The risk of biodiesel production by trans-esterification of oils

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1. Introduction

Trans-esterification of triglycerides of virgin oils or refined/edible oils by using methanol and alkaline catalysts [1-3] is nowadays largely adopted (Figure 1).

![Image](image_url)  

**Fig. 1.** Trans-esterification reaction of triglycerides by methanol to methyl esters (biodiesel) and glycerol.

The R groups in Figure 1 are generally fatty acid chains (C12 to C20) as laureate, palmitic, stearic or oleic acids. The alkaline-catalyzed reaction is performed at about 60°C (near boiling temperature of methanol) and ambient pressure in simple batch, stirred tank reactor [4], or combined stirred tank reactor (STR) at 400 kPa [5,6] with high yields. Sodium or potassium hydroxide, or their methoxides (e.g. potassium methanolate, CH₃OK) are typically adopted as catalysts. Typical molar ratio of methanol to triglycerides in alkaline-based process is 6:1 [7], i.e. higher than stoichiometric, in order to drive the equilibrium to maximum ester yields. Furthermore, methanol excess improves the reaction rate and reduces the residence time.

The products exiting from the main reactor are in two liquid phases, which are separated by settling tank often followed by centrifugation. The two streams, the glycerol-based and the Fatty Acid Methyl Esters (FAMEs) which constitutes 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. Due to FAME and glycerol thermal instability, vacuum distillation at low temperature (below 150°C) conditions are adopted in this stage.

Often, before the methanol distillation, FAME and glycerol-based streams are neutralized with mineral acids. The methanol stream is then purified by vacuum distillation to remove water and other contaminants before its recycling to the reactors [4].

To achieve the stated technical international standard (EN 14214, ASTM D6751) the FAME stream is then purified with water in liquid-liquid extraction washing column. The purified
FAME stream is further dehydrated by water vacuum distillation. After neutralisation, crude glycerol with 85% purity is typically obtained. The main impurities are the salts derived from catalyst neutralization. Several techniques are then proposed to purify crude glycerol but the most used is 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. Soaps 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, a pre-treatment process at 70°C, 400 kPa, with methanol and sulphuric acid is generally adopted in order to reduce to negligible values the amount of FFAs before trans-esterification reaction. This pre-treatment phase includes a methanol recovery by vacuum distillation for removing water before alkaline trans-esterification. Furthermore, the necessity of sulphuric acid neutralization before the trans-esterification stage leads to larger use of basic catalyst and salts production. For the sake of completeness, it should be cited that several studies are under development for new processes based on a single acid catalysts as sulphuric, phosphoric, hydrochloric or organic sulfonic acid [3,5]. These acid-based processes do not require pre-treatment, but are characterized by slow reaction rate and larger methanol to triglycerides ratios, which can reach 30:1 to 50:1 for optimal yields. The increased amount of reactant leads also to the use of larger reactor and distillation towers and subsequent increased safety and economical issues. Furthermore, additional hexane-based and methanol/water stages are introduced in the case of low cost feedstock oils for limitation of emulsion. Another disadvantage of the acid-catalyzed process is related with the corrosive action of the liquid acid catalyst and to the high quantity of by-products: a plant of 10,000 t/y of biodiesel co-produces 2000 t/y of CaSO₄ [3,8]. To the author’s knowledge, no commercial plants are under exercise with acid-based processes.

Processes at very high temperature and pressure without catalyst (e.g. supercritical condition: 350–400 °C; 100- 250 bar), have been also proposed in the literature, but the problem linked with the high investment cost necessary for this type of technology has limited their diffusion [9].

2. Results and discussion

The relevant accidents occurred in the biodiesel industry in the last decades have been recently presented and analysed in the open literature [10-13]. Results are not reported here for the sake of brevity, but they show clearly that methanol and methoxides fires or explosions are essentially related to transportation activities, maintenance operations and, in few and relatively small accident cases, the tank farm area where few tons of methanol are stored (buffer tank and recycling tank). Hence, the production process during normal operation has a very good record on accidents with respect to the most toxic and flammable materials.

On the other hand, some anomalies result if considering the entire process, and more in particular the neutralisation steps. Indeed, several large accidents have occurred after using sulphuric acid as neutralisation agent of glycerol-based by-products, either before after the distillation operation for methanol separation or after the same operation. Almost, all accidents reported in the literature have occurred in USA, whereas no accidents are reported in Europe, despite the Seveso Directive applies for most of large biodiesel production plant due to the large amount of methanol, i.e. information on near-misses or accidents are due to the authorities when occurring. Eventually, as cited above, our analysis has concluded that the main difference is due to the use
of sulphuric acid instead of the phosphoric acid, as generally advised. That because the prices of goods and commodities have been dramatically affected and increased by worldwide economical crisis of last years, and the sulphuric acid has become by far cheaper than the phosphoric acid, despite the production of sodium or potassium phosphate as fertilizer. Indeed, the use of the cheaper acid in this low-revenue industry may be hazardous if large excess of acid and higher temperature (eventually produced by the reaction of sulphuric acid with glycerol by-product reagents) are produced. The main reaction is possibly the formation of propenal, or acrolein, following classical dehydration reaction from glycerol [14]:

\[
\text{K}_2\text{SO}_4 \text{ or } \text{KH}_2\text{SO}_4 \quad \text{or } \text{H}_2\text{SO}_4 \quad \text{Heat}
\]

\[
\text{HO}_3\text{OH} \quad \rightarrow \quad \text{H}_2\text{C} = \text{C} = \text{O}
\]

*Fig. 2. The reaction of glycerol to acrolein.*

The reaction needs heating of liquid to 170°C or above. Sulphates may catalyze the formation rate of acrolein, whereas the sulphuric acid may decrease the decomposition of the same gaseous substance [15]. Acrolein is strongly toxic and may cause severe irritation to operators. The boiling point is 53°C and may be pressurise the neutralisation reactor. If sparked, it may explode in the vapour section. Further analysis are however necessary for complex mixtures as the glycerol by-product, which contains also other FAMEs residual, the catalyst, soaps and others. E.g. when large excess of sulphuric acid a competitive reaction of methanol to dimethyl-sulphate, however characterised by very slow rate, should be also considered; or methanol and proton may form di-methyl ether, which is highly flammable and may ignite easily, but in the presence of water [16]. All these reactions need however high temperature, which may only obtained by the occurrence of local inefficient heating during reaction of sulphuric acid with alkaline catalyst.

3. Conclusions

Biodiesel safety is mainly related to methanol fires and explosions. However, it should be noted that most of accidents involving methanol have occurred in “backyard” utilities, where discontinuous operations are adopted, especially during maintenance activities. On the other hand, the number of plants with capacity larger than 100,000 tons per year is constantly growing worldwide. For such large plants, where safety management is more aware of hazards, the number of accidents involving methanol is negligible and could be the main reason for the absence of large scale accidents in Europe, where backyard plants are rare. Economical reasons have addressed to the use of sulphuric acid in the neutralisation process of glycerol by-products, thus introducing new risks, due to the pressurisation of the reactor when excess acid is used. To this regard, it is important to note that, in general, several operations involving large use of chemicals and large consumption of energy are necessary for the purification of transesterification products, and that these problems are mainly addressed by the use of homogeneous catalysts, which are not easy to remove from the reaction products. A solution is the use of heterogeneous catalysts but, to the author’s knowledge, only one process by the Institute Français du Petrole (IFP) is operative in the world. When heterogeneous catalysis is adopted, neutralization step, biodiesel washing and glycerol distillation may avoided or simplified. On the other hand, the process is more hazardous for the higher pressure (200°C – 250°C, 40 bar – 70
bar) and temperatures adopted. Further analyses are required for effective advantages, in terms of risks, for the two catalytic options.

4. References