Accidental rate in Biodiesel production plants

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In a recent work, the authors showed that the trend of accidents affecting biodiesel (BD) industry follows the production trend, which is increasing worldwide due to environmental issues and climate change action plans (Marmo et al., 2017). The analysis presented a risk figure for the sector that seems above the expectation with respect to "more traditional" facilities adopting similar technologies, revealing the misconception of "green = safer". Indeed, the number of biodiesel production plants is rapidly growing around the world, and the related technologies are developing to full industrial scale within a brief time. Most of the plants adopt the consolidated transesterification process technology; despite supercritical process technology has almost achieved the build-up stage.

To better address and characterise the problem of the high accidental rate in biodiesel industry, an in-depth statistical analysis of past accidents was performed and is presented in this paper. The set of records analysed 93 events, from 2003 to 2017 have been selected to depict the most relevant factors affecting the accidental rate, such as:

- Plant characteristics: size, location, capacity, production technology;
- Plant lifetime: plant life stage, operating time;
- Accident Scenario: type of event, substances involved, losses, fatalities and injured.

An overview of the results is hereby summarised: The majority of the records accounts for events in the US, which is currently the main biodiesel manufacturer. The more frequent scenario is relative to fire and explosion, while the highest fatality is due to explosion events.

A relatively low lifetime could be accounted for investigated BD plants, as more than half of events occurred in the earlier years from plants' start-up and relative low number of plants withstand without an event in the long term. Accidents occurred mainly in start-up phase, or in operating stage, when some maintenance operations are performed on structures and equipment. Considerations could be done analogously on variables as production capacity, plant section (where accident happened), equipment involved, with respect to the accidental rate, referred to the overall operating time of the plant, belonging to the considered category (depending on size, section, etc.). Accidental rate, referred to overall operating time of the plant, could also be referred with respect to different variables as production capacity, plant section, equipment involved and sort by previously defined categories (size, section etc.).

The findings of this work could also help to individuate the more adequate risk assessment techniques for this peculiar industrial sector and to suggest correct risk moderation measures.

Introduction

In the last 20 years, biofuels production has gained attention worldwide and acquired relevance with respect to traditional fossil fuels, due to their "green" specifications. Among others, Biodiesel had some critical benefits: it could be produced form renewable resources, it has a high grade of biodegradability and feedstocks and technologies are economically convenient.

Biodiesel production has been constantly growing in the period considered in this work (2006-2016), if the drop occurred in 2008, meanwhile oil price crisis, is disregarded. Major BD producer were first located in the Northern hemisphere (US, Germany), though recently Asian region entered the market with large production capacity (Indonesia, Thailand), as well as Southern America countries (Brazil, Argentina).

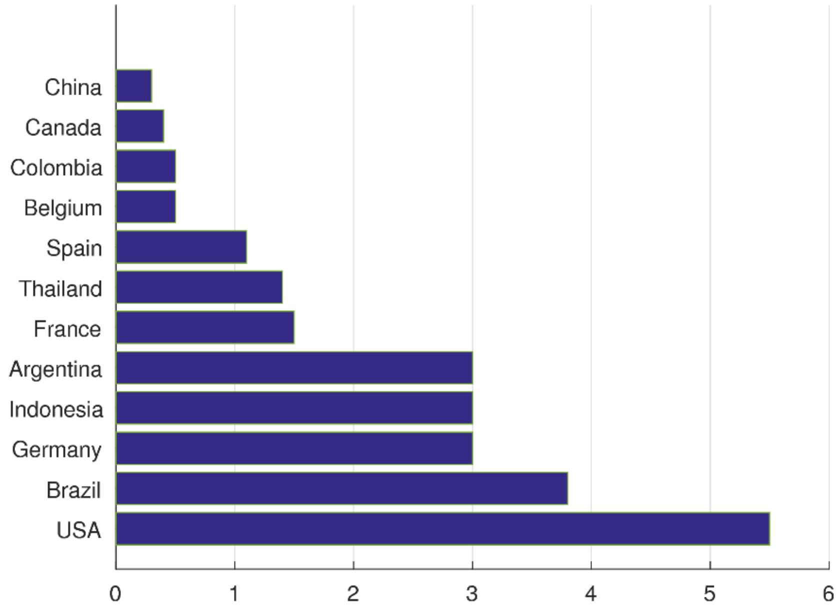

Figure 1: Biodiesel production sort by country, from [Biofuels Annuals, 2017, USDA Foreign Agricultural Service], 10^3 millions liters.

The process to convert oily and high fatty acids content substances into Biodiesel, that is Fatty Acid Methyl Ester, are different, depending on feedstocks or process technology. The global most adopted technology is the Transesterification process, from which "conventional" Biodiesel is obtained. Transesterification reaction allows the use of multiple feedstocks to generate a fuel with properties similar to conventional diesel: triglycerides (oils and fats) are converted in alkyl esters by the addition to reagents of catalysts (acid, base or enzymatic).

This type of process, independently from catalyst type, do not require complex plant site. Typical equipment of the conventional chemical industry could work for Biodiesel production, i.e. distillation columns, dryers, vacuum stripping units, washing and mixing tanks, gravitational separators.

The process conditions are relative mild: the maximum Temperature sets around 200°C and the process is performed at atmospheric pressure. Stronger process conditions are expected for super-critical process technology (around 250°C, 10 MPa), while plants are still at the lab scale (Parvizsedghy and Sadrameli, 2014).

Despite this safe framework, the binomial greener equals to safer is not a priori true, as several accidents have been reported in the whole biofuels industry (Casson Moreno et al., 2015). Authors have previously underlined (Danzi et al., 2017) how, among biofuels, biodiesel have a peculiar accident history which could be related to its manufacturing specifications. In this work, we assumed that, due to the proper user-friendly industrial equipment needed for biodiesel production and purification, a slightly higher risk degree could be accounted for this industry sector (with respect to traditional chemical industry) as a result of an underestimation of the perceived hazards, due to this safety misconception.

Dataset built-up

Records of past accidents involving biodiesel plants were collected from different sources as ARIA Database (French Ministry of Ecology Sustainable Development and Energy, 2017); the JRC eMARS (Major Accident Hazards Bureau, MAHB, 2002), European Joint Research Centre; the Infosis ZEMA (Deutsch Umwelt Bundesamt, 2017), and The Loss Prevention Bulletin (IChemE, 2017). Among the records 4 different scenario were selected as the most representative: Fire, Explosion, Multiple scenario (Fire & Explosion) and Release.

A total of 93 events were included in the database, covering the last 14 years and ranging from 2003 to 2017.

Each accident record consists of several variables, which characterise the event, the variables are defined as plant characteristics (capacity, life-stage, technology and feedstocks), plant production life-time (stage and age when accident occurred) and scenario features (substances, equipment involved, losses and injured).

Common or recurring aspect were defined by imposing different categories to variables, as to study the influence of these latter with each other's, Table 1 reports dataset structure and the division in categories.

Table 1: Dataset structure, main variables and sub-categories.

VARIABLES							
SCENARIO	**CAUSES**	**TYPE OF EVENT**	**LOCATION**	**FEEDSTOCK**	**PLANT STATUS**	**TECHNOLOGY**	**SUBSTANCE**
Fire	Component failure	Accident	Process unit	Soybean Oil	Strat-up	Basic-catalysed	Reagents
Explosion	Equipment failure	Incident	Process tank	Other veg. oils	Normal operation	Acid-catalysed	Products
Multiple Scenario	Operational error	Near Miss	Storage tank	Multi-feedstocks	Maintenance	Enzymatic-catalysed	Feedstocks
Asphyxia	Maintenance error	Mishap	Utilities	Waste cooking oil	Shut-down	Others	Chemicals
Release	Na-Tech		Line	Brown grease	Unknown	Unknown	Mixture
	Spontaneous combustion		Warehouse	Others			Catalysts
	Unknown		Unknown	Unknown			Others

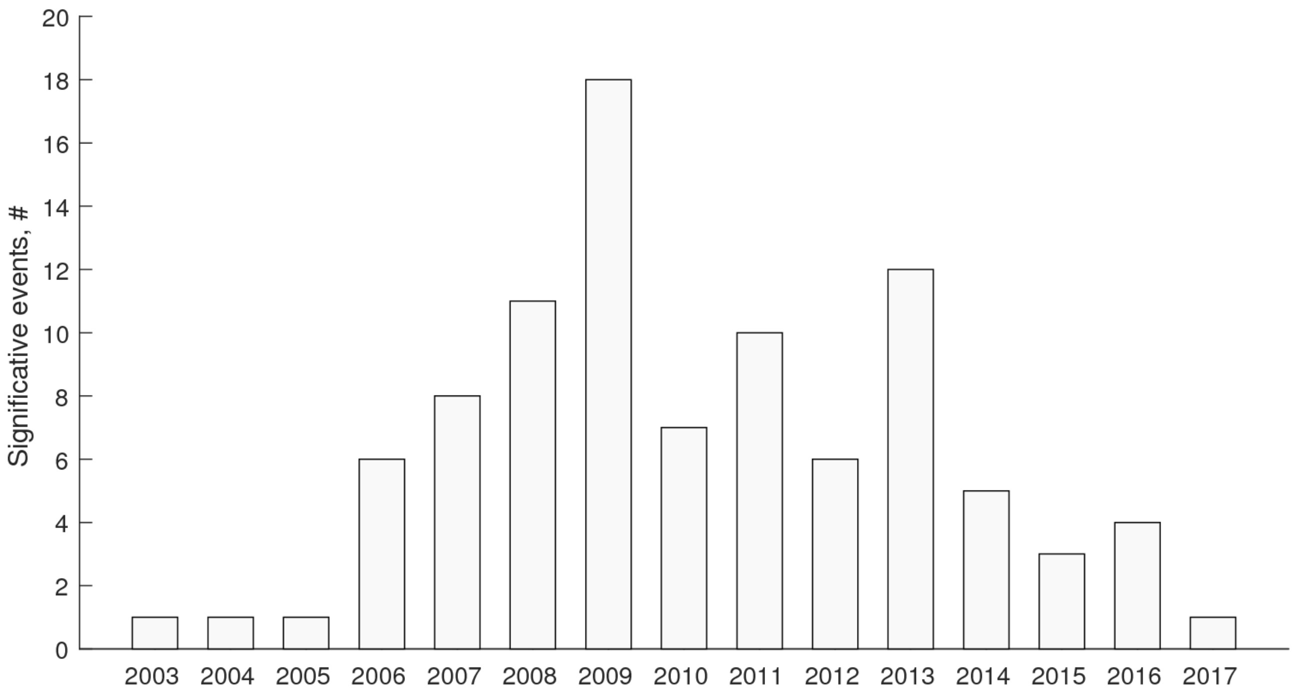

Figure 2: Dataset events distribution in the time period considered.

Results and discussions

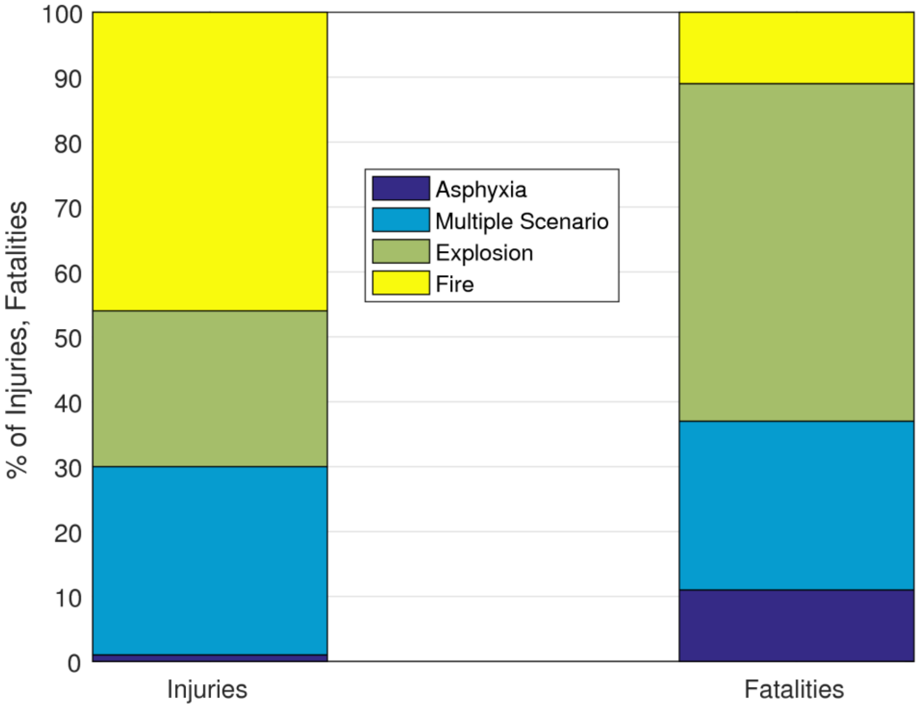

Figure 3: Injuries and losses associated to most common scenario in biodiesel industry accidents.

In order to have a clear view of the accident distribution of biodiesel industry, the study first focused on the primary characteristics of BD plants investigated, in terms of production capacity, feedstocks and technology adopted. Over the half of the plants included in the dataset have a capacity smaller than 100 ktonn/year: this occurrence is mainly due to the size distribution of US plants, as this production capacity range represents almost the 70% of the existing US installations. This picture has been previously reported also by Salzano et al. (2010a), where the US accident incidence was associated to the peculiar size of plants: "backyard facilities" (defined as smaller than 35 ktonn per year plant) are common in US and represent a third of the total account (National Biodiesel Board, 2017). In these cases, is less probable that a systematic risk analysis is applied and plant safety is likely to be compromised in advantage of cutting investment costs.

Recently larger plants have also been involved in accidents (particularly in Europe), thus requiring a more detailed investigation on the effectiveness of personal training and formation, since human errors seemed to be the major cause, in particular when a maintenance procedure is in progress.

The most common accident scenario is fire (41% of the cases), followed by explosion (22%). A relevant percentage is associated to multiple scenario, involving both fire and explosion (17%). The most severe scenario, if consequences are considered, is explosion, which represent more than half of the total fatalities reported, while 61% of total injuries is associated to multiple scenario (Figure 3).

The study of influencing variables on accident distribution and fatality incidence could also allow some considerations and suggestions on safety critical aspects. In this work, fatality rate has been studied with respect to both plant characteristics and type of scenario.

Dataset reports that accidents fatality is greater as plant age is lower, as 85% of fatalities occurred after 5 years from the plant production start and injury rate inside this time range equals almost the 65% of the total amount.

As plant size is considered, a relevant 61% of total injuries is registered for small size plant, defined as plant with production capacity lower than 30 ktonn per year. Fatality rate is more equally distributed with respect to plant size, while if cumulative data are observed the 75% of deaths occurred in plants with lower than 100 ktonn per year capacity.

A clear picture derives from plant stage incidence on fatality rate: maintenance stage is the deadliest among all, accounting for 18 to 28 total fatalities observed in dataset. This outcome has been previously underlined by other authors (Salzano, 2010a and 2010b, Riviere and Marlair, 2010), nevertheless in-works accidents with very similar dynamics still happened recently (case study reported in Marmo et al., 2017). If maintenance-related accidents are considered on a 3-years period based, similar values characterised the 2006/2008 and the 2015/2017 intervals (23% and 25% respectively). Operating stage resulted is characterised by the higher percentage of injuries, 43 (39% on totality), even if a similar value related to not-determined stage (42 cases).

Maintenance error was found the most frequent cause of accident in biodiesel industry followed by equipment failure, operational error and component failure. Accident descriptions, where detailed, allows to connect direct actions and events to causes of the accidental scenario.

If maintenance is took into account, it is worthy to note that almost all related accidents are related to welding-cutting operations performed on equipment during maintenance stage (16 to 17). The "hot work" operation and the accident dynamics is found similar in different cases: workers used acetylene torch to add/remove joints from a tank, which is thought to contain any flammable substances, when eventually an ignition took place and a flash fire/explosion is produced.

As could be seen from Table 2 fatality and injury incidence are greater for the Maintenance and Operational errors category. A higher fatality is associated to maintenance, coherently with those reported above concerning the plant stage in which accident occurred.

Table 2: Fatality and injury incidence, with respect to direct accident causes

Fatality		**Injury**	
Maintenance errors	0.66	Unknown	0.39
Operational errors	0.15	Operational errors	0.28
Na-Tech events	0.11	Maintenance errors	0.22
Component failure	0.04	Na-Tech	0.04
Unknown	0.04	Equipment failure	0.04
		Component failure	0.02
		Spontaneous combustion	0.01

The most frequent "Operational errors" identified in biodiesel industry are the implementation of a wrong procedure and the wrong implementation of a correct procedure. An interesting aspect in Equipment failure and Component failure is related to the fact that they represent sources of ignition, where the weaker component seemed to be the heating controller, whether on process line or in the feedstock storage section of plants. It is worthy to note that a relevant number of cases are due to spontaneous combustion (mainly of oily rags from feedstock refining operations).

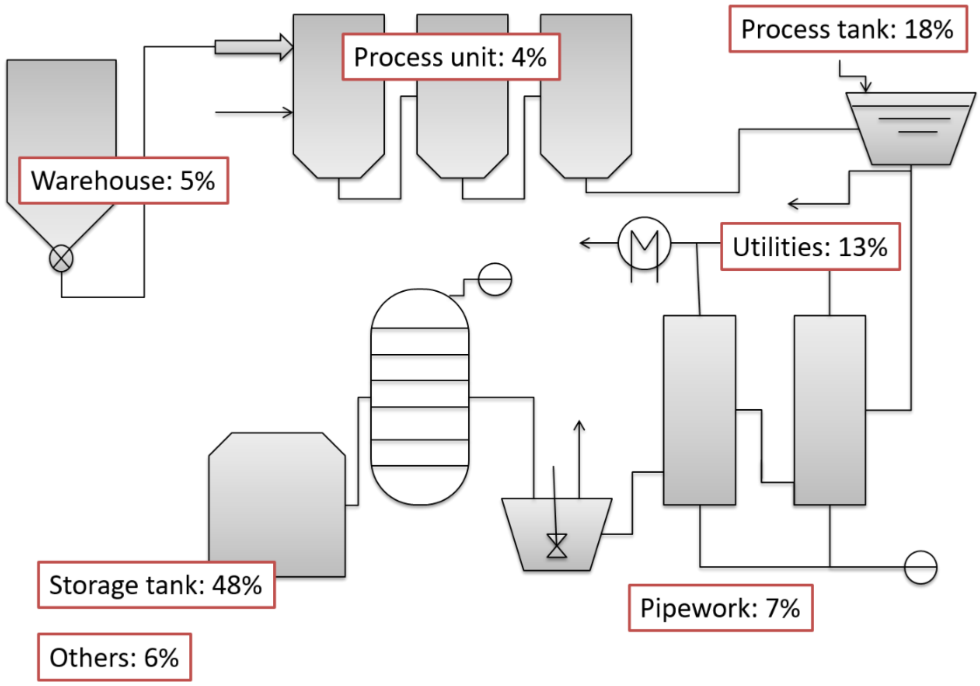

Figure 4: Accident distribution with respect to main unit involved.

The main unit involved in accidents is reported in Figure 4

Tanks constitutes the 66% of total unit involved. In this category are included buffer tanks, storage tanks of reagents, by-products and process tanks, such as those devoted to neutralization or pretreatment of feedstocks. A relevant percentage is due also to utilities, whose failure could contribute to escalate the severity of scenario (see also Marmo et al., 2017). Process units rarely are primarily involved in accidents.

A high fatality incidence is finally associated to accidents involving tanks as primary event unit, as reported in Table 3 while if injuries are considered, the incidence is almost equally distributed among storage, process tanks and other equipment.

Table 3: Fatality and injury incidence with respect to main unit involved in accidents

Fatality		**Injury**	
Storage tank	0.68	Others	0.31
Unknown	0.14	Process tank	0.26
Process tank	0.11	Storage tank	0.25
Warehouse	0.04	Unknown	0.09
Line	0.03	Line	0.05
		Warehouse	0.02
		Process unit	0.01
		Utilities	0.01

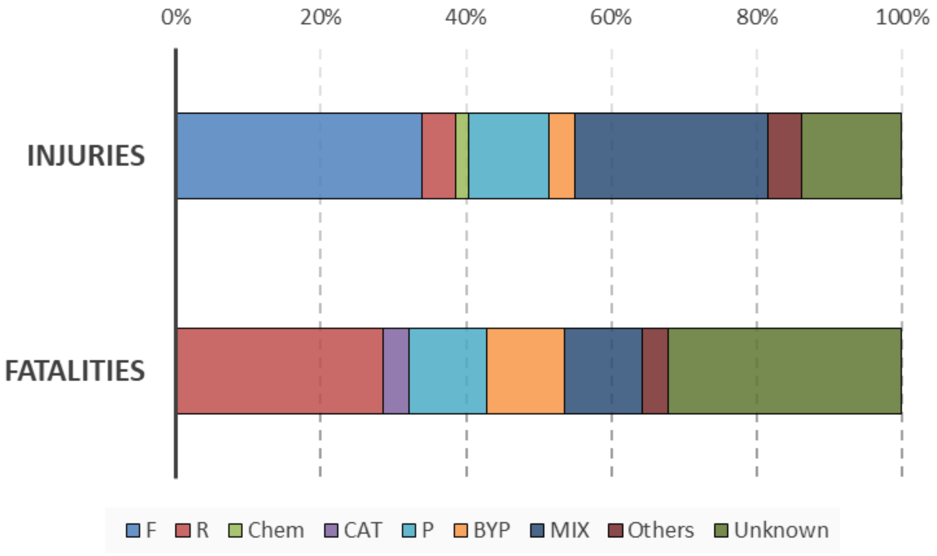

Figure 5: Injuries and fatalities count sort by substances mainly involved in accidents, where F: Feedstocks, R: Reactants, Chem: Chemicals, P: Products, BYP: By-products, MIX: Mixtures.

Methanol is reported by many works (Nair, 2010, Riviere et al., 2014, Fabiano et al., 2012) as the main responsible of fire and explosion hazards in biodiesel plants. Its low flash point (12° C, closed cup) implies an enhanced risk not only in loading/unloading or processing operations, but also in storage section. Direct cause of fire/explosion scenario are inappropriate operational actions, but also inadequate storage equipment, such as non-earthling or grounding tanks. Indirect cause could be inappropriate spacing or unintentional deviation from design intent.

In our dataset Methanol and Sodium Methylate (as catalyst) are found mainly responsible for explosions, while less flammable substances are involved in the majority of fires (such as biodiesel and non-refined oils, respectively product and raw feedstock of the process). Kwok et al. (2013) detailed investigated explosion hazards related to catalysts like methoxides in biodiesel processing.

The term "Mixture" in Figure 5 and Figure 6 refers to volatile compounds, mainly methanol vapours, glycerol and sulphuric acid. In our dataset at least 2 events are related to violent exothermic reaction due to excess amount of acid in the neutralization step. Mixture account for the 24% and 20% for Explosion and Multiple E & F scenario, respectively, thus provoking the 10% and 26% of total fatalities and injuries.

Furthermore, batch processing is generally adopted in biodiesel manufacturing facilities (particularly at small scale), thus implying peculiar hazards related to bad mixing operations. This could result in undesired strongly exothermic reactions, as that occurring when methanol is added to hot oil (Nair, 2010) and other cases reported in the present dataset.

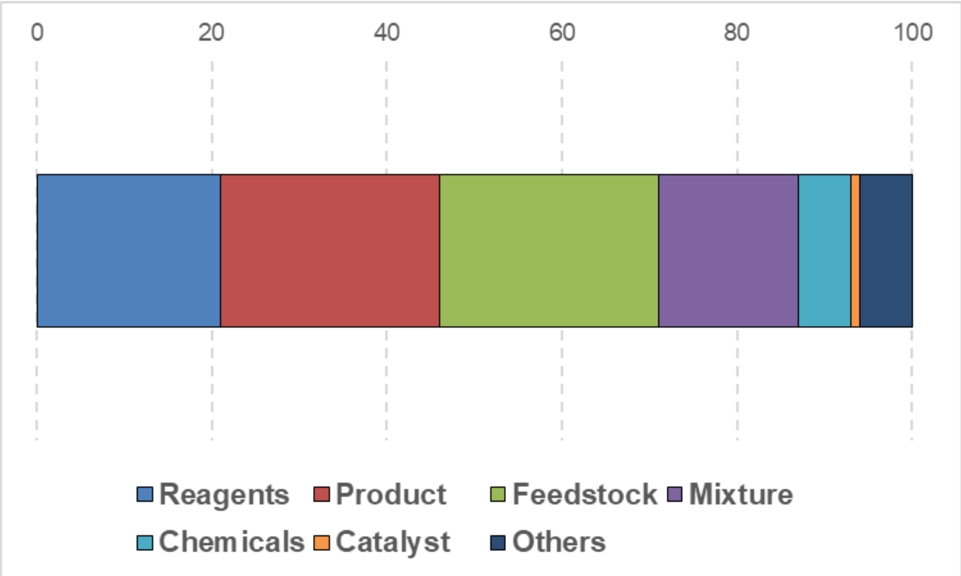

Figure 6: Accident distribution with respect to substances involved.

Methanol related accidents were underlined as the main cause of explosion in small BD facilities by Salzano (2010a). A slightly different figure come out in this work, due to the inclusion in dataset of events occurred after 2010, which interested methanol related accident in larger capacity plant (100ktonn per year), mainly located in EU and Asia. Fatality incidence for larger plants (from 100 up to 300 ktonn per year) is not negligible (25%) and in the last 3 years those accidents accounts for the 62.5% of total cases. However, it seemed that with larger capacity than 100ktonn per year, reactants are not mainly involved in accidents, maybe due to increasing attention with safety issues of methanol.

Table 4: Events distribution, fatalities and injuries (in % and cases) with respect to plant-lifetime at the moment of accident

	Events	**Fatalities**	**Injuries**
Within 2 years	0.35 (26)	0.40 (8)	0.16 (15)
Within 5 years	0.35 (26)	0.45 (9)	0.47 (44)
Within 8 years	0.19 (14)	0.10 (2)	0.09 (8)
Within 13 years	0.11 (8)	0.05 (1)	0.28 (26)

Table 4 reports the accident distribution with respect to plant lifetime when event occurred. The 70% of accidents occurred within 5 years from the starting of the plant. This data clearly represent the accident incidence of BD plants and could be explained if safety issues are considered: a combination of limited experience in operational processes by the plant owners and managers, lack of safety culture in the plant management structure, which turns into poor training of in field operators, lack of standardized instructions for peculiar operations of those type of facilities.

Furthermore, as previously reported in this paper, safety literature on BD plants did exist (even if has to be furtherly widen), but poor attention was paid by plant managers and S&H managers to it or to previous case studies and accidents investigations.

The high number of events in the earliest years of plant production reflects in a high percentage of fatality and injury incidence also, as depicted in Table 4. This lack of safety awareness could be limited to small scale plants ("backyard" facilities), but the same figure is evinced from dataset for medium and large plants, where an enhanced safety culture should be present. There, an inadequate mitigation and prevention should turn minor events to major accidents, escalation being possible due to the larger flammable substances inventory and hold-up.

A consideration could arise form dataset on the shift to large scale production of biodiesel, occurred in recent years. It is worthy to note that accident causes, from 2006 on are mainly Equipment, Component Failure and Operational error, while prior to 2006 the main cause is maintenance errors. This may be related to the growth in plant scale and consequent increase of plant complexity.

Finally some considerations could be done if this dataset outcomes is compared to the analysis performed by Riviere in his work (Riviere and Marlair, 2010). Here the authors defined different clusters of accidents in biofuel industry according to correspondence analysis among variables considered more relevant, such as location, product involved and scenario. If location is concerned, tanks are individuated as main unit involved in biofuel accidents.

A cluster is individuated as the more representative for biodiesel accidents. The 61% of accidents in this group occurred in tanks and the 33% of accidents is related to maintenance activities. Accidents considered happened during plant stop for the 14% of cases. The more common scenario is fire and/or explosion, which accounts for the 89%. Data obtained from our dataset are almost coherent to Riviere's works and could be used to identify different clusters of accidents among accidents related to the biodiesel manufacturing industry.

Conclusions

The analysis of past accident in biodiesel industry allowed to define a severe risk figure for the sector that seems above the expectation with respect to more traditional facilities adopting similar technologies, revealing the misconception for which "green = safer".

Several activities and operations in the bio-based industry could imply relevant major accident hazards, although are often underestimated. Among others, maintenance stage has to be carefully regarded, as our dataset associated to it a high fatality incidence (64%). Direct causes of maintenance errors are mainly correlated to not appropriate welding/cutting operations on tanks, scenario which represent the 94% among maintenance related accidents. As injury incidence is concerned, it comes out that operational errors is responsible for the 28% of cases, revealing how training and hazards knowledge of operators about peculiar BD processes and substances has to be improved.

It is worthy to note that in several episodes a joint cause of inadequate maintenance and operational procedures contribute to raise the accident severity, as reported in dataset event description and in other case studies, (Marmo et al., 2017). The stage at which most of accidents occurred is operational, while a 46% of cases occurred during transient phases (start-up, shut-down) and plant stopping (maintenance), confirming the critical issues of these stages on safety (Ostrowski and Keim, 2010).

A final critical aspect underlined in this work concerned the early occurrence of accidents in plant lifetime. The large majority (70 %) of the events recorded, occurred in the earlier phase of production (within 5 years), pointing out a general lack of safety culture and risk perception in biodiesel production industry.

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