Health and Safety Executive

Inspection of biodiesel sites

SPC/Enforcement/137

Target Audience:
HID Staff in CI 1-4 (Bands 0-4) and RCOs,
Relevant FOD Inspectors and HSAOs,
Local Authorities

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Purpose

1. In recent years there has been a significant increase in the production of biodiesel in the UK. The commonest process is called transesterification, and requires the mixing of hazardous chemicals to form the biodiesel. This document addresses the various hazards associated with that process, and offers guidance towards reducing the risk to personnel.

Note: Bioethanol is made by a different process, and will be covered in a future SPC.

Background

2. The size of operations ranges from large-scale continuous processes (i.e. 250,000 tonnes per year) through medium sized batch units (8 tonnes/batch/day) to very simple bucket chemistry scenarios. Each scale of process has similar hazards from the substances handled, and they can all be dealt with in a similar manner, though the risk consequences will increase with the scale of production.

3. The majority of operations are not expected to be covered by the Control of Major Accident Hazard (COMAH) Regulations 1999 as amended, and inspectors should be aware of the sub-COMAH guidance.

4. However, a limited number of installations will be COMAH Lower Tier (LT) possibly due to the quantities of methanol on site, which is a named substance under Schedule 2 of the regulations, with a 500 tonne LT threshold. Note that solid metal alkoxides (Sodium and Potassium Methoxide) are substances that carry a subsidiary risk - corrosive C: R14 risk phrase “reacts violently with water”. Some solutions of metal methoxides in methanol are also classified as R14 depending on the concentration (Hazard Table). This class of substance is covered by COMAH Category 10 in schedule 2 Part 3 with a 100 tonne LT threshold.

5. Inspectors should be aware that Hazardous Substances Consent may be required for sites storing quantities of certain substances if they are above the threshold levels set out in the Planning (Hazardous Substances) Regulations 1992 (as amended). Guidance on land use planning issues, which can be complex, can be found at http://www.hse.gov.uk/landuseplanning/lup.htm#Legislation

6. The end product is either sold to petrochemical companies for blending and sale at the forecourts, or is stockpiled by the manufacturer for their own use.

7. Equipment for production on a large scale is generally purpose built, and should comply with the various CE-marking and ATEX Directive requirements. In a few cases, inspectors may find equipment that has been recovered from chemical processes and repiped to allow biodiesel manufacture. This kind of equipment may be equipped with flameproof electrical equipment. If that equipment has been properly inspected and maintained at the correct frequency, it should be safe for continued use, but equipment which is subjected to a substantial modification has to be ATEX-certified.

8. Smaller production units can be bought from various parts of the world in mail-order kit form with basic instructions. Such units will still have a requirement to comply with product safety legislation even if they are not used in connection with a work activity. These units may be found unsafe for such production processes as they may present an uncontrolled source of ignition, and appropriate action (see Enforcement section) may be required to suspend their use or make them safe for continued operation. Where inspectors are concerned that a product for use at work is unsafe by design or manufacture they should contact their regional Product Safety Team. Products intended for consumer use should be referred to the local Trading Standards Officer.

9. If a person makes biodiesel for their own use, and this is not connected with a work activity, then health and safety legislation does not apply. However, the individual is still responsible under civil law for ensuring that the effects of any incident, e.g. a fire or explosion, do not harm third parties.

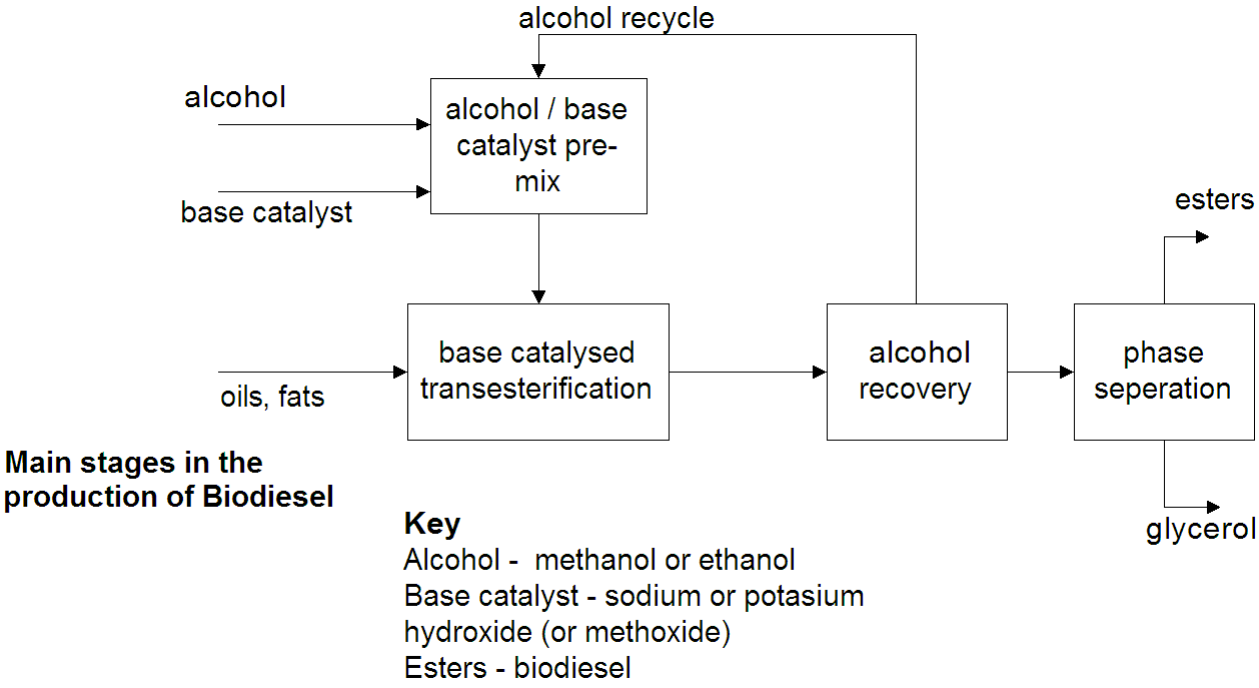
10. At large production installations (i.e. where the product is sold on) the production operation is normally supervised and operated by competent chemists, engineers, and process technicians who are generally knowledgeable of chemical hazards. Operators of such sites should be able to provide evidence on competence in the form of relevant experience and training for both supervisory and production staff.

11. As the scale of production falls, inspectors may find that operator competence diminishes, with the result that many smaller operators may experience large numbers of incidents.

Incident History

12. There have been a number of incidents both in the UK and worldwide involving methanol fires of varying severity. Other incidents include chemical burns, biodiesel and glycerol fires, and environmental releases. Further information can be found in the HSL report, PS/07/03 ‘Exploration of the range and scale of biodiesel production and the identification of key hazards and controls’. This can be found in TRIM Folder 1.9.3.288

Chemistry of process - basic outline of normal process



Main stages in the production of Biodiesel

Key
Alcohol - methanol or ethanol
Base catalyst - sodium or potasium hydroxide (or methoxide)
Esters - biodiesel

13. The most common process starts with potassium or sodium hydroxide being mixed with methanol to produce the methylating agent, potassium or sodium methoxide (sometimes known as methylate instead of methoxide). Alternatively, the metal methoxide can be purchased as a solid, or a ready-made solution in methanol. When the metal hydroxide or solid metal methoxide is dissolved in methanol, an exothermic reaction takes place, which should have been subject to a robust risk assessment. This methoxide solution is then slowly mixed with the vegetable oil/animal fat/waste cooking oil and stirred at temperatures of up to 60°C for a predetermined period of an hour or more. There will probably be some form of reflux distillation to collect and contain the methanol vapour from the reacting mixture. If a faster reaction is required, the process may be carried out under pressure and at higher temperatures. Assistance from a local process safety specialist may be of value for those processes that appear more complex or do not follow the standard pattern outlined here.

14. The mixture is allowed to settle, and the upper layer removed, washed with acidified water to neutralise any residual caustic, and either centrifuged or dried by distillation or an agent such as a molecular sieve. The dried, clarified product is biodiesel. It may still contain some methanol and so have a lower flashpoint than normal diesel.

15. The lower layer is mainly glycerol with residual methanol and caustic. It can be treated to yield food grade glycerol or burnt as waste (although an EA authorisation may be required). Other disposal methods may also be available (animal feedstuff for instance). In some cases it has been disposed of through the domestic sewer. This can introduce the potential for flammable and toxic methanol vapour to accumulate in the sewer with unknown effect. Such discoveries should be promptly drawn to the attention of the Environment Agency (EA) or Scottish Environment Protection Agency (SEPA) . (See below.)

16. Larger facilities may undertake methanol recovery, but where this is not done, the operator should ensure that the waste stream does not pose an environmental or flammable hazard due to the presence of methanol. Any drummed waste from the process should be treated as highly flammable, toxic and corrosive unless proven otherwise.

Environmental Issues

17. The production of biodiesel for commercial purposes is regulated under the Pollution Prevention and Control (PPC) Regulations 2000. However, production by an individual or a small group of individuals for their own use is not usually counted as commercial production. Similarly, production of less than 5000 litres per year (200 tonnes per year in Scotland) is not usually counted as commercial production.

18. If the biodiesel producer is not required to hold a PPC Permit, the storage of waste oil is regulated under the Waste Management Licensing regulations. However, the EA does allow operators to store up to 5000 litres and treat up to 250 litres at any one time without being required to meet the requirements of the Waste Management Licensing Regulations.

19. Also, if the producer does not hold a PPC permit then any discharges to sewer should be made under a Trade Effluent Consent which is acquired from the local sewerage undertaker. In Scotland they could also have a CAR licence from SEPA under the Water Environment (Controlled Activities) (Scotland) Regulations 2005.

20. The EA can be contacted via their National Customer Contact Centre (NCCC) on 08708 506 506 which will notify the relevant area team if inspectors have any concerns relating to environmental issues. SEPA can be contacted via their Communication Centre on 0800 80 70 60.

Risk Assessment

21. In all cases, the sites are expected to comply with the requirements of all the relevant legislation concerning risk assessments, particularly the Dangerous Substances and Explosive Atmospheres Regulations (DSEAR) 2002, the Management of Health and Safety at Work Regulations (MHSW) 1999, The Control of Substances Hazardous to Health Regulations (COSHH) 2002, the Manual Handling Operations Regulations (MHOR) 1992, and the Regulatory Reform (Fire Safety) Order (RR(FS)O) 2005 for England and Wales and the Fire Scotland Act F(S)A 2005 for Scotland.

Hazards - chemical reactive, toxic, explosion/fire, physical (slipping etc)

22. The main hazards are expected to include:-

- Fire (methanol, biodiesel, glycerol)
- Explosion (arising from a confined release of methanol)
- Chemical reaction hazards between methanol and the metal hydroxide
- Toxicity of methanol
- Environmental release
- Corrosive properties of acids and alkalis

23. A table of hazards is included in Appendix 1 to this SPC, but inspectors should note that this list is **not** exhaustive, and as stated above, dutyholders should carry out their own risk assessments.

24. Further information on specific hazards and control measures can be found in relevant HSE publications as noted in the table and the References section at the end of this guidance.

Enforcement Action

25. It is expected that where standards fall well below those that would be expected for the management of similar risks, proportionate enforcement action will be taken. This may include a range of issues such as management failings, failings involving the handling of hazardous substances and other occupational health and safety issues.

26. Sites that do not come under the COMAH Regulations may still have the potential to have incidents comparable to those at COMAH sites. When using the EMM, inspectors should consider use of both Risk Gap Table 2.1 (single and low casualties), and Table 2.2 (multiple casualties) depending on the scale of the operation.

27. Inspectors should also consider enforcement action under other legislation as appropriate eg COSHH for health issues

In particular:

28 Methanol should not be handled in open vessels, and containment should be undertaken as far as is reasonably practicable. Where this has not been carried out to an acceptable standard, enforcement action should be considered

29. Prohibition of production equipment which does not comply with the requirements of ATEX should be considered. Where there is any uncertainty, support should be requested from local process safety specialists.

30. Where there are matters of evident concern, inspectors should consult with the Fire Authority, the Local Authority and the Environment Agency as appropriate.

Further help and advice should be sought from the local Process Safety specialist, and/or other specialist disciplines, if required.

Further information / action by inspectors

31. If other novel processes are found that do not utilise the process described below, please send details to the named contact, who may be able to advise further.

32. Where inspectors find any chemicals which are not listed in this SPC, they should contact the local Process Safety specialist for advice.

33. Further guidance and information is available in the HSL report PS/07/03 ‘Exploration of the range and scale of biodiesel production and the identification of key hazards and controls’. This can be found in TRIM Folder 1.9.3.288

34. These premises may be a higher risk for visiting staff due to the issues surrounding taxation on fuels. Inspectors should refer to the following guidance regarding concerns about personal safety http://intranet/yourhealthsafety/safety/violencetostaff.htm

35. Any comments or queries relating to the information contained within this SPC should be directed to Sally Hawkins HID CI4B VPN 523 3391 or the local Process Safety specialist.

References

For general information on fire and explosion the following link is invaluable:
Fire and explosion: Further information and guidance

Other references include:

Dangerous Substances and Explosive Atmospheres Regulations (DSEAR) 2002

Management of Health and Safety at Work Regulations (MHSW) 1999

Control of Substances Hazardous to Health Regulations (COSHH) 2002

Manual Handling Operations Regulations (MHOR) 1992, and the Regulatory Reform (Fire Safety) Order (RR(FS)O) 2005 for England and Wales and the Fire Scotland Act F(S)A 2005 for Scotland.

Carriage of Dangerous Goods and Use of Transportable Pressure Equipment Regulations 2007

Personal Protective Equipment at Work Regulations (PPEW) 1992

The storage of flammable liquids in containers HSG51 HSE Books 1998 ISBN 0717614719

Safe use and handling of flammable liquids HSG Books 1997 ISBN 0717613313

Appendix 1 Hazard Table

Hazard	Possible control measures and/or mitigation
1. Transport and storage	
Methanol is a highly flammable liquid and burns with a very pale blue flame. Flash point is 11°C, boiling point is 64°C.	Control measures for flammable liquids (HSG 51, HSG140, HSG176). Risk assessment, hazardous area classification and other requirements under DSEAR. Further guidance is available in L134, L135, Ll136, L137, L138 and on the HSE website The Dangerous Substances and Explosive Atmospheres Regulations 2002 Fire separation of process and storage. Control of methanol vapours at source. Control of reactor temperature. Possibly heat sensors for fire detection. Transfer operations (dispensing/decanting) should be performed away from the storage area. Sources of ignition should be controlled.
Confined vessel entry may be necessary.	Guidance on isolation procedures is available in HSG 253. Guidance on work in confined spaces is available in HSG 101.
Methanol storage along with other materials such as oxidisers or combustibles	Guidance on storage of dangerous substances is available in HSG 71 Chemical Warehousing.
Contamination of less flammable materials with methanol can reduce the flash point considerably.	Flash point testing may be necessary. Controls for flammables can be applied to waste streams.
Methanol is toxic. Methanol odour threshold is above exposure limit.	Total containment should be possible. Where area ventilation is used, it should be suitably rated for flammable atmospheres. Guidance on LEV is available in HSG 37, HSG 54 and HSG 140. Note: DSEAR ACOP L136 para 46 onwards, and particularly para 51 wrt ventilation.
Carbon bed absorbers have the potential for a fire in the solvent or absorber. Downstream abatement systems can present uncontrolled ignition hazards.	Consult the local Process Safety specialist. Further advice can be found in Discipline Information Note SI5/062
N2 inerting may be used at larger installations: asphyxiation risk.	Oxygen sensors can be used to detect low oxygen atmosphere. (Note: Many flammable gas analysers will only indicate in air and not in nitrogen.)

Hazard	Possible control measures and/or mitigation
Corrosive materials: Sodium/potassium hydroxide/acids. Chemical burns and material incompatibilities possible. Acids, for example 98% sulphuric acid, are used on some plants. Sulphuric acid has different corrosion properties at different dilutions, and can be corrosive at lower concentrations to certain materials. Sulphuric acid in contact with iron and some steels may yield hydrogen, explosions of trapped quantities of hydrogen within tanks and tankers have been recorded.	Need for emergency showers/eye wash, also alarms, lone working considerations and correct PPE. Tanks and pipework should be designed to an appropriate standard. If there are any concerns, assistance should be sought from a specialist. Bunding. Acid stores should be bunded with acid-resistant materials.
Palm oil/linseed oil can self heat if soaked into insulation. Steam trace heating is often applied and this increases the likelihood of self-heating/combustion.	Regular maintenance and inspection as required under PUWER. Prompt removal and replacement of contaminated insulation.
Caustic reacts with atmospheric CO2 to give carbonates, which could go on to cause blockages.	Containers with a good seal to protect from the environment. Good stock management prevents ageing of stock. Procedures for clearing blockages.
Sulphuric acid has a high heat of mixing with water.	Acid should be added to water, not water to acid.
The ground at biodiesel plants is notoriously slippy, due to a coating of waxy, soapy oils. It has been claimed that normal shoes and PPE/RPE are attacked by biodiesel.	Avoid spills. Good housekeeping, especially floor cleaning. Oil-resistant footwear. Regular inspection/maintenance of PPE/RPE, including BA hoses. Selection of suitable materials for PPE/RPE.
The tyres of vehicles may not be compatible with the biodiesel/waxy material which covers the ground at biodiesel sites.	Good housekeeping. Clean up of spillages and regular inspection/maintenance of vehicles.
Spillages on road surfaces – some oils may solidify.	Good housekeeping. Emergency procedures developed in accordance with the risk assessment.
Smaller scale operators are likely to use a variety of containers which may not be compatible with the materials they hold.	Assessment of material compatibilities carried out before use.
Solid hydroxides such as KOH and NaOH are hygroscopic and can suffer from clumping, which can then lead to blockages and a subsequent manual handling problem.	Procedures for clearing blockages.

Hazard	Possible control measures and/or mitigation
Sodium/Potassium methoxide is caustic and can cause severe damage to mucous membranes and eyes. Pure material reacts violently with water. Strong solutions of the metal methoxide in methanol may also react violently with water.	Avoid spills and leaks. Absorb spills onto inert material. Do not let methanolic solutions dry-out - clean up immediately. Obtain a safety data sheet (where possible) and consult a Process Safety specialist if there is any concern over the strength of solution and potential reactivity and/or CHIP classification.
Mixing of incompatible materials can occur by addition to the wrong tank.	Use of different fittings, adequate labelling, written operating procedures, verification of contents of supply tankers and containers.
Some oils may solidify in storage. This can lead to blockages and possible loss of containment. Steam or electrical trace heating may be in use for such oils, which bring their own hazards. If trace heating is used to unblock a solidified pipe, but the heating is not evenly distributed along the pipe, solid plugs can be formed which block the pipe and lead to bursting.	Procedures for clearing blockages. Emergency procedures developed in accordance with the risk assessment.
The finished biodiesel product degrades on storage, and the flash point will probably fall as it breaks down into a fatty acid and methanol.	Good stock control. Avoidance of incompatible materials.
2. Alcohol/base pre-mix	
A flammable methanol/air mixture is likely in the vessel airspace.	Control of ignition sources. Consideration should be given to inerting, venting to a safe place, explosion relief and the use of flame arrestors. Note: Flame arrestors may require regular inspection and cleaning to prevent them becoming clogged up with oils, etc. Guidance on flame arrestors is available in HSG 158.
Smaller “kits” may not have ATEX approved electrical equipment.	Hazardous area classification under DSEAR determines the need for explosion rated electrical equipment.
Methanol vapours in reaction vessel likely to be above exposure limits, also problem of venting, leaks.	Total containment should be possible. Where area ventilation is used, it should be suitably rated for flammable atmospheres. LEV should be external to the vessel, and care should be taken that it does not induce a flammable atmosphere in the vessel. Guidance on LEV is available in HSG 37, HSG 54 and HSG 140. Note: DSEAR ACOP L136 para 46 onwards, and particularly para 51 wrt ventilation. A scrubber or vapour recovery system may be necessary.
NaOH/KOH are usually supplied in pearl form, but dusts may arise if breakage of the pellets occurs. NaOH/KOH are substantially corrosive. There are manual handling and PPE concerns since most dosing operations are manual.	Containment is the preferred control measure. Use of suitablee RPE/PPE. Eyewash and emergency showers should be available.

Hazard	Possible control measures and/or mitigation
Alcohol/base mixing is known to be an **exothermic** step. Usually methanol is in excess and provides a heat sink, but if materials were added the wrong way round, then evaporation or boiling of methanol could occur, or possibly frothing, and heating would occur. This may lead to overpressure in the vessel.	Add base to methanol. Temperature measurement and adequate control/cooling should be provided.
Possibility of static build-up during addition of solid base.	Earthing and electrical continuity reduce the risk of static discharge. Avoid use of non-conducting materials.
Layering of caustic under methanol can occur with resulting sudden exotherm when mixing is started. Loss of agitation may lead to an accumulation of undissolved base and subsequent hotspots.	Start mixing before caustic added and monitor reactor agitator. Efficient and reliable agitation.
Smaller operations may use open tanks, where flammability and toxicity limits will almost certainly be reached.	Use of entirely contained processing should be possible, although venting will be required unless system is designed for pressure.
Hydrogen generation due to presence of base.	Materials containing zinc/aluminium should be avoided.
Seal/gasket materials need to be correct for use with methanol/base mixtures.	Adequate selection of materials of construction
The dosing of corrosive solids into the mixing vessel often involves manual handling.	Use of suitable engineering solutions.
Use of solid sodium methoxide as a catalyst can lead to a flammable dust.	Generate methoxide in situ by reaction of base and methanol. Otherwise will need dust explosion prevention & control measures as required by DSEAR.
3. Acid Pre-Treatment	
Hydrochloric acid can constitute a toxic hazard due to its vapours.	Appropriate PPE, use of RPE for spills.
Acids are corrosive and should be handled accordingly.	Guidance on the storage and handling of HCl/HNO3 acids is available in HSG 235. Guidance on sulphuric acid is available from the National Sulphuric Acid Association.
If nitric acid is used, this might lead to unstable compounds being produced with the organics present. Nitric acid is a strong oxidising agent and presents a serious fire hazard in contact with combustible materials such as straw and paper.	Use of an alternative acid is preferable.
HCl causes stress corrosion cracking of certain grades of stainless steels.	Standard stainless steels should generally not be used with chloride ion / halides.
Use of novel acids.	If any acids are used, which are not mentioned above, then consult the local Process Safety specialist.
4. Esterification Reaction	

Hazard	Possible control measures and/or mitigation
Methanol is generally used in excess and a flammable mixture is present above the reacting mixture.	Control of ignition sources. Consideration should be given to inerting, venting to a safe place, explosion relief and the use of flame arrestors in process vents. Note: Flame arrestors should not be placed in pressure relief lines. Flame arrestors may require regular inspection and cleaning to prevent them becoming clogged up with oils, etc. Guidance on flame arrestors is available in HSG 158. Note: DSEAR ACOP L136 para 46 onwards, and particularly para 51 wrt ventilation. It may be unacceptable to vent to atmosphere and a scrubber system or vapour recovery system may be necessary.
Location of equipment in small scale operations – sheds, garages, farm buildings etc.	Adequate separation and ventilation is necessary. Storage and processing should be kept separate. No more than 50 litres of highly flammable liquid should be kept in the workroom. Combustible materials should not be kept near flammable materials. Buildings and workrooms should be substantial, and of generally non-combustible material. Further guidance is available in HSG140 and DSEAR ACOPs.
Generally carried out in some form of batch reactor, but larger scale producers may use 'process intensification' continuous processes.	Process intensification techniques are generally considered safer as they are a means of reducing the quantities of substances present. Alternatively, a semi-batch process can be used where addition of the final reactant is controlled. However, novel reactors and processes have their own specific hazards that would need assessment on a case-by-case basis. If in doubt, contact the local Process Safety specialist.
Correct material required for reaction vessel and pipework.	Avoid aluminium or metals containing zinc due to the possibility of hydrogen generation. Where there are concerns, specialist assistance should be sought.
Loss of agitation may lead to incorrect temperature measurement (i.e. not where reaction is taking place).	Adequate agitation should be provided. Note the level of temperature sensors during reactor filling, and level controls.
Too much water/too much free fatty acid leads to formation of soap and associated emulsion.	Procedures in place to deal with failed batches.
Soaps/solids formed may clog bursting disc.	Adequate inspection and maintenance procedures. Pressure measurement between bursting disc and relief valve where used in conjunction to indicate failure of bursting disc.

Hazard	Possible control measures and/or mitigation
'Failed' batches may contain higher than expected amounts of free methanol and/or methylating agent.	Lower than expected flash point. Failed batches should be assessed before disposal for flammability properties. Bulking up poorly characterised 'waste' batches can initiate unplanned reactions.
5. Alcohol Recovery	
Purification by distilllation - recovery of methanol	Ideally this should be carried out in the open air or in well ventilated buildings, and in sealed vessels. The process should have been fully assessed through a HAZOP or similar, and should have been subjected to a DSEAR assessment. Vents from the process should terminate in unoccupied areas of safety, and should be fitted with flame arrestors.
6. Biodiesel/Glycerol Phase Separation	
If methanol carried over from the reaction is not fully removed, it will lead to the biodiesel product having a lower than expected flashpoint. Unexpected ignition.	Routine flashpoint testing of batches.
Use of centrifuges could be a source of ignition.	Hazardous area classification under DSEAR determines the need for explosion rated electrical equipment.
High noise levels during the use of centrifuges.	Noise assessment.
7. Laboratory Analysis	
In smaller workplaces the laboratory equipment may be situated in the main work area.	Ensure all laboratory equipment which is in an area subject to Hazardous Area Classification is suitable for use in that area.