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Safety and Chemical Exposure Evaluation at a Small Biodiesel Production Facility

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Case Study
Safety and Chemical Exposure Evaluation at a Small Biodiesel Production Facility

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INTRODUCTION

Biodiesel is a renewable fuel produced when agricultural feedstocks such as vegetable oils, rendered animal fats, and used cooking oils are reacted with alcohol in the presence of a catalyst to form fatty acid esters, glycerin, and soap in a process known as transesterification. Because of economics and process considerations, methanol is the most commonly used alcohol in the transesterification process producing fatty acid methyl esters.[(1)] Potential hazards of biodiesel production include (1) use of large quantities of methanol, (2) use of caustic chemicals as catalysts, (3) physical hazards, and (4) potential exposure to aldehydes.

The biodiesel industry recognizes its most significant hazard as methanol. The properties of methanol, both physical and chemical, make it a particularly hazardous chemical. Methanol is highly flammable, and exposures can cause a wide range of deleterious health effects. It is easily absorbed by all routes of exposure. Methanol is metabolized to formaldehyde that is then converted to formic acid, which can accumulate in the human body. Methanol toxicity is mediated, in large part, by the formic acid metabolite. Studies have shown that short-term inhalation exposure to 200 ppm methanol results in blood methanol concentrations of less than 10 mg/L with no observed increase in blood formic acid concentration.[(2)] Acute methanol toxicity includes visual disturbances leading to blindness, mild dermal irritation, dizziness, giddiness, permanent motor dysfunction. and possibly death.[(3–5)] Chronic exposure to methanol may result in headache, dizziness, giddiness, insomnia, nausea, gastric disturbances, conjunctivitis, visual disturbances, and blindness.[(3)] The Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) and the National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL) for methanol is 200 ppm time-weighted average (TWA). The short-term exposure limit (STEL) for methanol is 250 ppm; the concentration that is immediately dangerous to life and health (IDLH) is 6000 ppm.[(6)]

The transesterification process would not proceed or would proceed very slowly without the addition of heat and a catalyst. The catalyst can be an acid or a base; however, in modern biodiesel production the catalyst is almost exclusively alkaline (sodium hydroxide, potassium hydroxide, sodium methylate, or potassium methylate). Different factors, including safety and economics, determine what the facility uses.[(1)] The agents are chemically similar and have similar hazardous properties. The primary safety concern is their caustic nature, as all the chemicals will cause severe chemical burns if they come into contact with human tissues. Sodium hydroxide and potassium hydroxide are sometimes added to the process manually, leaving the operator vulnerable to exposure. Sodium or potassium methylates are often premixed with methanol (alcoholates) and frequently used by large-scale biodiesel producers and offer benefits over sodium and potassium hydroxide. There are no established exposure limits for alcoholates; guidelines for safe handling are a hybrid between those of methanol and sodium or potassium hydroxide.[7,8]

Acrolein can be produced from glycerin through several specific chemical processes.[5,9] Though the temperatures required are greater than those used in the biodiesel production process,[9] and required catalysts are not used, some concern was expressed by fire professionals because of the presence of heated glycerin. Acrolein exposure can occur by inhalation, ingestion, skin and/or eye contact. Symptoms and sequelae of exposure include irritation to the eyes, skin and mucous membrane; decreased pulmonary function; delayed pulmonary edema, and chronic respiratory disease. The OSHA PEL and NIOSH REL for acrolein is 0.1 ppm TWA. NIOSH gives a STEL value of 0.3 ppm and an IDLH value of 2.0 ppm.[6]

With any industrial-scale production there are innate physical hazards. During this project these hazards were evaluated during preliminary plant tours (Visit 1). Specific items evaluated during Visit 1 include fire suppression and detection, chemical storage, noise, equipment, and slick floors. According to OSHA, falls account for the majority of workplace injuries.[10] This is not an unforeseen issue with biodiesel production; however, it has not been determined if slick floors lead to an uncommonly high occurrence of falls in the industry.

METHODS AND MATERIALS

NIOSH conducted an environmental and safety evaluation of a small biodiesel production facility in the southeast region of the United States. The evaluation was part of a larger ongoing research project to evaluate potential hazards in the biodiesel industry. On an initial safety assessment performed during Visit 1, NIOSH industrial hygienists were escorted by an employee representative familiar with the facility (Employee 1). In addition to the safety inspection, Visit 1 was used to gather information to develop a site-specific air sampling plan.

During Visit 2, area air monitoring for methanol was performed in the main production area. This area had the greatest potential for methanol exposure based on the process design and a report by Employee 1 that this area had a strong methanol odor during production. Methanol assessment was performed during Visit 2 using a real-time monitor, a MIRAN SapphIRe Portable Ambient Analyzer (Thermo-Fisher, Franklin, Mass.). In addition, Gastec direct-reading methanol detector tubes no. 111L (scale 40–1000 ppm, $n = 1$) (Gastec Corp., Ayase-shi, Kanagawa, Japan) were used. screening for volatile organic compounds (VOCs) in air was performed in both the production and the refinement area using thermal desorption tubes containing graphitized carbon and carbon molecular sieve sorbents at a flow rate of 0.01 L/min and analyzed using NIOSH analytical method 2549. Gastec direct-reading detector tube no. 93 (scale 10–800 ppm, $n = 2$, scale 3.3–10 ppm, $n = 4$) were used to detect acrolein at potential sources, such as heated glycerin tanks.

OBSERVATIONS

General Observations

The biodiesel facility visited by NIOSH investigators is a small producer of biodiesel that employed approximately 20 people and included research and development, laboratory, and production. In 2008 the facility produced one million gallons of unblended biodiesel fuel (B100). The facility occupied a major portion of a small industrial park and was the only fuel-related industry in the park. The building originally housed a metal fabrication business and had been retooled for biodiesel production and refinement. The facility housed a research and development area, production and refinement area, a fuel quality assurance laboratory, fuel washing area, and fuel storage area.

Fall Prevention Assessment

The floors, elevated catwalks, and fixed ladders at the facility were extremely slick, especially in the fuel wash and storage areas. It was difficult at times to maintain traction even while wearing anti-slip boots. The facility was not in compliance with OSHA walking-working surfaces standards.[11]

Methanol Air Monitoring Assessment

The facility had an external bulk methanol storage tank; however, at the time of Visit 1 pre-mixed sodium methylate was being used as the catalyst. Sodium methylate was delivered to the facility in 275-gallon bulk transport totes pre-mixed with methanol. The alcoholate was pumped from the tote to the process tank by electric pump and hose. Facilities that use more than 10,000 pounds of methanol ($\sim$1500 gallons) are required to comply with the OSHA process safety management (PSM) standard of highly hazardous chemicals.[12] This facility and most industrial-scale biodiesel producers fall into that category. This particular facility did not have a fully implemented PSM plan at the time of either visit. Area air samples were collected on Visit 2 during the transesterification of a batch of biodiesel in the main production room (Figure 1). The room had two exits, a large door leading to the interior of the building, and a small door to the exterior of the building. The door to the exterior remained open throughout the air sampling period; this is the normal operating condition.

The background methanol level in the room, during non-production times, remained fairly constant throughout at less than 10 ppm according to the MIRAN SappIRe. Concentrations were monitored throughout the room and on all levels (midlevel, lower catwalk, upper catwalk, and the pit area). When biodiesel production was started, methanol concentrations immediately increased. For the first hour of production, concentrations increased from background to 300 ppm. At this point the MIRAN SapphIRe was placed on a desk in the room while detector tube samples were taken. During this period (28 min) the methanol concentrations recorded by the MIRAN peaked at 785 ppm (Figure 2), and several Gastec

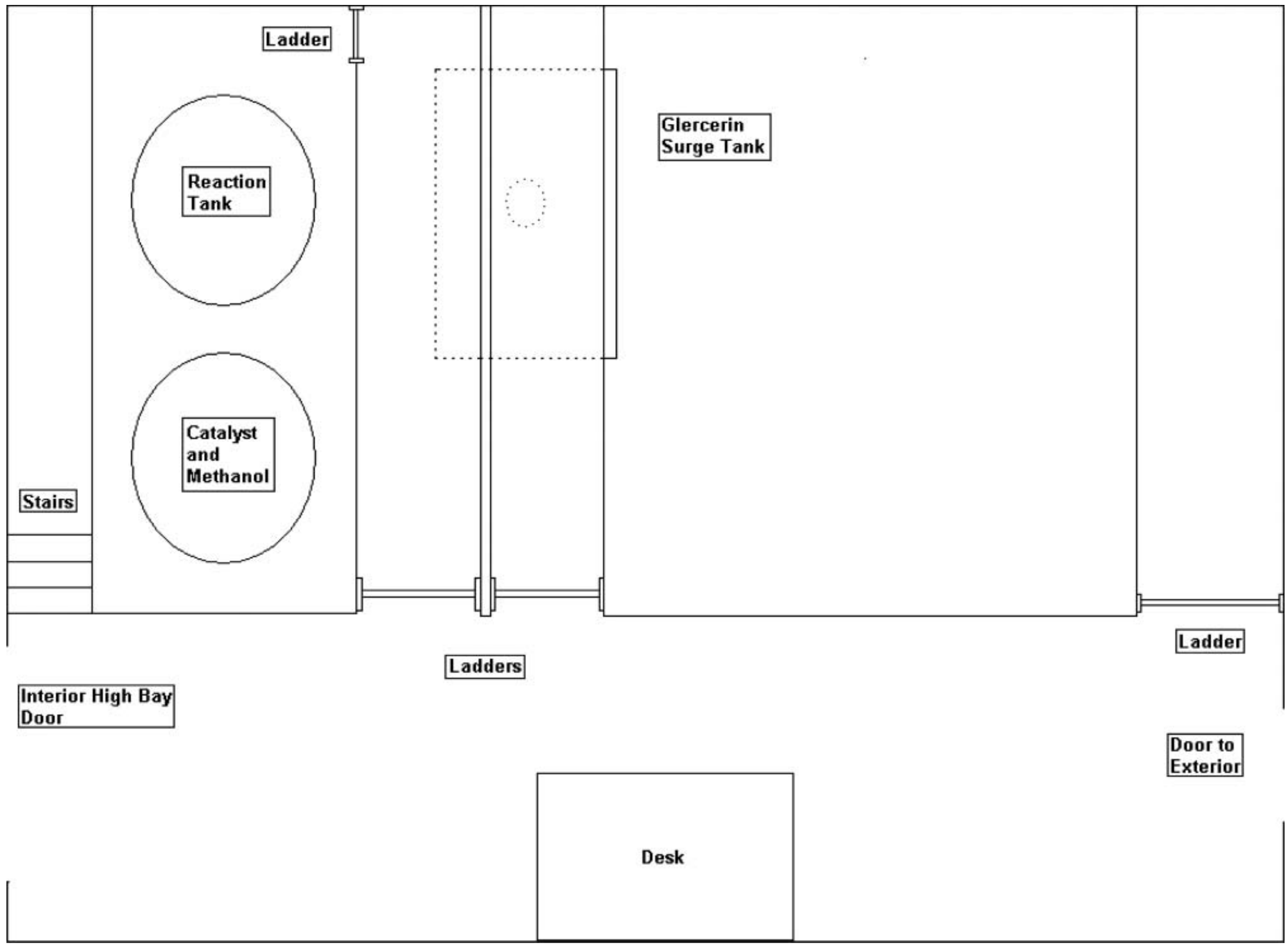

FIGURE 1. Main production room where methanol area air sampling was performed. Map is not to scale.

direct-reading methanol detector tube samples near the surge tank were greater than 1000 ppm (off scale for the detector tubes). After the transesterification process was completed, methanol concentrations quickly returned to background levels. The entire transesterification process took approximately 2 hr. During this period workers were present intermittently but for periods that exceeded 15 min.

Acrolein Evaluation and Volatile Organic Compounds Screen

The acrolein direct-reading detector tubes did not indicate the presence of any sources of acrolein. The VOC screen was insignificant for an exposure characterization.

Chemical Storage and Handling

Sodium methylate was supplied to the facility as a solution in methanol and dispensed from 275-gallon bulk totes. The operator empties the tote using an electric pump and hose. Exposure to methylate solution could occur in the case of spillage; however, the operator reported using a rubber apron, rubber gloves, and plastic full-face shield. Once the catalyst has been mixed with the methanol or, in this case, the premixed solution is pumped into the tank, the catalyst is pumped into the reaction tank. The specific volumes and concentrations vary with the feedstock moisture and free fatty acid content.

Chemical storage at the facility was, for the most part, compliant with existing regulations. The facility used flammable material storage cabinets for small-volume containers and segregated chemicals by hazard class and compatibility, with two exceptions: a drum rack containing four large drums labeled isopropyl alcohol, acetone, and sodium hydroxide, and one drum reported to be muriatic acid. The drums were used for dispensing, and there was evidence of spillage. These drums were in the research and development section of the facility. Acids, bases, and flammables should not be stored together. Acetone is potentially explosive in the presence of acids. Neither the rack nor the barrels appeared to be electrically grounded. The other concern was the washing and reuse of bulk chemical totes. Several totes were being used to hold what appeared to be waste products. The totes retained their original hazard placards, which is in violation of the OSHA hazard communication standard[13] and the OSHA occupational exposure to hazardous chemicals in laboratories standard.[14]

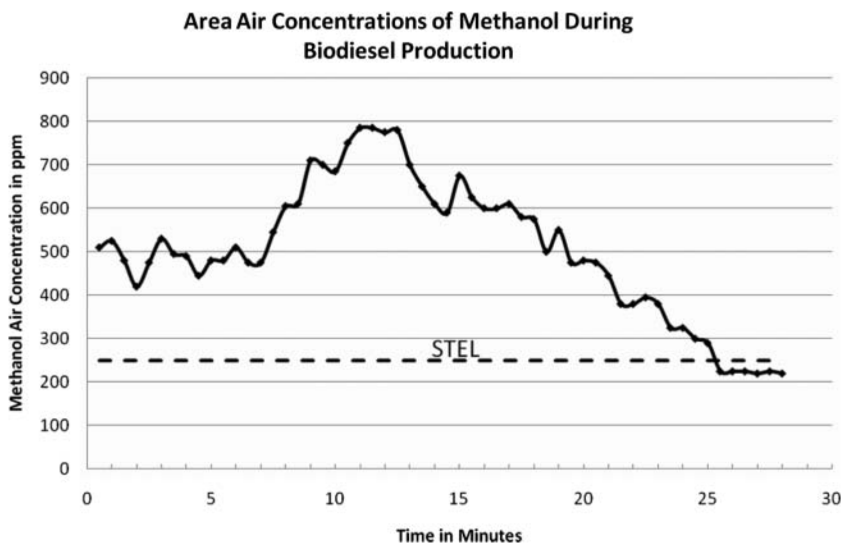

FIGURE 2. Methanol concentrations during the transesterification of feedstock using the MIRAN SapphIRe Portable Ambient Analyzer. The instrument was located at the desk in the main production room.

Personal Protective Equipment

Limited personal protective equipment (PPE) was available. Employee 1 reported that the employer did not provide formal PPE training. An employee in the research and development department was observed operating an angle grinder while wearing a half-face respirator with organic vapor cartridges installed rather than the appropriate particulate cartridges. A full-face shield, rubber apron, and gloves were available for the transfer of sodium methylate to the alcohol and catalyst mixing tank. Steel toe shoes, hard hats, or safety eyewear were not required by the employer. Most employees were observed wearing wraparound protective eyewear.

RECOMMENDATIONS

After Visit 1, it was recommended that the facility comply with the OSHA PSM standard. Such implementation was expected to provide added benefits, such as improving employee knowledge of operation, improving and maintaining accurate process safety information, and possibly increasing productivity. Slick floors, elevated catwalks, and ladders were identified as potential hazards, and it was recommended that an employee-run health and safety program be instituted with regular inspections. It was also recommended that regular, thorough cleaning be part of the facility's preventive maintenance plan. In addition, employees should be encouraged to attend to small spills immediately. It was recommended that a standard personal protective equipment plan, with training, be developed for the facility. This plan should include when, where, and what type of PPE is required. This would most likely be done in accordance with implementing PSM standards. Area monitoring for methanol was suggested for a later visit. The final recommendation was that the OSHA general industry standards be regularly reviewed to ensure compliance.

During Visit 2, methanol area monitoring was performed and demonstrated that the methanol concentration exceeded the STEL during biodiesel production. Area sampling was conducted during this visit to allow for identification of point source or process-related methanol vapor release. Operators were present for greater than 15 min during times of peak methanol air concentrations in the area of the monitor. It was recommended that the system be sealed or local ventilation be installed to control the methanol vapors.

FOLLOW-UP AND DISCUSSION

Following Visit 1, the large drums had been segregated according to hazard class and compatibility, and the bulk storage and transportation totes were placarded correctly.

Following Visit 2, the PSM standard had been implemented at the facility, and as a result, regular employee training was implemented. The surge tank had been eliminated from the process and replaced with a vented closed tank. The facility representative reported this was an appropriate tank for the process. The facility cleans the floors regularly with a high-pressure steam cleaner and addresses spills as soon as possible.

The biodiesel industry is composed of backyard producers who produce for themselves, local cooperatives that produce only for their members, start-up facilities that produce on a small scale, and conglomerates producing on a large scale. This particular facility had grown to produce sufficient quantities of product and to employ sufficient numbers of workers to move them into the regulatory framework. A similar pattern has occurred at other facilities visited as part of this research project. As a result, growing pains are more than a cliché for this industry. As an example, on the day prior to Visit 1, this particular biodiesel producer experienced a serious incident that injured two contracted workers and required production to be shut down. While incidents do happen, such incidents would be less likely if health and safety standards were implemented and protections were in place.

It is imperative that as this industry develops, health and safety professionals are involved in helping companies evaluate their facilities and apply the appropriate components of the regulatory standards. This particular company and its employees provided an excellent example and should be commended for their transparency and desire to improve health and safety, not to mention the real steps they have taken toward that goal.

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