Fire and explosion risk in biodiesel production plants: a case study

Luca Marmo, Applied Science and Technology Department, Politecnico di Torino, Turin (Italy), luca.marmo@polito.it
Enrico Danzi, Applied Science and Technology Department, Politecnico di Torino, Turin (Italy)
Leonardo Tognotti, Dipartimento di Ingegneria Civile e Industriale, Università di Pisa, Pisa (Italy)
Valerio Cozzani, LISES, Department of Civil, Chemical, Environmental and Materials, Università di Bologna (Italy)
Ernesto Salzano, LISES, Department of Civil, Chemical, Environmental and Materials, Università di Bologna (Italy)
Valeria Casson Moreno, LISES, Department of Civil, Chemical, Environmental and Materials, Università di Bologna (Italy)
Daniela Riccio, Alchim sas, Chieri (TO), Italy

Biodiesel production facilities are widespread in the world as the demand for “green” fuels increase continuously. So, the number of accidents increases with the number and the capacity of plants.

In this paper, the fire and explosion risks in biodiesel production facilities are discussed. Beside some evident risk sources such as flammable storage tanks, we have shown that process deviations may give a relevant contribution to the overall risk and that two critical aspects may be: the excess of the amount of residual methanol in the streams fed to the phase separation step (e.g. biodiesel/unreacted separation after reaction, or glycerin/fatty acids separation), which can affect separation efficiency, and the condensation of flammable vapour streams.

Keywords: Accident investigation, Biodiesel production, Fire, Explosion

Introduction

The hazards related to biodiesel production are increasing with the increasing plant capacity, due to the high complexity of the process units, to the increasing scale of the equipment and to the larger amount of needed chemicals (Salzano 2010a, Olivares 2014). In fact, while biodiesel is considered as a “safe fuel”, its production involves highly flammable chemicals as methanol and sodium methylate, which raise the vulnerability of the biodiesel process to fires and explosions (Acheson et al., 2011).

Several accidents involving biodiesel plant have occurred in the US in recent years (Riviere and Marlair, 2010). About 14% among them involved explosions and fire in the tank storage area of plant and 22% occurred during tank storage operations (overfilling, leaks and localized fires). Furthermore, McElroy (2006) underlines the risks related to relatively small plants (up to 35000 tons/y) due to their “scale up” nature and the attempt to get into the business at minimal costs by entrepreneurs, thus neglecting safety issues. Besides, Olivares et al. (2014) report human intervention errors and lack of training in safety procedures as the main causes of accidents.

Recently the first accident in an Italian biodiesel plant occurred. A violent explosion of a fatty acid tank caused three fatalities. The study of this case can provide useful indications to widen the panorama of the hazard of biodiesel production facility. That case is used in this paper with the aim to discuss the fire and explosion risks of biodiesel plants. It emerges that, beside some evident sources such as the flammability risks in the storage tank area, also process deviation may be a relevant risk source. Furthermore, two safety critical issues have been recognized: a possible excess in the amount of residual methanol in the streams fed to the phase separation process (e.g. biodiesel/unreacted separation after reaction, or glycerine/fatty acids separation), which can affect the separation efficiency, and the condensation of streams containing flammable vapours.

Eventually, the conclusions drawn from the investigation of past accidents could bring some additional information and lessons to the safety issues related to biodiesel production, with regard to errors in design of equipment and of the control philosophy.

Relevant accidents and incidents in biodiesel industry happened from 2004 to 2013

In order to support the findings of the present paper, a selection of relevant accidents and incidents occurred in 10 years in biodiesel industry has been done and presented. The selection has been done on the basis of a literature review (Olivares et al., 2014; Casson Moreno and Cozzani, 2015; Salzano et al., 2010a, 2010b) and a deep web search, including specialized database and web sites such as ARIA (2016), JST (2016), MARS database and the Loss Prevention Bulletin (2016).
Figure 1 shows the trend of worldwide relevant accidents and incidents occurred from 2004 to 2013 in biodiesel industry. According to the definition proposed by Rathnayaka et al. (2011), we have defined as “accident” an event that may cause one or more fatalities or permanent major disabilities, relevant financial loss, and/or that is mentioned on national media, whereas “incident” is defined as an event that could cause considerable harm or loss that may also cause a major health effect or injury (temporary disability or permanent minor disability), localized damage to assets and environment, considerable loss of production and considerable impact to company reputation.

A total of 61 events have been included in our analysis, in the considered period:

- 67% of them took place in North America, and in particular 63% in the US;
- 13% in Europe (more than half in France);
- 9 % in South America;
- 6 %in Asia, and
- 4 % in Australia.

The trend of accidents recorded in Figure 1 follows the global biodiesel production trend (displayed in Figure 2), showing a progressive increase until 2010 biodiesel production recession. In 2011, biodiesel production started to increase again and so the number of accidents. The number of records in the last years of the considered period (i.e. 2012 and 2013) might be affected by uncertainties, such as short-term under-reporting.

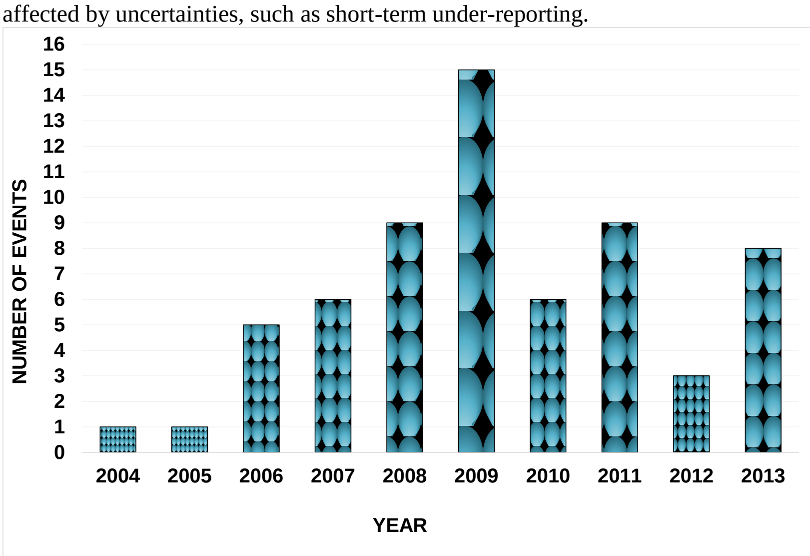

Figure 1: Trend of relevant accidents and incidents related to biodiesel industry happened from 2004 to 2013.

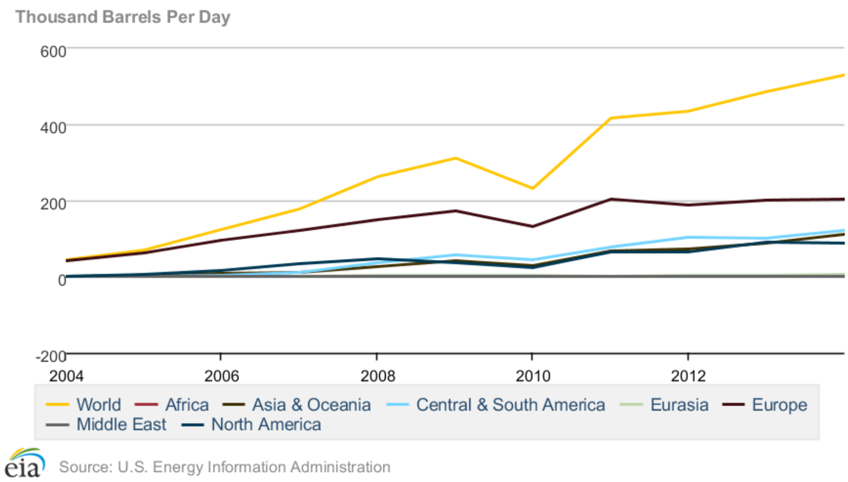

Figure 2: Biodiesel production trend from 2004 to 3024. Source: U.S. Energy Information Administration, EIA, 2016.

The events caused a total number of 68 injuries and 21 fatalities. In Figure 3, a statistical analysis on the type of scenario involved in the events analysed and reported in Figure 1 is proposed. The most common scenario is fire, followed by explosion. It has to be noted that, on top of them, in 15 % of the cases summarized in Figure 1, cascading events involving fires and explosions have been reported.

In Figure 4, the type of causes related the accidents and incidents in biodiesel industry selected for the analysis and reported in Figure 1 is shown. The outcome of the figure is that most of the causes of unwanted events are related to the failure of components (e.g. heating elements, mechanical seals, etc.), and by both operational and maintenance errors. For what concerns the maintenance errors, it is worth mentioning that almost all of them are related to welding and cutting operations during equipment maintenance.

Another important aspect to be pointed out is that the analysed accidents and incident occurred in 61 % of the cases in the production area of the plant, whereas 33% in the storage area (for 6% of the cases, the location was not defined).

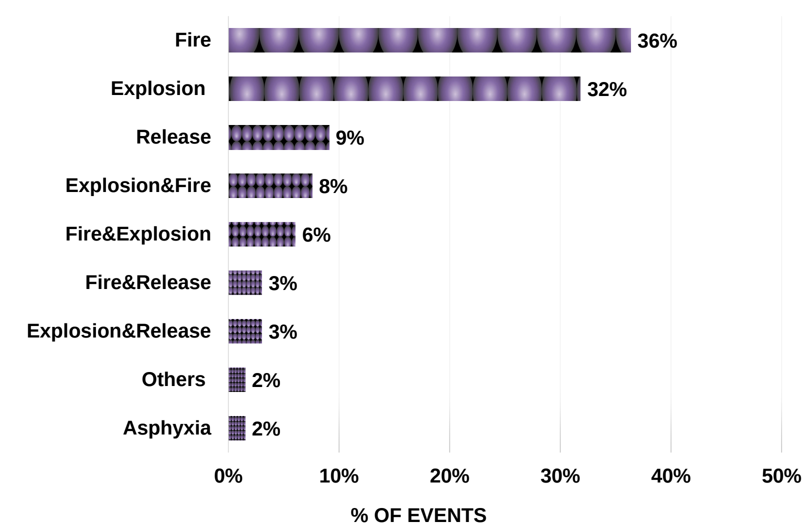

Figure 3: Type of scenarios the accidents and incidents in biodiesel industry selected for the analysis and reported in Figure 1. When two scenarios are considered (e.g. Explosion&Fire or Fire&Explosion), a cascading effect is considered, starting from the first scenario.

Consolidated and upcoming Technologies for biodiesel production

Classical transesterification processes starting from vegetable oils or animal fats to produce Fatty Acids Methil Esters (FAMEs) are consolidated at the level of production facility. The size of the facilities is on average small, as can be seen from Figure 5. In most cases, transesterification is performed by using Methanol and a basic catalyst. In general Sodium Methylate is used. The use of Ethanol or an acid catalyst is much less widespread. Further details can be found in existing literature.

The transesterification is an equilibrium reaction. It implies that to achieve sufficient conversion cascade of reactors are generally used. The output of the reaction section separation of FAMEs from the polar phase (excess Methanol, glycerine and fatty acids) is needed. FAMEs and the polar phase are not miscible and gravitational separation is generally adopted. FAMEs still contain Methanol that is recovered via distillation (atmospheric and/or vacuum) and condensation. The polar phase is furtherly separated as it contains Methanol and a valuable amount of fatty acids. Further recovery of the Methanol is obtained via distillation. The bottom stream is then acidified such to separate the glycerine phase from the fatty acids. Residual Methanol remains in the glycerine phase as it is more polar than Fatty Acids.

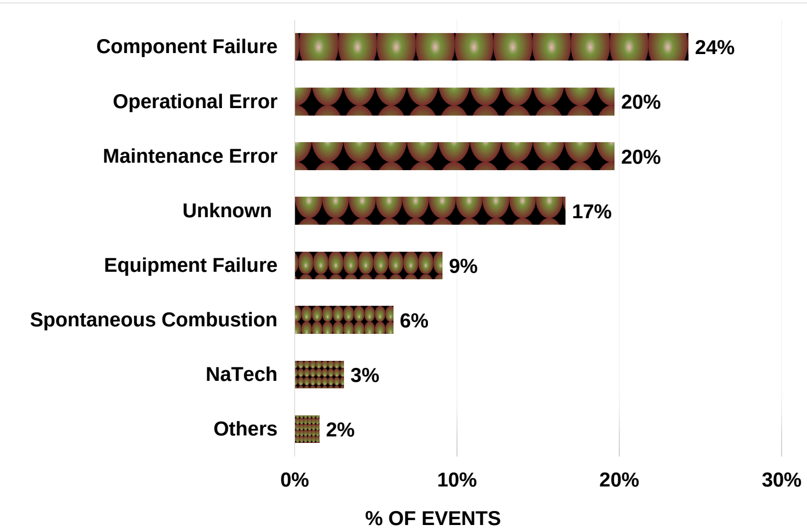

Figure 4: Type of causes related the accidents and incidents in biodiesel industry selected for the analysis and reported in Figure 1

Supercritical processes are at a scale up stages. According to Parvizsedghy and Sadrameli (2014), these processes may allow using low-price oils with high content of FFA. So, they are expected to spread in the future. The reaction conditions will be more severe than in traditional plants, as operating pressure is expected to range up to 50-100 MPa and temperature may reach 300°C. This will imply the plant to contain a huge number of pressurised equipment's, piping's and joints. The risk associated to these more severe operative conditions was discussed by Parvizsedghy and Sadrameli (2014), who observed that the risk in supercritical biodiesel processes will increase because of high pressure and high inventories of flammable materials. They observed that pressurized liquid inventories were the most hazardous items and jet fire was identified as the most likely incident scenario. They determined vulnerability distances in the range 70-190 m for humans and from 61 to 159 m for domino effects.

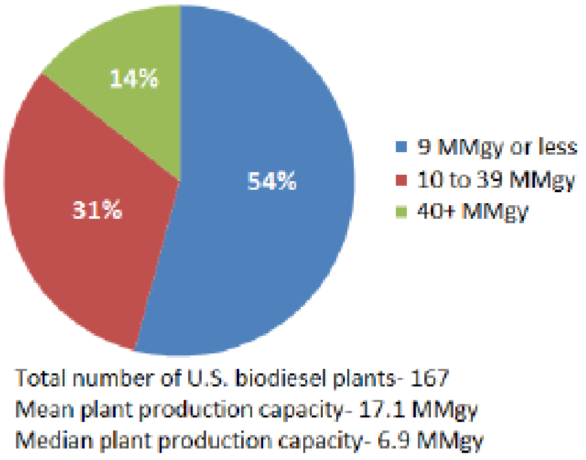

Figure 5: Size of ethanol and biodiesel plants in USA (Hoagland, 2013)

A case study of an explosion in a biodiesel plant

In 2013, a 200.000 T/Y biodiesel plant in southern Italy was hit by an explosion and fire that killed three workers and provoked serious material damages to an intermediate storage area. The incident occurred in a biodiesel production facility that processed waste vegetable oils and animal fats to convert them to FAMEs by using a transesterification process. A pre-treatment process upstream transesterification units served to refine the feedstock oils and to reduce the impurities in the reaction. The capacity of the plant was of about 200 t/d biodiesel production.

The sections of the plant were the followings:

- Degumming section of feed waste oils (200 t/d);
- Decolouration section (200 t/d);
- Deacidifaction section (200 t/d);
- Transesterification section (main reactors) (200 t/d);
- Glycerol distillation section (35 t/d).

The overall design of the plant is specified in the next Figures 6-8. The Pre-treatment section is shown in Figure 6. As a feedstock of raw waste oil is introduced in the process several refining operations have to be made. Raw oils are processed in the degumming unit (b and d in Figure 6) and then the decolouration unit (c e and f). Then, the feedstock is deacidified through two columns (g, h), the first working in light void conditions in order to maximize the efficacy of the vapour stripping. From these units two streams are obtained: one constituted by the fatty acids removed from the oils and the other constituted by the refined oils, which proceed to the esterification section, shown in Figure 7. Fatty acids are stored to an intermediate tank to be recycled to the reaction section.

The transesterification section is carried out in a series of three reactors (a, b and c in Figure 7). Methanol is added here in the process, together with the catalysts. The remaining elements of this section perform to the purification of FAMEs and the recovery and recycle of by-products and reactants in excess. FAMEs are then separated from the polar phase by several operations as physical phase separation in a gravitational separator (d in Figure 7, eliminating the polar fraction from biodiesel), evaporation and condensation of methanol to be recycled, elimination of residual soaps and drying of biodiesel to grant its characteristics to be those required by current technical standards (UNI EN 14214).

Last process section performs the recovery of the polar fraction from the reaction section (Figure 8). Here, separation of methanol, glycerine and residual fatty acids is obtained in a distillation column (a), a decanter (b) and a second distillation column (c, working at a high grade of void).

A key element of the accident dynamics is represented by the decanter, indicated with a "b" in Figure 8. In this vessel, a gravimetric separation should have produced two streams: the light one with a major content of fatty acids and the polar, heavier fraction composed of glycerol and methanol.

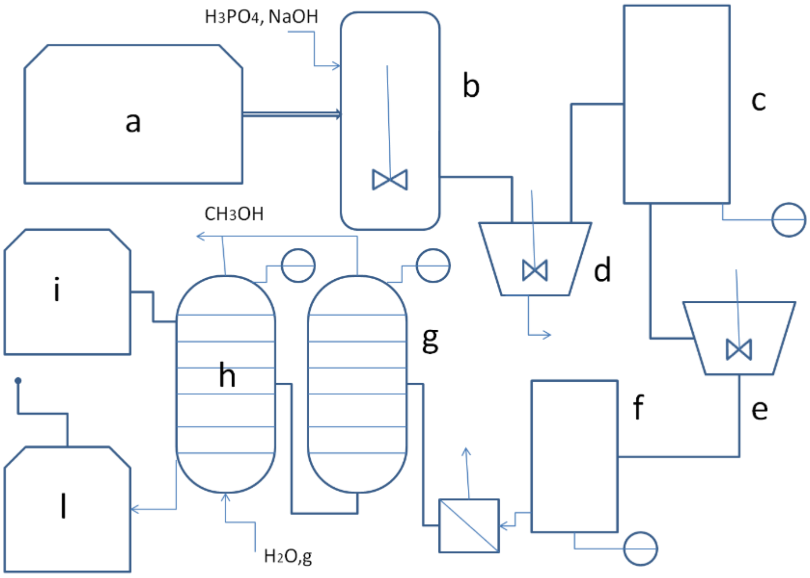

Figure 6: Pre-treatment section of the plant. Oil storage (a); degumming units (b and d); decolouration units (c e and f); deacidification columns (g and hf anf g); fatty acid storage (l); refined oils (i).

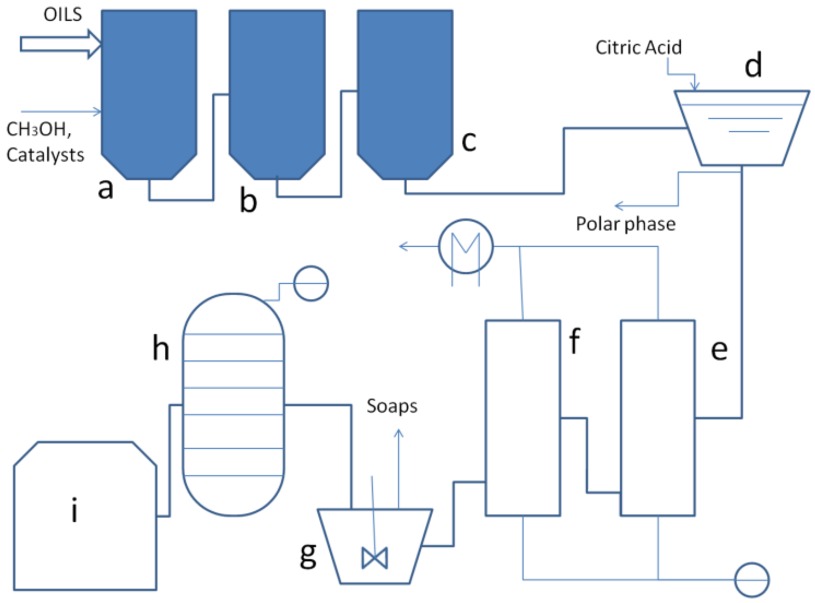

Figure 7: Trans-esterification and biodiesel purification section. Reactors (a, b, and c); gravitational separator (d); evaporator (e and f); elimination of residual soap (g); drying unit (h); storage unit (i).

Target Methanol concentration in the inlet stream should have been around 6÷10%. According to design calculations the Methanol should remain in the polar phase at a concentration of about 15% and almost no methanol should remain in the non-polar, lighter stream mainly composed of fatty acids. The fatty acid stream was conveyed to the intermediate storage tank hit by the explosion occurred (indicated as "i" in Figure 6).

Dynamics of the accident and discussions

At the time of the accident the plant was in the start-up phase because it did not operate yet except for some short test runs. The explosion (Figure 9) occurred in the 50 m^3 fatty acid intermediate storage tank whereas the three victims were doing some hot works to realize some new piping that were supposed to allow direct discharge of fatty acids from incoming trucks. The tank was named “D 503”.

The tank had not been placed out of service nor purged as it was expected to contain non-flammable liquids. Contrarily to expectation, the tank inventory was contaminated by a significant amount of Methanol (18% w/w, Flash point <18°C°). As the workers attempted to make a hole in the tank roof with an angle grinder an ignition occurred. The tank broke at the bottom welding and the deflagration blew the tank to a 60-meter missile-like flight (Figure 10, Figure 11). The methanol vapours present in the tank has been ignited by the overheating by the angle grinder used by one worker on the top of the tank. Three workers were operating on the tank, two were on a lifting basket, the third close to the tank bottom.

The three workers died for the burst. A localized fire developed in the containment basin where the tank was located. It was easily extinguished by the internal fire brigade.

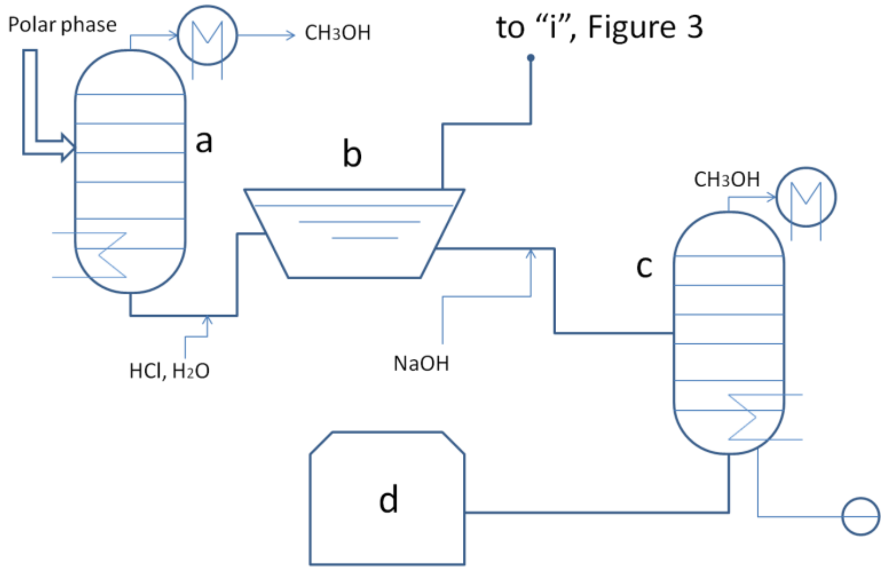

Figure 8: Glycerine and methanol recovery section. Distillation columns (a); decanter (b); second distillation column (c); storage unit (d).

Figure 9: the explosion as seen from a nearby surveillance camera. Time frame ca. 0.25 s

Once ignited the flame front has ran along the tank and generated extremely hot combustion gases that had to be responsible for the pressure rise in the tank and the consequent failure of the basement connections. During the first phases of lifting of the tank the combustion has continued and involved the remained unburnt methanol causing the flash fire outside the tank to run over the operators on the top of the lifter.

The flash fire resulting has determined the critical scenario: generally, in the area involved by the flames or next to, a radiant heat power of about 150 300 KW/m^2 is generated. The starting value for lethal effect is around 7 KW/m^2, while the high lethality threshold is equal to 12.5 KW/m^2.

Figure 10: the thank landed 60 m away from its original location in the backstage close to the blue lifting machine.

Figure 11: scrap on the tank roof and the tool used at the moment of the accident

Reasons for the presence of Methanol in the tank

The tank D503 was supposed to contain fatty acids mainly recovered from raw oils in the pre-treatment section. A smaller stream of fatty acids was conveyed to D503 from the gravitational separator used to separate glycerine from Fatty acids in the post treatment section. Methanol was not supposed to be present in any of the cited streams. The reasons for the unexpected presence of Methanol in the tank, which served as intermediate storage for the fatty acids separated from the glycerine stream downstream of FAME recovery, were essentially two, both related to poor plant design:

- an improper design of the tail vapor condenser which discharged the condensed in the separator used to recover the fatty acids from the glycerine stream
- poor design and control of the chilling water piping network devoted to supply cold water to the vapour condensers. The network was not provided of any temperature or flow control device, as a consequence some condensers were highly inefficient.

Figure 12 reports the scheme of the decanter d707-17 (indicated as "b" in Figure 8) used to separate the glycerine-like phase from the fatty acids. The lighter fatty acid phase was conveyed to D503.

During the investigation, several samples were collected around the plant to detect any abnormal methanol concentration in different streams of the process. Samples were analysed to determine the content of FAMEs, Fatty acids, Methanol and the flash point. The concentration of methanol in the inlet and outlet streams of the decanter D701-17 is shown in Figure 12. Here the anomaly could be found in the very high methanol concentration in the outcome pipe on the right, where only fatty acids should have collected if the process were in normal operation conditions.

The stream indicated as "LA1401795" in Figure 12, with about the 70% of methanol, was sampled from the piping connecting the decanter to the D503 tank. Consequently, an abnormal concentration of methanol had to be found here also.

The reasons for the anomalous methanol concentration in D701-17 counts in the architecture of the vapour condensers and chilling water network, as seen in the next Figure 13.

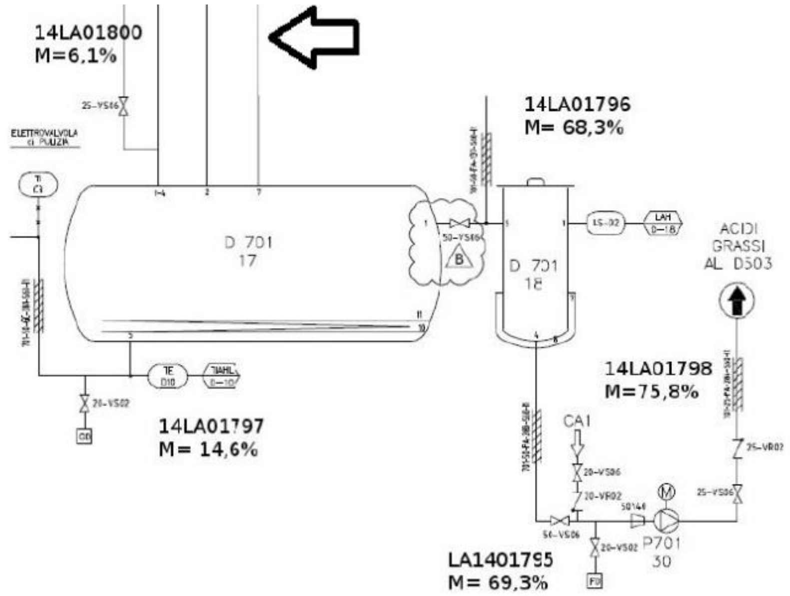

Figure 12: Detailed scheme of D701-17 tank and inlet/outlet streams, Methanol concentration indicated as M%, as sampling evidences reported. The arrow indicates the pipe connecting the separator to the methanol condenser.

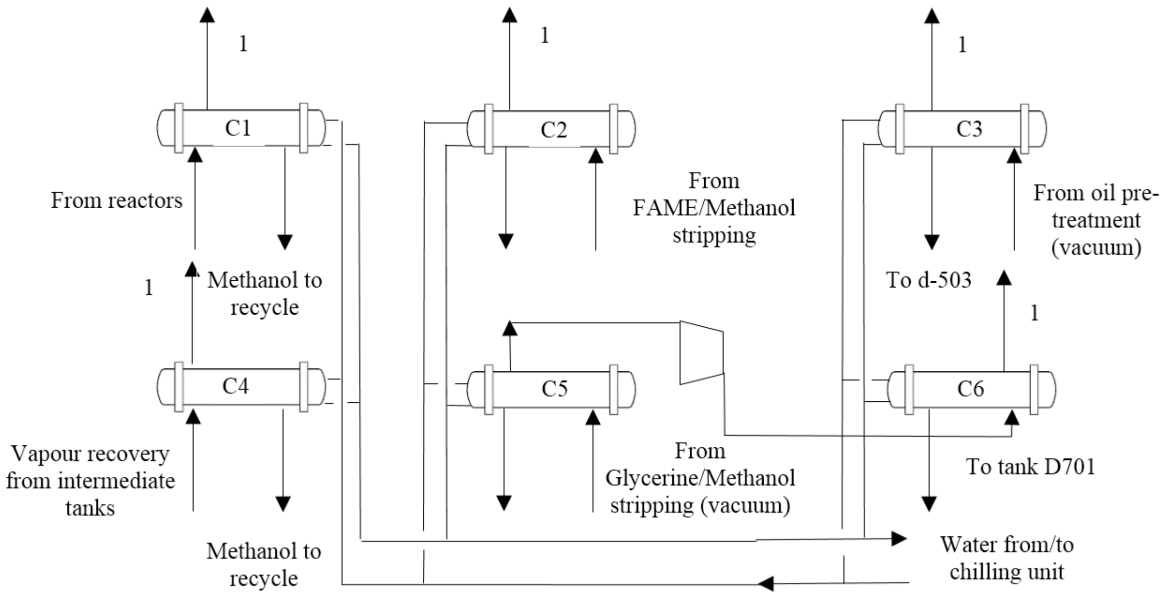

Figure 13: Simplified scheme of the condensers and chilling water network. 1 = exhaust treatment.

The cold-water network was not provided with any temperature or flux control device so water distribution was not optimized. Condensers C5 and C3 were operated at a significant vacuum (design 80 mmHg) as they served the vacuum methanol recovery section and the oil pre-treatment column. As water flow to condenser C5 was too low, its operating temperature was higher than the set point. The working pressure was about 150 mmHg, which is the vapour pressure of Methanol at the temperature of 30°. So, Methanol vapour was only partly condensed and a significant amount was entrained to condenser C6 where it condensed at atmospheric pressure. The liquid from C6 was transferred to D701 and then to tank D503.

The direct consequence of these two issues was the poor methanol vapour recovery by the condensers dedicated to that task, such that the methanol was condensed by the Fatty acid condenser and conveyed to the storage tank.

Discussion

The accident described in this paper could easily be ascribed to a gross disregarding of working procedures, as is well known since long time as an elementary principle of safety implies to avoid hot works on closed tanks not placed out of service and purged. It is worth pointing that almost all of the incidents whose cause has been classified as "Maintenance error" are related to welding and cutting operations during equipment maintenance, so the present case study is representative of approximately 20 % of the unwanted events affecting biodiesel facilities.

A deeper insight into the accident root causes provides a different viewpoint with a general value on the biodiesel process safety. The starting point is the totally unexpected presence of a flammable mixture in tank D503. The investigation demonstrated as the presence of Methanol in the tank was due to several issues, listed below.

a) *Lacks related to the plant control devices*

The chilling water network to the condensers was not provided of any device to properly control the water flow and/or temperature to the condensers. As a consequence of insufficient water flow to vacuum Methanol condensers, no adequate working temperature and pressure were obtained in all the vacuum Methanol recovery equipment. This caused excess uncondensed Methanol vapours to leave the vacuum condensers. As only low volatiles species as fatty acids were expected to leave vacuum methanol condensers as vapour phase, these flows were pressurized and sent to an atmospheric condenser from where the produced liquid phase was sent to the glycerine-fatty acids separator. Along this path the uncondensed Methanol flowed into the tank. D503. It has to be noted that tank D503 was not identified as possibly containing a flammable liquid.

b) *Lack of proper plant design*

Water temperature and flow measuring and control devices were built as designed. The lacks described in the previous point were consequence of the design strategy, which evidently suffered of poor risk analysis as the event of a malfunction leading to the presence of a flammable liquid in tank 503 was not identified.

c) *Lack of personnel and management awareness*

Beside the evident unawareness of the hazard of performing hot work on a closed vessel, also some indicators of not optimized process conditions were disregarded. The most evident was the anomalous high pressure value in the vacuum stripping units devoted to Methanol recovery. Pressure of 150 mmHg instead of the expected 80 mmHg was reported by the plc. Vacuum column pressure was driven by the Methanol steam pressure reached in the vacuum condensers, which in turn was determined by the chilling water temperature. Moreover, the company management was totally unfamiliar with chemical plant exercise as they came from completely different business area. As a consequence, no corrective actions were planned to improve the awareness of the personnel to malfunction indicators.

d) *Lack of plant risk analysis*

A proper risk analysis using typical methodologies such as Hazop would have easily revealed the event of unexpected methanol flow in equipment other than expected.

e) *Lack of process deviation awareness*

Apart from the case studied presented here, it should be noted that most of the separation processes widely used in the classical biodiesel manufacturing process, such as FAME/polar phase out of the reaction section, and glycerine/Fatty acids are based on phase separation. The methanol content of the system could affect to a great extent the efficiency of the separation process, as demonstrated by Marrone et. al. (2007) in the case of Methanol-Glycerine-Fatty acids. An increase of Methanol results in a decrease of density difference between the two phases, a decrease in the stratification velocity. At very high Methanol content the phase separation no longer occurs. So, anomalous Methanol content in the inlet flows to separators may result in incomplete/inefficient phase separation driving to the presence of flammable phases elsewhere than expected.

Conclusions

Biodiesel production via conventional transesterification adopts well known and consolidated technologies. The plant, the process and the equipment are those typical of the industrial chemistry in use since the first half of the last century. Investments needed to build a biodiesel plant from scratch are relatively low compared to other green technologies.

"Green" energies are often wrongly perceived as safer than the petroleum-derived products. However, the raw materials to produce biodiesel require several treatments using hazardous materials (e.g. methanol and sodium methylate for the transesterification) or severe process conditions (e.g. supercritical processes).

Indeed, it was recently discussed elsewhere (Casson Moreno and Cozzani, 2015) that the number of major accidents in bioenergy production plants is increasing fast in the last years and a comparison with the number of accidents in oil refining activities showed that the increasing trend is specific of bioenergy sector. Furthermore, an estimation of major accident frequency in bioenergy industry showed that the risk associated to this industrial sector seems to be within the ALARP region. In particular, for the case of biofuels (biodiesel and ethanol) a slightly higher accident frequency was estimated with respect to biogas plants (Casson Moreno et al., 2016), and this might be reasonably derived from the higher complexity of biofuel processing (Rivière and Marlair, 2010).

Due to the strong demand of green fuels and to public incentives and strategies to improve the green fuel output, the number of low to medium capacity biodiesel plants has rapidly grown worldwide. The case study presented here demonstrates that the combination of the aspects just mentioned above may have lead sometimes to a critical underestimation of the real hazard of such activities driving to the feeling that a biodiesel plant is a "safe car" that almost anyone could drive. The same reason could explain the low level of automation and instrumentation observed in case of the accident here discussed.

Points discussed above suggest that a proper analysis of root causes of biodiesel related accidents may help to deepen the awareness of technical and managing open issues in the traditional biodiesel industry and more in general in the bioenergy production (Paltrinieri et al., 2013; Casson Moreno et al., 2014).

In the light of these arguments, hazards studies of the new biodiesel processes such as those adopting the supercritical technologies devoted to better understand which process deviations may lead to hazardous consequences potentially rising to accidents are needed.

References

Acheson, B., Kwok, Q., Turcotte, R., Janès, A, Marlair, G., 2011. On the Fire and Explosion Risks Triggered by use of Sodium or Potassium Methoxides as Catalysts for the Production of Biodiesel. Sixth Int. Semin. Fire Explos. Hazards 978–981.

ARIA Database, 2016. http://www.aria.developpement-durable.gouv.fr/find-accident/?lang=en.

Casson Moreno, V., Cozzani, V., 2015. Major accident hazard in bioenergy production. J. Loss Prev. Process Ind. 35, 135–144.

Casson Moreno, V., Papasidero, S., Scarponi, G.E., Guglielmi, D., Cozzani, V., 2016. Analysis of accidents in biogas production and upgrading. Renew. Energy 96, 1127–1134.

EIA, 2016. U.S. Energy Information Administration [WWW Document]. URL http://www.eia.gov/beta/ (accessed 2.6.17).

Hoagland K., Comparing Plant Capacities of U.S. Ethanol & Biodiesel Industries, Biomass magazine, n. 9801, December 13, 2013.

JST Failure Knowledge Database, 2016. http://www.sozogaku.com/fkd/en/.

Loss Prevention Bulletin, IChemE, 2016. http://www.icheme.org/lpb

Marrone L., Pasco L., Moscatelli D., Gelosa S. Liquid-Liquid Phase Equilibrium in Glycerol-MethanolFatty Acids Systems, Chemical Engineering Transactions, Volume 11, 2007

McElroy, A. K. Getting serious about safety. Biodiesel Magazine, 2006, September.

Olivares, C.R.D., Rivera, S.S., Mc Leod, N.J.E., 2014. Database for accidents and incidents in the biodiesel industry. J. Loss Prev. Process Ind. 29, 245–261.

Paltrinieri, N., Dechy, N., Salzano, E., Wardman, M, Cozzani, V., 2013. Towards a new approach for the identification of atypical scenarios, Journal of Risk Research, 16, 337-354.

Parvizsedghy, R., Sadrameli, S.M., 2014. Consequence modeling of hazardous accidents in a supercritical biodiesel plant. Appl. Therm. Eng. 66, 282–289.

Rathnayaka, S., Khan, F., Amyotte, P., 2011. SHIPP methodology: Predictive accident modeling approach. Part I: Methodology and model description. Process Saf. Environ. Prot. 89, 151–164.

Rivière, C., Marlair, G. The use of multiple correspondence analysis and hierarchical clustering to identify incident typologies pertaining to the biofuel industry, Biofuels, Bioproducts and Biorefining Volume 4, Issue 1, January 2010, Pages 53-65.

Salzano, E., Di Serio, M., Santacesaria, E., 2010a. Emerging risks in the biodiesel production by transesterification of virgin and renewable oils. Energy and Fuels 24, 6103–6109.

Salzano, E., Di Serio, M., Santacesaria, E., 2010b. Emerging safety issues for biodiesel production plant, Chemical Engineering Transactions 19, 415-420.