

Emerging safety issues for biodiesel production plant

E. Salzano¹, M. Di Serio², E. Santacesaria²

¹Istituto di Ricerche sulla Combustione, Consiglio Nazionale delle Ricerche
Via Diocleziano 328, 80124 Napoli (IT)

²Dipartimento di Chimica, Università di Napoli »Federico II«,
Via Cintia 80126, Napoli (IT)

Biodiesel is a very attractive bio-fuel because of its environmental benefits. Indeed, it has lower content of air pollutants per net energy than diesel; it is nontoxic and can be produced from renewable sources with high energetic efficiency.

Quite clearly, despite biodiesel status as a safe substance, the production process can be dangerous as methanol and other flammable reactants such as sodium methylate can leave plants vulnerable to fire and explosion if not properly engineered and operated. But further issues are emerging for the increasing capacity of plants, which have driven up on-site volumes of highly hazardous chemicals, thus resulting in higher risks for the scale-up. In this paper, insights of risks within this fairly new industry are presented.

1. Introduction

Biodiesel may be defined as the mono-alkyl esters of long chain fatty acids from vegetable oil or animal fat. Its use is constantly growing as it yields 90% to 40% more energy than energy invested in producing it [Hill et al., 2006; Wesseler, 2007]. For these and other economical/environmental reasons related to the use of renewable sources, every year new industrial plants, with increasing capacity, are going to be built worldwide.

Among biodiesel chemical processes, trans-esterification of triglycerides of virgin oils or refined/edible oils by using methanol and alkaline catalysts [Ma et al., 1999; Pinto et al., 2005; Lotero et al., 2005; McElroy, 2006] is nowadays largely adopted (Figure 1). The R groups in Figure 1 are generally fatty acid chains (C12 to C20).as laurate, palmitic, stearic or oleic acids. The alkaline-catalyzed reaction is performed at about 60°C (near boiling temperature of methanol), and ambient pressure with high yields in simple batch, stirred tank reactor [Van Gerpen et al., 2004] or in continuous process as Plug Flow Reactor or combined stirred tank reactor (STR) at the same temperature, 400 kPa pressure [Zhang et al., 2003; Conneman and Fischer, 1998]. Sodium or potassium hydroxide, or related methoxide are typically adopted as catalysts, Typical molar ratio of methanol to triglycerides in alkaline-based process is 6:1 [Freedman et al., 1986]. This ratio needs to be higher than stoichiometric to drive the equilibrium to maximum ester yields. Due to this large methanol excess the intermediate species di- and mono-glycerides are only present at very early stage of reaction. Furthermore, Nouredini and

Zhu (1997) have demonstrated the trans-esterification reaction occurs in mass transfer-controlled regime in first stages, hence methanol excess improves the reaction rate and reduces the residence time, whereas a kinetically-controlled regime occurs only afterward.

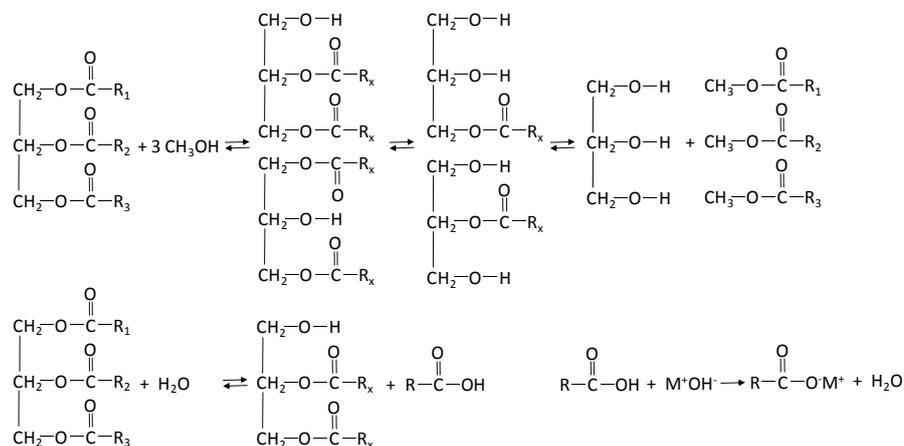


Figure 1. Trans-esterification reaction of triglycerides by methanol to methyl esters (biodiesel) and glycerol, and competitive reaction of free fatty acids to soap and water.

The products from reactor are in two phases which are separated by settling tank and following centrifugation. The two streams, one containing 50% glycerol and most catalyst, the other rich of Fatty Acid Methyl Esters or FAMES, which constitute the main final product of biodiesel, are both separated from methanol in distillation towers with few stages (typically five), due to the large differences in the boiling point of the components.

The produced glycerol and FAMES (Fatty Acid Methyl Esters) which constitute the main final product of biodiesel, are then separated from methanol in distillation tower with five stages or more, due to the large differences in the boiling point of the components. However, due to FAME and glycerol thermal instability, vacuum distillation and temperature below 150°C is adopted. The products, methanol and catalysts are then purified by liquid-liquid extraction in water washing column at 60°C and after catalyst neutralization by H₃PO₄ by final vacuum distillation.

Many low cost feedstock oils (e.g. waste cooking oil) are available for biodiesel production. Unfortunately, those oils contain often large amounts of free fatty acids (FFAs), which react with alkali catalysts to produce soaps (e.g. potassium or sodium oleate) and water. Soap of saturated fatty acids tend to solidify at ambient temperature, thus forming un-desired gel and semi-solid mass. Furthermore, the water can hydrolyze the triglycerides thus forming a new fatty acid and diglycerides. Eventually, pretreatment at 70°C, 400 kPa, with methanol and sulfuric acid is typically used to reduce the amount of FFAs. This stage is however followed by glycerin washing stage to remove water before alkaline trans-esterification and methanol recovery by vacuum distillation at 70°C.

Acid-catalyzed trans-esterification (by sulfuric, phosphoric, hydrochloric or organic sulfonic acid) is largely ignored because slow reaction rate and large methanol to

triglycerides ratio, which should be raised at 30:1 to 50:1 for optimal yields, hence introducing larger reactor and distillation towers. Furthermore, additional hexane-based and methanol/water stages are introduced in the case of low cost oils for limitation of emulsion. However, it does not require pre-treatment, and studies are under advancement, even if, to the author's knowledge, no commercial plants are under exercise [Zhang, 2003].

Feedstock with very high concentration of FFA are also esterified with methanol under high pressure and temperature, rather than using the catalyst process, in continuous tubular reactor at 100 bar and temperature between 180°C and 240°C. Methanol and water are then separated from the oil phase in de-methanolisation/de-watering column.

2. Accident case histories in biodiesel power plant

Any industrial plant processing flammable materials may incur in severe accidents. Within oil and chemical industries, Duguid (1998) have stated that most incidents occur during shutdown (15%), start-up (14%), maintenance (11%) and abnormal operations (13%), e.g. 50% of the total number of accidents. Furthermore 22% of total incidents are related to tank usage. Remaining 38% of accidents may be related to process.

With specific reference to the plant operations, thus excluding transportation accidents with following fire of biodiesel outside the border of process site, historical analyses [ASB, 2008; Saraf, 2009] have demonstrated that almost all accidents refer to methanol vapors. In some cases, domino effects produced fires of oil stored in the plant. More specifically, according to Saraf (2009), in 3-year period (2006-2009) there were 8 fires and 6 explosions in biodiesel facilities in the U.S., i.e. 5 incidents per year. These data are quite impressive if considering that in most cases the total destruction of plants occurred and that the number of large plant operating in US is about 200.

In Table 1, a short description of accidents occurred in the sole year 2009 is reported.

Date	Plant	Location	Scenario	Description
May 24	Minnesota Soybean	Brewster (MN)	Fire, Explosion	Causes not known
Jun 15	Midwest Biorenewables	Toledo (OH)	Fire No injuries	A vacuum-control valve on vacuum-refining vessel failed to work, causing implosion
Jul 17	Columbus Foods	Chicago (IL)	Explosion 2 workers injured	Workers mixing chemicals
Sept 24	New Eden Energy	St. Cloud (FL)	Fire, Explosion No injuries	Accident started in a warehouse containing tons of methanol and biodiesel

Table 1. Short description of accidents occurred in US in 2009 involving biodiesel.

The common point between the companies listed in Table 1 is the relatively low dimension and capacity of plants. Quite strangely, no injuries or major incidents are reported in recent years in Europe for the biodiesel industry, over 65 plants operating (data of 2006). This evidence should be clarified but it is clearly related to the dimension of plants.

3. Emerging risks of biodiesel production

Despite biodiesel oil status as safe substance [Krawczyk, 1996], the production process can be dangerous as methanol can turn plants to be vulnerable to fire and explosion, if not properly engineered and operated. However, several issues are emerging due to the increasing capacity of plants, which have driven up on-site volumes of highly hazardous chemicals, thus resulting in higher risks. Indeed, plants with capacity larger than 100,000 tons year⁻¹ has been proved to be the only processes economically feasible with higher-value virgin oil, yielding higher net annual profit and lower break-even price [You et al., 2008]. Economical considerations for the increase of production are similarly related to the increasing cost of vegetable oils and, for low cost feedstock, to the introduction of pre-treatment process for acid-catalysed trans-esterification.

That trend is clear in Figure 2, which shows the plant capacity distribution and number in US (as elaborated from data published in www.biodiesel.com, 2008). The production ranges from few tons per year to 300,000 tons/year production plants. Most of plant works with multiple feedstock hence both virgin oils and waste oils.

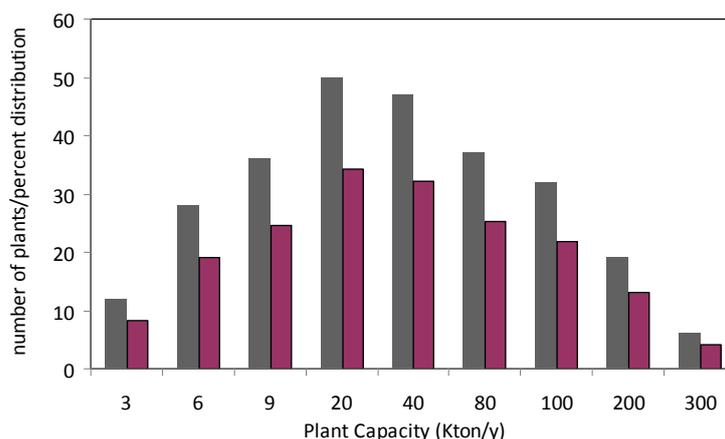


Figure 2. Number (left bar) of active biodiesel production plant in US and percentage distribution (right bar) vs. plant capacity. Elaboration from www.biodiesel.com, 2008.

The growing plant capacity clearly enhances the hazard of biodiesel production and the consequences of accidental scenarios, due to the increased complexity of plants, due to the number and dimension of equipment, due to the larger inventory of chemicals. The modification in plant characteristics when increasing the plant capacity may be observed if checking data of Zhang and ASB, i.e. comparing 8000 tons/year and 100,000 tons/year production plant (Table 2).

Quite clearly, the total risk is increased by more than an order of magnitude in the case of FAME distillation tower and washing column. Two or more order of magnitudes should be than considered for 300,000 tons/year plants. These data should be finally combined with failure frequencies of equipment as given by ASB (2008), as in Table 3. For the evaluation of Table 3 and for the following analysis, it should be noted that the ASB plant in Hong Kong is a recent 100,000 m³ capacity plant. A buffer tank for total

capacity of 500 m³ of methanol (working time of about two weeks) is adopted. Hence, 1 barge (1000 tons) per week is normally received by the nearby harbor. In the case of impossibility of sea transport of methanol, 2 road tanker (10m³) per day are used.

Type		8000 tons/year	100,000 tons/year
Transesterification Reactor	DxL,number	1.8x5.4, 1	2.7x8.1, 3 parallel
Neutralisation Reactor	DxL,number	0.3x1.0, 1	0.7x2.3, 1
Washing Column	DxH,number	0.8x10.0, 1	0.8x10, 12 parallel
FAME Distillation Tower	DxH0,Number	1.2x12.0, 1	1.2x12, 12 parallel
Methanol Buffer Tank	Vol m ³	5	500

Table 2. Equipment size and costs for biodiesel industry by varying production capacity. D, L and H are diameter, length and height, respectively in m (ASB, 2008).

Vessels	Leak Freq. (per year)	Rupture Freq. (per year)
Esterification vessel	2.2×10^{-4}	2.0×10^{-5}
Methanol buffer tank	1.1×10^{-4}	1.0×10^{-5}
Pipe reactor 350m	1.75×10^{-4}	3.5×10^{-5}
Methanol recycle tank	1.1×10^{-4}	1.0×10^{-5}
MEK buffer tank	2.2×10^{-4}	2.0×10^{-5}
Road Tanker	-	2.0×10^{-6}

Table 3. Failure Frequencies in Process Area and transportation (ASB, 2008).

The work of ASB (2008) has presented also the main contribution to Potential Loss of Life (PLL) and the societal risk for a 100,000 tons/year plant located on the coast of Hong Kong. The absolute value of PLL is 6.83×10^{-7} per year for the specific condition of that site. The study evaluates also the relative contribution of each scenario over the entire set of analyzed accident, which may then be generalized.

More than half (55%) of PLL per year is given by methanol leak or rupture from pipeline resulting in explosion of vapors (VCE). The total contribution of methanol is 70% if adding the risks related to the trans-esterification reactor, the methanol tank risks and the neutralization tank.

With respect to the societal risk, the process risks represent almost the total risk per year for a total number of fatalities N between 3 and 10. For greater values of N, the tank farm accidents are the only contribution. Transportation risks are comparable to other risks only for N = 10 and for 1 person.

References

- ASB Biodiesel (Hong Kong) Limited, Development of a Biodiesel Plant at Tseung Kwan O Industrial Estate, Environmental Impact Assessment Report -Executive Summary, Environmental Resources Management, Hong Kong, 6 October 2008.
- Conneman J., Fischer J., Biodiesel in Europe 1998: Biodiesel processing technologies, Liquid Biofuels Congress, Brasil, 1998.
- Freedman, B., Pryde, E.H., Mounts, T.L., Variables affecting the yields of fatty esters from transesterified vegetable oils. *Journal of the American Oil Chemists' Society*, 1984, 61,1638-1643.
- Duguid, I.M. Analysis of past incidents in the oil, chemical and petrochemical industries, *Loss Prevention Bulletin, IChemE*, 1998, 142, 3-6.
- Harvey et al. 2003, Continuous Oscillatory Flow Reactor (OFR)
- Hill J., Nelson, E., Tilman, D., Polasky, S., Tiffany D., Environmental, economic, and energetic costs and benefits of biodiesel and ethanol biofuels, *Proc. Natl. Acad. Sci.* 2006, 103, 11206–11210.
- Krawczyk T., 1996, Biodiesel. *INFORM 7*, 801-822.
- Kreutzer U.R., Manufacture of fatty alcohols based on natural fats and oil, *J.Am.Oil Soc. Chem*, 61, 343-348, 1984.
- Lotero E., Liu Y., Lopez D.E., Suwannakaran K., Bruce D.A., Goodwin Jr. J.G., Synthesis of biodiesel via acid catalysis, *Ind. Eng. Chem. Res.* 2005, 44, 5353–5363.
- Ma F., Hanna M.A., Biodiesel production: a review, *Bioresour. Technol.* 1999,70, 1–15.
- Mannan M.S., Wang, Y., Zhang, C., West, H.H., Application of Inherently Safer Design Principles in Biodiesel Production Process, *Proceedings of Hazard XIX, Instituto of Chemical Engineers, Manchester, UK*, 28-30 2006, pp.982-989.
- Noureddini H., Zhu D., Kinetics of Transesterification of Soybean Oil, *J.Am. Oil Soc. Chem*, 1997, 74, 1457-1463.
- Pinto A.C., Guarieiro L.L.N., Rezende M.J.C., Ribeiro N.M., Torres E.A., Lopes W.A., de P.Pereira P.A.; de Andrade J.B., Biodiesel: An Overview. *J. Braz. Chem. Soc.* 2005, 16, 1313–1330.
- Van Gerpen J.; Shanks B.; Pruszko R.; Clements D.; Knothe G.; Biodiesel Production Technology, August 2002- January 2004, NREL/SR-510-36244, National Renewable Energy Laboratory, Colorado.
- Wesseler J., Opportunities ('costs) matter: A comment on Pimentel and Patzek "Ethanol production using corn, switchgrass, and wood; biodiesel production using soybean and sunflower, *Energy Policy* 2007, 35, 1414–1416.
- You Y.-D., Shie J.-L., Chang C.-Y., Huang S.-H., Pai C.-Y., Yu Y.-H., Chang C.H., Economic Cost Analysis of Biodiesel Production: Case in Soybean Oil, *Energy & Fuels*, 2008, 22, 182–189
- Zhang Y., Dubè M.A., McLean D.D., Kates M., Biodiesel production from waste cooking oil: 1. Process design and technological assessment, *Bioresour. Technol.*, 2003, 89, 1-16.
- Saraf S., <http://risk-safety.com>.