atmospheres.
- 4.3.6.7.7 Hydrogen Electrostatic Ignition Sources Hydrogen has a low MIE. Safeguards / control measures are required to eliminate low energy electrostatic discharges capable of igniting hydrogen. Particular care must be taken to control electrostatic risks associated with:
  - personnel; controlled by the use of antistatic footwear and flooring providing a resistance to earth <  $108\Omega$ .
  - the use of non-conductive (e.g. plastic) components.

#### 4.3.6.8. **Lightning**

- 4.3.6.8.1 Where required, an approved lightning protection system, installed in accordance with the Standard for the Installation of Lightning Protection Systems, shall be provided for the extraction process.
- 4.3.6.9 Electromagnetic fields in the frequency range from 9 kHz to 300 GHz

4.3.6.1.1.2 In line with risk assessment conducted

4.3.6.10 Electromagnetic radiation in the frequency range from 300 GHz to 3million GHz

4.3.6.1.1.3 In line with risk assessment conducted

#### 4.3.6.11 **Ionizing radiation**

4.3.6.1.1.4 In line with risk assessment conducted

#### 4.3.6.12 **Ultrasonic**

4.3.6.1.1.5 In line with risk assessment conducted

4.3.6.13 Adiabatic compression, shock waves, gas flows

4.3.6.1.1.6 In line with risk assessment conducted

#### 4.3.6.14 **Chemical reactions**

4.3.6.14.1 Catalyst (fresh and spent) conveyors shall be of a design that minimizes the possibility of ignition of product deposits. The use of nitrogen gas may be considered to reduce the risk of auto-

ignition of spent catalyst.

4.3.6.14.2 Insulation materials soaked with oils and fats may generate hot spots and smolders. Hot surfaces (as such tracings) will accelerate this process. Insulation will be designed as to avoid ingress of / soaking with oils and fats

### 4.4 Management of change

- 4.4.1 Before making any changes to hydrogen containing equipment, an assessment has to be made and all identified control measures have to be implemented (inclusive of training, instructing relevant staff and adapting written procedures and instructions).
- 4.4.2 A pre start-up inspection is conducted before the change is made effective.
- 4.4.3 The whole change process is documented.

### 4.5 Emergency preparedness

- 4.5.1 All employees shall be trained in the necessary actions to be taken in time of emergency, including emergency shutdown procedures.
- 4.5.2 Personnel shall be trained as to the location of exits.
- 4.5.3 All personnel shall be trained in the use and limitations of each type of fire-fighting equipment on the premises, including control valves for the water spray systems.
- 4.5.4 A fire brigade, if established, shall be composed of selected personnel on each shift and shall be trained as a unit with each person assigned definite responsibilities in case of an emergency.
- 4.5.5 Periodic drills shall be held to ensure that employees can carry out the procedures in 4.5.1 through 4.5.4.
- 4.5.6 Emergency safety devices or systems provided in the plant shall be periodically tested in accordance with established procedures and a record made thereof.

# 5. Zone classification of Hydrogenation unit guidance and appropriate equipment categories : proposal

The proposed zoning in this chapter is based on implementing all measure as described in this FEDIOL guide.

Zone classification	Zone	Zone	Electrical/Mechanical	Remarks
outside equipment		dimensions	equipment	* See additional remark
Area description			category	below
Inside hydrogenation process	2		II 3G	Unless otherwise specified below
Hydrogen truck unloading- hoses and connections in tanker bay	1	2 m around	II 2G	
Hydrogen truck connection/disconnection and discharge	1	2 m around	II 2G	
Seals				In accordance with equipment supplier
Entrapment if not properly vented	1		II 2G	See also 4.3.5.2
Building fans or purge systems	1	Within 5 m around exhaust point	II 2G	
	2	In area between 5 and 10 m around exhaust point	II 3G	
Equipment vent lines and safety or pressure relief valves	1	Min. 2 m around and vertical column above depending on the flow released	II 2G	

\* Additional remark: local zones (usually spheric form) should be extended with a vertical cylinder upwards of at least 5 m high and reaching minimum 3 m above any building or equipment in the direct neighborhood.

			(continued)
Zone classification inside	Zone	Electrical/Mechanical equipment	Remarks
equipment		category	
Area description			
Hydrogen equipment up to isolation valves	1	II 2G	
Hydrogen storage tanks	0	II 1G	
Pumps	-	-	In accordance with the suppliers and the instruction manual.
Building fan and ducts	1	II 2G	

# Annex 1. Comparing NFPA with "ATEX" Directives

Summary of comparing NFPA with ATEX

	NFPA 497 and 499	ATEX (1999/92/EC)	
Application Focus on ignition from failure of electrical equipment		Electrical and mechanical equipment could provide ignition source not only through failure.	
Zoning Class1 Division 1 and 2 have no comparison in ATEX			
	Zone 0-2 comparable to ATEX	Zone 0-2 comparable to NFPA	
	Class II, division 1 comparable to zone 20	Zone 20 comparable to Class II, division 1	
		Zone 21 no comparison in NFPA	
	Class II, division 2 comparable to zone 22	Zone 22 comparable to Class II, division 2	

Equipment classification for suited use in zone /classified areas NFPA 70 also refers to zone 0,1,2, and 20, 21, 22 as these are IEC :

Zone	NFPA 70 (applies to electrical only)	1999/92/EC refers to 94/9/EC (applies to electrical and mechanical)
0	Class I division 1	Group II, category 1G
1	Class I division 1	Group II, category 1G or Group II, category 2G
2	Class I division 1 or Class I Division 2	Group II, category 1G or Group II, category 2G or Group II, category 3G
20	Class II Division 1	Group II, category 1D
21 Class II Division 1 Group II, cated Group II, cated		Group II, category 1D or Group II, category 2D
22	Class II Division 1 or Class II division 2	Group II, category 1D or Group II, category 2D or Group II, category 3D

	NFPA 497	1999/92/EC
Class I,	is a location	
Division 1	(1) in which ignitable concentrations of flammable gases or vapors can exist under normal operating conditions, or	
	(2) in which ignitable concentrations of such gases or vapors may	
	exist frequently because of repair or maintenance operations or	
	because of leakage, or	
	(3) In which breakdown or faulty operation of equipment or processes	
	vapors and might also cause simultaneous failure of electrical	
	equipment in such a way as to directly cause the electrical	
	equipment to become a source of ignition. [70:500.5(B)(1)]	
Class I,	is a location	
Division 2	(1) in which volatile flammable liquids or flammable gases are	
	handled, processed, or used, but in which the liquids, vapors, or	
	gases will normally be confined within closed containers or closed systems from which they can ascane only in case of accidental	
	rupture or breakdown of such containers or systems or in case of	
	abnormal operation of equipment, or	
	(2) in which ignitable concentrations of gases or vapors are normally	
	prevented by positive mechanical ventilation, and which might	
	become hazardous through failure or abnormal operation of the	
	ventilating equipment, or (2) that is adjacent to a Class I. Division 1 location, and to which	
	(3) that is adjacent to a class 1, Division 1 location, and to which ignitable concentrations of gases or vanors might occasionally be	
	communicated unless such communication is prevented by	
	adequate positive-pressure ventilation from a source of clean air	
	and effective safeguards against ventilation failure are provided.	
	[70:500.5(B)(2)]	
		./.

#### NFPA Zoning versus ATEX

(continued)				
	NFPA 497	1999/92/EC		
Class I, Zone 0	<ul> <li>is a location</li> <li>(1) ignitable concentrations of flammable gases or vapors are present continuously, or</li> <li>(2) ignitable concentrations of flammable gases or vapors are present for long periods of time. [70:505.5(B)(1)]</li> </ul>	Zone 0	A place in which an explosive atmosphere consisting of a mixture with air of flammable substances in the form of gas, vapor or mist is present continuously or for long periods or frequently	
Class I, Zone 1	<ul> <li>is a location <ol> <li>in which ignitable concentrations of flammable gases or vapors are likely to exist under normal operating conditions; or</li> <li>in which ignitable concentrations of flammable gases or vapors may exist frequently because of repair or maintenance operations or because of leakage; or</li> <li>in which equipment is operated or processes are carried on, of such a nature that equipment breakdown or faulty operations could result in the release of ignitable concentrations of flammable gases or vapors and also cause simultaneous failure of electrical equipment in a mode to cause the electrical equipment to become a source of ignition; or</li> <li>that is adjacent to a Class I, Zone 0 location from which ignitable concentrations of vapors could be communicated, unless communication is prevented by adequate positive pressure ventilation from a source of clean air and effective safeguards against ventilation failure are provided.</li> </ol> </li> </ul>	Zone 1	A place in which an explosive atmosphere consisting of a mixture with air or flammable substances in the form of gas, vapor or mist is likely to occur in normal operation occasionally	
			./.	

			(continued)	
	NFPA 497	1999/92/EC		
Class I,	is a location	Zone 2	A place in which an explosive	
Zone 2	(1) in which ignitable concentrations of flammable gases or vapors are not likely to occur in normal operation and, if they do occur, will exist only for a short period; or		atmosphere consisting of a mixture with air of flammable substances in the form of gas,	
	(2) in which volatile flammable liquids, flammable gases, or flammable vapors are handled, processed, or used but in which the liquids, gases, or vapors normally are confined within closed containers of closed systems from which they can escape only as a result of accidental rupture or breakdown of the containers or system, or as a result of the abnormal operation of the equipment with which the liquids or gases are handled, processed, or used; or		vapor or mist is not likely to occur in normal operation but, if it does occur, will persist for a short period only.	
	(3) in which ignitable concentrations of flammable gases or vapors normally are prevented by positive mechanical ventilation but which may become hazardous as a result of failure or abnormal operation of the ventilation equipment; or			
	(4) that is adjacent to a Class I, Zone 1 location, from which ignitable concentrations of flammable gases or vapors could be communicated, unless such communication is prevented by adequate positive-pressure ventilation from a source of clean air and effective safeguards against ventilation failure are provided.			

	NFPA 499	1999/92/EC		
Class II, Division 1	<ul> <li>is a location <ol> <li>in which combustible dust is in the air under normal operating conditions in quantities sufficient to produce explosive or ignitable mixtures, or</li> <li>where mechanical failure or abnormal operation of machinery or equipment might cause such explosive or ignitable mixtures to be produced, and might also provide a source of ignition through simultaneous failure of electric equipment, through operation of protection devices, or from other causes, or</li> <li>in which combustible dusts of an electrically conductive nature may be present in hazardous quantities.</li> </ol> </li> </ul>	Zone 20	A place in which an explosive atmosphere in the form of a cloud of combustible dust in air is present continuously, or for long periods or frequently	
		Zone 21	A place in which an explosive atmosphere in the form of a cloud of combustible dust in air is likely to occur in normal operation occasionally.	
Class II, Division 2	<ul> <li>is a location <ul> <li>where combustible dust is not normally in the air in quantities sufficient to produce explosive or ignitable mixtures, and dust accumulations are normally insufficient to interfere with the normal operation of electrical equipment or other apparatus, but combustible dust may be in suspension in the air as a result of infrequent malfunctioning of handling or processing equipment and</li> <li>where combustible dust accumulations on, in, or in the vicinity of the electrical equipment may be sufficient to interfere with the safe dissipation of heat from electrical equipment or may be ignitable by abnormal operation or failure of electrical equipment. [70:500.5(C)(2)]</li> </ul> </li> </ul>	Zone 22	A place in which an explosive atmosphere in the form of a cloud of combustible dust in air is not likely to occur in normal operation but, if it does occur, will persist for a short period only.	

# Annex 2. Guidance on electrical equipment in Equipment Directive 94/9 EC

The equipment is based on the location of its intended use and the categorized according to the level of "ignition protection" provided.

Group	Level of	Ignition source	
	Very high	High	N/A
II	Cat 1	Cat 2	Cat 3

The level of protection required for each of the Group II cat is summarized below :

Level o	of	Category Group II	Performance of protection
protection			
Very High		1	Two independent means of protection or safe even when two faults occur
High		2	Suitable for normal operation and
			frequently occurring disturbances or equipment where faults are normally
			taken into account
Normal		3	Suitable for normal operations

There is a clear link between Group II cat and hazardous areas (zones) as defined in ATEX. This relationship is shown in the table below:

Each category requires sub-division depending on its intended duty.

G = gas, vapor or mist

Gases, Vapors
Zone 0 - category 1 G
Zone 1 – category 1 G or 2 G
Zone 2 – category 1 G, 2 G or 3 G

./.

#### (continued)

It should be noted that where an equipment user's ATEX risk assessment determination of safety based on explosion protection (venting or suppression) reduces risk to an acceptable level, a lower category of equipment can be used.

#### Temperature classification

Hot surfaces represent potential ignition sources and the maximum surface temperature of equipment should be considered. A common approach is to use the T class.

When selecting apparatus according to temperature classification, the maximum surface temperature or the T class of the apparatus should be specified to avoid ignition sources of the potential flammable atmosphere.

T class is normally assigned basis the temperature rise tests assuming ambient temperature not exceeding 40 °C. In other cases revert to the supplier in particular hen equipment is installed inside the insulation.

T class	Maximum surface temperature °C	
Τ1	450	
Т 2	300	
Т 3	200	
Τ4	135	
Т 5	100	
Т 6	85	

Temperature classes

#### Guidance in a draft European Code of Practice:

"Electrostatics - Code of Practice for the avoidance of hazards due to static electricity", which has been published by British Standards as a published document ref:-PD CLC/TR 50404:2003.

#### Gases / Vapors

Based on published material test data (PD IEC 60079-20:2000); **new equipment for hazardous area** should be selected based on the guidance below.

MATERIAL	T CLASS	<b>APPARATUS GROUP</b>
Hydrogen	T1	IIC

(continued)

Additional requirements may be required regarding T Class if the ambient temperature exceeds 40°C.

ZONE	GROUP & CATEGORY
0	1G
1	1G or 2G
2	1G, 2G, or 3G

Any existing electrical equipment within the defined hazardous areas should be surveyed to ensure it meets the standards outlined below.

ZONE 0	TYPE OF PROTECTION
0	Ex i(a)
	Ex s
1	any of the above or
	Ex d
	Ex i(b)
	Ex p
	Ex e
	Ex s
	Ex m
	Ex o
	Ex q
2	any of the above or Ex n

T Class and apparatus group should be as recommended for new equipment.

Existing non-electrical equipment within the defined hazardous areas must be of good design and construction, properly installed and well maintained following a formal preventive maintenance program.