

HEALTH AND SAFETY IN BIODIESEL MANUFACTURE

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A simple process to convert vegetable and animal oils into an alternative and "green" fuel for diesel engines has resulted in a rapid increase in the number of producers of biodiesel in the last 3–4 years, particularly amongst small companies. However, the manufacture of biodiesel can be hazardous if suitable precautions are not taken, as it involves the storage, handling and use of several hazardous substances. Unfortunately, a significant number of new biodiesel producers have little or no experience of chemical processing. In addition, the benefits have prompted some equipment manufacturers to produce kits, for converting waste oils to biodiesel, that have become hazardous during use. In some cases the instructions have been found to be inadequate, so that the hazards have not been fully understood. A number of serious accidents and injuries have already occurred and there is concern that, as the number of producers continues to grow, this trend will increase.

In order to avoid this happening, HSE is producing free basic guidance on the measures necessary to achieve safe production of biodiesel through their website, and detailed advice for enforcement staff to assess such processes. This paper reviews the basic process, identifying the main physical and chemical hazards that need to be assessed to produce a safe process operation. Some of the incidents are also discussed. In addition, the paper examines some issues that have been addressed by inspectors.

INTRODUCTION

A simple process to convert vegetable and animal oils into an alternative and "green" fuel for diesel engines has led to a rapid increase in the number of producers of biodiesel in the last 3–4 years, particularly amongst small companies. However, the manufacture of biodiesel can be hazardous if suitable precautions are not taken, as it involves the storage, handling and use of hazardous substances. Unfortunately, a significant number of new biodiesel producers have little or no experience of chemical processing. In addition, the benefits have prompted some equipment manufacturers to produce kits, for converting waste oils to biodiesel, that have become hazardous during use. A number of serious accidents and injuries have already occurred and there is concern that, as the number of producers continues to grow, this trend may increase.

This paper reviews the basic process, identifying the main physical and chemical hazards that need to be assessed to ensure safe process operation. In addition, some typical issues that have been addressed by inspectors during the course of their inspections are outlined. Some of the incidents that have occurred are discussed, along with planned guidance in order to assist companies to manufacture the materials safely.

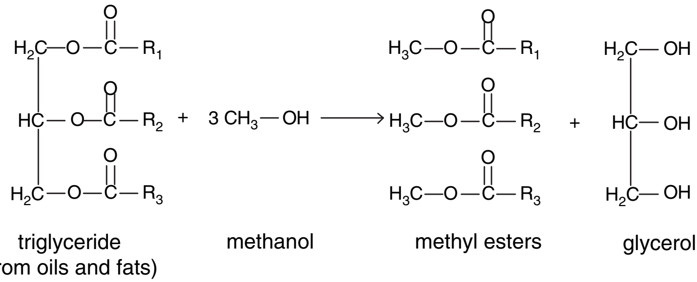

Figure 1. Transesterification reaction for the manufacture of biodiesel

OUTLINE OF MAIN PROCESSES INVOLVED

Feedstock oils are relatively unrefined, and although they can be used directly as fuel in diesel engines, they may eventually choke the engine. However, if the oil is broken down into smaller molecular units it can be used as a direct replacement for diesel.

The reaction commonly used to do this is given in Figure 1. An alkali metal hydroxide or methoxide catalyst is mixed with an excess of dry methanol, and added to the oil with agitation. Reaction times vary with temperature and efficiency of agitation, but are typically up to 8 hours at room temperature dropping to 1–2 hours at 55°C.

The methanol reacts with the oil to form a fatty acid methyl ester (FAME) and Glycerol, which is formed as a by-product. On standing, the two layers separate although, if the alkali ratio is incorrect, soaps may form which can lead to foaming and subsequent separation problems.

The densities of glycerol and biodiesel are approximately 1.3 and 0.9 respectively. The two layers are immiscible so that separation is fairly quick and clean. In larger continuous or batch systems, centrifuges are used to separate the two layers. Some producers choose to wash and dry their biodiesel product to bring it to the correct specification[1], whereas others use particulate filters and molecular sieves or similar. Material that does not meet this specification may damage engine components.

The waste products from the process include glycerol, water washings and excess catalyst, all contaminated with methanol. Specialist companies often remove the glycerol on contract for free as it can be used for a variety of purposes including cosmetics and food additives when cleaned. Direct disposal to the drain can pollute the public sewer.

INCIDENTS INVOLVING BIODIESEL

Several incidents are known to have occurred at biodiesel plants. Most were fires involving methanol or other combustible materials associated with biodiesel manufacture. A significant number were due to the corrosive properties of some of the materials involved. These include:

- A biodiesel plant was destroyed by fire when methanol was spilt during a transfer operation outside the plant building and ignited. Most of the inventory of raw material and product was saved, but the plant was entirely destroyed. The ignition source is unknown.
- An operator was burnt when caustic was being charged into the reaction vessel. The materials boiled over as the result of an uncontrolled exothermic reaction.
- Methanol/catalyst solution leaked onto unprotected electrical equipment when it was being charged into a reactor and ignited.
- Whilst oil/methanol/catalyst mix was being heated to the reaction temperature, vapour escaped from a poorly sealed lid on the reactor and was ignited by unprotected electrical equipment.
- Reaction mixture leaked from a large vertical reaction vessel (approximately 20 cubic metres) and ignited. The subsequent fire destroyed the plant and equipment. It is believed that material leaked either from a manhole cover near the base of the vessel or from a flange in the feed-pipe. There were a number of potential ignition sources in the vicinity, including a boiler and a portable inspection lamp.
- A homeowner, who was involved in domestic production of biodiesel, forgot to turn off the heating element when he left for the weekend. The element overheated which led to a huge fire and the shed and equipment being destroyed. The shed had also contained various materials used in the manufacture of biodiesel, along with some of the finished product, and these seeped into the ground during the fire.
- A company was pumping product biodiesel from a road tanker into IBCs which ignited. The subsequent fire killed 2 people. The ignition source is unknown.
- Approximately 7000 litres of biodiesel escaped into a bund from the lid on a filter pot on a transfer line at a biodiesel blending plant. This was found to have been caused by a vibrating pump.
- Electrical wiring faults have been blamed for other process fires.
- One UK company[2] was fined £24,000 and ordered to pay £5,282 in costs under environmental legislation. Used cooking oil escaped from the site and entered a local watercourse. Local residents reported a strong chip-shop like smell. It was found that they had failed to bund storage vessels and were fined for the release of the cooking oil.
- In the US[3], one person was killed whilst welding on top of a storage tank at a biodiesel plant. The storage tank contained biodiesel, and an explosion occurred followed by a fire. This fire spread to other storage tanks containing glycerine and other flammable materials, which exploded. A large part of the plant was destroyed in the fire, and a second person was injured whilst trying to rescue the man who died.
- Maintenance work involving a grinding operation on a vessel containing methanol is believed to have caused a separate explosion.
- An operator was injured by contact with solid potassium hydroxide on a biodiesel production facility whilst trying to clear a blockage in a reactor feed chute with a screwdriver.

> This took about 2 hours. The blockage occurred due to the potassium hydroxide absorbing water from the atmosphere, and possibly methanol vapour being drawn up through the chute. Blockages had occurred in the past and a variety of methods were used to clear them. When the operator tried to remove his chemical suit and PVC gloves with a knitted cuff, skin from his wrist came away with the glove. A skin graft had to be performed on the affected area.

The accidents continue to occur.

HAZARDS

Regardless of the scale of operation the hazards are the same: a combination of flammable, toxic and corrosion hazards depending on the stage of the process. In particular:

Methanol

This is a highly flammable and toxic liquid. It will freely burn in the open air or explode if confined in a vessel or room and ignited. Whilst all precautions should be taken to avoid leaks of flammable vapours into the workroom, leaks and spillages may still occur and it is necessary to take further precautions to reduce the likelihood of their ignition. In areas where such materials are handled, companies are required to identify the areas where flammable atmospheres may exist, for example due to a leak, and determine their likely extent. Such areas are classed as hazardous and should be classified into zones, depending upon the likelihood of their occurrence. In such areas ignition sources such as naked flames should be excluded and only suitably protected electrical equipment should be used. Further information is given in reference 4. It should be noted that the presence of methanol can also render the product and any waste materials flammable, depending upon the way the biodiesel is manufactured.

The catalyst

This is normally potassium hydroxide, sodium hydroxide or sodium methoxide, sometimes in methanol solution, but often as a dry flake or prill. All are corrosive and sodium methoxide is violently water reactive and toxic. Powdered methoxides are a dust explosion hazard, and highly corrosive.

Feedstock oil

If clean and pure it should not be a health problem. However, if the source is unknown or of doubtful quality, then it should be treated as contaminated. Oils are a serious slipping hazard if spillage or contamination outside sealed vessels occurs. Oils can seep into lagging and many can self-combust following a period of chemical degradation. All oils are combustible and will add fuel to any developing fire.

Glycerol

This material is combustible (with a flash-point of 160°C). However, it may be contaminated with methanol and caustic, with their associated hazards, including a potential reduction in flash-point. Unless the initial by-product quality is reliably monitored, then prudence dictates that it should be regarded as contaminated until it has been suitably purified.

Biodiesel

If certified to BSEN 14241:2003[3] it may be regarded as combustible (its flash-point is approximately 150°C). It has rather unusual solvent properties, and will attack some common engineering polymers, including polyvinyls, natural rubber, some gasket and hose materials and metals, including copper, tin and zinc[5]. The effect can increase with heating and ageing of the biodiesel. It is also hygroscopic, and can absorb up to 1500 ppm water from the air. If even slightly contaminated with acid or alkali, biodiesel may be hydrolysed to fatty acids and methanol. This reaction also occurs more slowly in the absence of water, so material stored for more than a couple of weeks may show evidence of a different flash-point than anticipated (which may be significantly lower). Unless this can be reliably prevented, then the product should be used as quickly as possible after production, or reclassified and stored and handled accordingly. Unfortunately this is not always appreciated.

Wash water

This may be contaminated with acid, alkali and methanol. It should be treated as corrosive, toxic and flammable unless tests determine otherwise.

Reaction hazards

The main reaction hazards identified are in the preparation of the base catalyst, which can be by one or more of the following methods:

- The direct addition of sodium or potassium to methanol: this reaction is very exothermic and should be the subject of a rigorous risk assessment, particularly as molten sodium is spontaneously combustible in air and the reaction produces hydrogen as a by-product. Fortunately this route is not generally available to smaller/domestic producers.
- The addition of dried hydroxide or methoxide to methanol which is also very exothermic (heat of dilution)

A much gentler heat of reaction is produced if the catalyst is supplied in methanol solution (although this has to be manufactured safely elsewhere!), and further diluted to the required strength on plant. This is normally the preferred option for smaller companies.

A further reaction hazard occurs when concentrated mineral acid is mixed with water. Addition of water to acids often results in violent boiling and ejection of the acid from vessels. Acids should be added slowly to water with cooling and agitation.

General hazards

These include:

- Corrosion of processing equipment, building fabric, and supporting structures through exposure to caustic and acids leading to premature weakening and catastrophic failure. A by-product of the corrosion process is hydrogen;

- Biodiesel can soften and dissolve a variety of polymers commonly used in safety equipment, such as plastic aprons and rubber boots, causing premature failure.

EXPERIENCE AND TRAINING OF OPERATORS

One of the issues identified as a result of inspections is that practical experience and knowledge of handling hazardous chemicals amongst operators is extremely variable, and tends to drop with reducing scales of production. Larger producers tend to use experienced staff that have previously worked on chemical plant. Their products are invariably sold on to petrochemical companies for blending with various proportions of diesel derived from fossil sources and quality control is important. However some smaller producers may be relatively inexperienced. They include farmers, taxi drivers, and operators of small transport companies who may have little or no training in the hazards. Many of these small producers produce the fuel for their own use. HSE is not responsible for regulating health and safety issues at many of these premises, instead it will normally fall to the Local Authority.

PRODUCTION SCALES AND EQUIPMENT RANGES

Biodiesel output rates from individual producers ranges from DIY operators producing a few tonnes per year, small commercial producers manufacturing 1000 to 10,000 tonnes per year often in skid mounted batch units, and continuous production plants manufacturing hundreds of thousands of tonnes per year. Equipment is variable in cost, quality and construction, and ranges from plastic kitchen buckets and sieves costing a few pounds through small scale commercial mixers and separators made of HDPE costing less than a thousand pounds, then up the scale to the skid-mounted batch units costing many tens of thousands of pounds to the multi-million pound continuous production units. In addition there is a growing trend to use redundant batch chemical production plant at minimal cost and outlay. The output from these units is comparable with the skid mounted batch units.

ISSUES AND HOW THEY HAVE BEEN ADDRESSED SO FAR

As a relatively simple chemical process, biodiesel manufacture has given few problems to the established chemical industry. They have approached it using the same risk assessment procedures applied to other chemical processes, with due account of legislative requirements such as DSEAR, COSHH etc. Problems such as unwanted soap or emulsion formation are systematically dealt with through standard technology. However, small-scale operations sometimes operate less efficiently. They may follow basic instructions that they obtain from various sources, such as the internet, and may fail to fully appreciate the hazards. Consequently they may be unable to develop or provide a safe process. Some smaller scale operations declare their activity to their property insurers, who may give guidance to protect property, however this may not extend to personal safety which is outside their remit.

As a result of our inspections, HSE inspectors have identified a number of issues that have required enforcement action to be taken, ranging from advice to issuing improvement or prohibition notices. These mainly relate to small and medium sized enterprises. Issues that have been addressed at various installations include:

- No risk assessments were carried out on any part of the process;
- No written instructions for the operators, other than the brochure provided with the kit which was not sufficiently detailed;
- Untrained and unqualified operators;
- The operator (self-employed) had no chemical knowledge of the process and minimal understanding of the hazards associated with the chemicals he was using, consequently he had received serious burns from potassium hydroxide;
- The use of unprotected or incorrectly rated electrical equipment, for example the standard of electrical equipment on the reactor and its immediate vicinity was unsuitable for use in a potentially flammable atmosphere;
- Poorly ventilated production areas fitted with domestic electrics (lights, power connections, water heaters etc.);
- The manufacturing operation was run in a room, approximately 5×6 m, at the side of a woodworking factory with inadequate fire separation. The room was cluttered with equipment, oils and chemicals. On one side was a methanol mixing vessel, a 1000 litre reactor, a pump and a separation vessel. On the other side was a (domestic) fridge and a gas-fired boiler.
- Process equipment obstructed the means of access and egress.
- Materials of construction were not fire resistant, and no physical fire barrier was provided between the operation and non-industrial activities in the building;
- A number of sites where methanol was supplied in plastic drums, and stored indoors in non fire resisting and/or unventilated areas for security reasons.
- A laboratory (used for wet titrations) was in the same compartment as production, and heavily contaminated with reactants and products;
- Taking into account the raw waste oil, methanol, biodiesel product and by-products there was a considerable amount of combustible or flammable material in the building, resulting in a high fire loading;
- The method of addition of caustic soda to the reaction vessel was not effective in preventing spillage and there was a clear risk of corrosion to equipment on the top of the reactor, including a relief valve, isolation valve and a quick release coupling;
- Product and feedstock have leaked making the workplace slippery;
- Unwashed and untested biodiesel product was left for weeks in thin carbon steel unbunded tanks, which then corroded and leaked.
- A reaction vessel provided with a loosely fitting lid so that flammable vapours were able to escape into the workroom;
- No fire fighting equipment was provided;
- The local fire brigade was unaware of the production activity;
- Inappropriate personal protective equipment (PPE) was provided

- Contaminated PPE dissolving or melting due to biodiesel contamination;
- Wash water and glycerol waste were treated as non-hazardous, even though they were contaminated with methanol and had a low flash point;

Advice has already been issued to inspectors on the main hazards, their means of prevention control and the action that they should take in inspecting such premises which can be accessed on the internet. In addition, a number of equipment suppliers have been approached due to the supply of equipment for biodiesel manufacture, which was not suitable for use in a potentially flammable atmosphere.

NEED FOR GUIDANCE

There is much health and safety guidance readily available that addresses the hazards associated with biodiesel manufacture, for example references 4 and 6 to 10. However, small producers may not be aware of such guidance. In order to address this, HSE is producing an information leaflet that will be available on the Internet. The purpose of the leaflet will be to give information on the hazards of the main processes involved and the measures necessary for their safe design & operation. It will concentrate on the conventional manufacturing process and associated operations, rather than more novel production processes (such as hydrocracking) and will be particularly aimed at small and medium-sized biodiesel manufacturing operations, including chemical companies, farms and transport companies. Where more detailed guidance is available, such as standards for suitable electrical equipment, then these are referred to in the guidance.

By consolidating the relevant guidance into an industry specific document and making it freely available for download, we hope to influence biodiesel producers at all scales to work safely.

CONCLUSIONS

1. There has been a rapid increase in the number of biodiesel producers in the last few years, in particular the number of smaller companies who are manufacturing it.
2. The manufacture of bio-diesel can be hazardous if suitable precautions are not taken, as it involves the storage, handling and use of hazardous substances, in particular toxic, flammable and corrosive substances.
3. Whilst many of the larger producers tend to use experienced staff that have previously worked on chemical plant, unfortunately a significant number of new smaller companies producing biodiesel have little or no experience of chemical processing, and may be unaware of all the hazards that the process introduces. They include farmers, taxi drivers, and operators of small transport companies. Many of these small producers produce the fuel for their own use and HSE is not responsible for regulating health and safety issues at many of these premises.

4. Consequently, HSE has already identified a number of issues at such facilities, which have resulted in enforcement action. Advice to inspectors on the action they need to take has also been issued.
5. In addition, several incidents are known to have occurred at biodiesel plants both in Britain and overseas. Most were fires involving methanol or other combustible materials associated with biodiesel manufacture. A significant number were due to the corrosive properties of some of the materials involved, or from poorly controlled mixing of reactive chemicals.
6. In order to address these issues, HSE is producing guidance that will address the hazards of the various substances and process steps, and advise companies on how they should be controlled. The guidance will be aimed particularly at small and medium sized companies and will be freely available on the internet.

REFERENCES

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