Biodiesel : a case study of the impact of new rules regarding the classification and labelling of physical and chemical properties of chemicals

Agnès Janes, Guy Marlair, Patricia Rotureau

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A.Janes, G. Marlair, P. Rotureau
Institut National de l'Environnement Industriel et des Risques (INERIS),
Parc Technologique Alata, BP2, 60550 Verneuil-en-Halatte, France, agnes.janes@ineris.fr, guy.marlair@ineris.fr, patricia.rotureau@ineris.fr

1. Introduction

Biodiesel and any co-products or intermediate chemicals produced and used from the biodiesel industry fall under the scope of the regulation related to chemical substances.

The criteria and methods for classification of physical hazards of substances and preparations used so far in the European Union were defined since 1967 in 67/548/EEC Directive [1] so called "substances Directive" and in 1999/45/EC Directive [2], dealing with preparations.

The European regulation CLP [3] - Classification, Packaging and Labelling - came into force on 20 January 2009 and implements the recommendations of Globally Harmonised System – so called GHS - in the European Union. CLP Regulation is an essential tool for the implementation of REACh Regulation [4]. The GHS is developed at the international level and describes the classification criteria of the hazards of chemicals. It also provides new harmonized elements related to safety information on these hazards. These are intended to develop new labels and material safety data sheets. It is expected that the 67/548/EEC and 1999/45/EC Directives are repealed with effect from 1st June 2015. It corresponds to the end of the transitional period before full implementation of the CLP Regulation for mixtures. Full enforcement for substances will be effective from 1 December 2010.

This paper provides a comparison between previous EU on the one hand and CLP on the other hand regulation criteria and methods, focusing on physical and chemical hazards. The impact of these new rules on the biodiesel industry is specifically investigated.

2. Update of new rules about physical and chemical hazards evaluation in EU

CLP Regulation modifies the rules on classification and labelling for substances and mixtures (hazard categorisation, labelling, MSDS ...). Enforcement of CLP involves the shift from 5 categories for physical hazards in the EU previous system to 16 classes in the new one. Some hazard categories are modified and new classes do appear.

Therefore, significant differences appear as to the assessment of physical hazards between the EU classification and labelling system applied so far and in the CLP Regulation:

- reorganization of the hazards already defined,
- definition of new hazard classes, such as "Gases under pressure", "Self-reactive substances and mixtures" and "Corrosive to metals",
- modification of criteria and thresholds for the classification and/or assessment methods. This is true for many hazard classes and differences are particularly significant for "Oxidising solids" and 'Explosives" classes. Only two hazard classes are strictly identical in the two classification systems: "Pyrophoric solids" and "Pyrophoric liquids".

As an example, table 1 below provides the changes involved for the classification and the labelling concerning the “Flammable liquids” class. Although the evaluation method - which consists in flash point measurement - does not change, thresholds selected for classification are modified. This increases the severity of classification.

Table 1: Comparison between “Flammable liquids” classification in old and new systems, based on ebullition temperature and flash point value

<table>
<tr><td>Flash point</td><td>< 0°C</td><td>< 21°C</td><td colspan="2">< 23°C</td><td>≤ 55°C</td><td>≤ 60°C</td></tr>
<tr><td>67/548/EC Directive</td><td>  if T_{eb} ≤ 35°C: Extremely flammable - R12
if T_{eb} > 35°C: Flammable - R11</td><td>  Easily flammable - R11</td><td colspan="2">No pictogram
Flammable - R10</td><td colspan="2">Not included in « Flammable liquids » class</td></tr>
<tr><td>CLP Regulation</td><td colspan="3">  if T_{eb} ≤ 35°C: Flammable liquid Cat. 1 - Danger - H224
if T_{eb} > 35°C: Flammable liquid Cat. 2 - Danger - H225</td><td colspan="3">  Flammable liquid Cat. 3 - Warning - H226</td></tr>
</table>

- T_{eb}: ebullition temperature
- Hazard statements:

R12: Extremely flammable	H224: Very highly flammable liquid and vapour
R11: Easily flammable	H225: Highly flammable liquid and vapour
R10: Flammable	H226: Flammable liquid and vapour

So far, every industry that uses a family of chemicals, such as biodiesel, is - more or less - impacted by the implementation of the CLP Regulation. It requires significant changes in current benchmarks related to classification and labelling of hazardous chemicals. This implies that each industry make an overview analysis concerning expected evolution.

3. How is the biodiesel industry impacted?

Biodiesel has been produced on an industrial scale in the European Union since 1992, largely in response to positive signals from the EU institutions. In the transport sector, it can be used both when blended with fossil diesel fuel and in pure form. Today, there are approximately 120 plants in the EU producing annually up to 6,100,000 tonnes of biodiesel. These plants are mainly located in Germany, Italy, Austria, France and Sweden [5].

Biodiesel is typically produced through the reaction of a vegetable oil or animal fat with methanol (which is preferred for cost reasons) or ethanol, in presence of a catalyst, to yield methyl or ethyl esters, i.e. mainly called FAME for fatty acid methyl ester and FAEE for fatty acid ethyl ester, and glycerine.

Biodiesel derived from rapeseed oil is the most common biodiesel available in Europe, while soybean biodiesel predominate in the United States [6]. Most common catalysts are sodium or potassium hydroxide, sodium or potassium methoxide and boron tri-fluoride [6] and [7].

In fact, “biodiesel” covers a wide range of products: there are about 50 substances on EINECS that may be manufactured and use as “biodiesel” [8]. The EU has published guidelines in compliance with CEN Standard - EN 14214 [9] - in order to insure consistent quality and performance. Despite these specifications, there is enough leeway as regards to the composition and physical and chemical properties of biodiesel.

Table 2 shows the changes involved for the physical and chemical hazards classification for the most common alcohols and catalysts used in the biodiesel industry. It indicates that among these examples, alcohols classification is impacted and two new classes appears concerning the catalysts.

For diesel fuel, FAME, FAEE, vegetable oils and glycerine, classification do not change, considering the “Flammable liquids” class. In both systems, all are excluded due to their high flash point value. In fact, it is known that biodiesel is better than diesel fuel in terms of sulphur content, flash point, aromatic content and biodegradability [6].

Classification in other physical and chemical hazard classes should be considered on a case by case basis, considering the physical and chemical properties, which may be obtained from standard tests. Particularly, it is known that sensitivity of vegetable oils to self-heating is highly dependent on its composition. This may lead to classify some of them in the “self-heating substances and mixtures” class.

Table 2: Harmonised physical and chemical hazards classification of some process chemical used in biodiesel production in both 67/548/EEC Directive and CLP Regulation systems [3]

Products (CAS number)	67/548/EEC Directive	CLP Regulation	Health and/or environmental hazards to be considered
Methanol (67-56-1)	Easily flammable R11	Flammable liquid cat. 2 H225	Yes
Ethanol (64-17-5)	Easily flammable R11	Flammable liquid cat. 2 H225	No
Sodium hydroxide (1310-73-2)	-	-	Yes
Potassium hydroxide (1310-58-3)	-	-	Yes
Sodium methoxide (124-41-4)	Easily flammable R11 - R14	Self-heating cat. 1 H251 - EUH014	Yes
Potassium methoxide (865-33-8)	Easily flammable R11 - R14	Self-heating cat. 1 H251 - EUH014	Yes
Boron trifluoride (7637-07-02)	-	Gas under pressure EUH014	Yes

Hazard statements:

R14 and EUH014: Reacts violently with water H251: Self-heating: may catch fire

4. Conclusion

Biodiesel has been demonstrated to have some significant environmental benefits in terms of limited global warming impacts**,** reduced emissions and greater energy independence.

Recent developments of the European legislation, such as CLP Regulation implementation, require every industry to assess the changes involved in classification and labelling of chemical used.

In the case of the biodiesel industry, CLP Regulation induces a more detailed classification of chemical and physical hazards, particularly considering some catalysts. Safety information about these hazards, especially concerning pictograms and hazards statements, is also significantly modified.

Although this is not constitutive of a real revolution, one has to get accustomed with these new practical references. It will take a while for people to shift from previous references to the new ones. This concerns the whole life cycle of chemicals and involves producers, users, authorities, emergency services...

Finally, for the majority of process chemicals used in biodiesel industry, changes in health and environmental hazards classification and labelling must also be investigated.

5. References

[1] Council Directive 67/548/EEC of 27 June 1967 on the approximation of laws, regulations and administrative provisions relating to the classification, packaging and labelling of dangerous substances. *OJ 196, 16.8.1967, p. 1–98*

[2] Directive 1999/45/EC of the European Parliament and of the Council of 31 May 1999 concerning the approximation of the laws, regulations and administrative provisions of the Member States relating to the classification, packaging and labelling of dangerous preparations. *OJ L 200, 30.7.1999, p. 1–68*

[3] Regulation (EC) No 1272/2008 of the European Parliament and of the Council of 16 December 2008 on classification, labelling and packaging of substances and mixtures, amending and repealing Directives 67/548/EEC and 1999/45/EC, and amending Regulation (EC) No 1907/2006. *OJ L 353, 31.12.2008, p. 1–1355.*

[4] Regulation (EC) No 1907/2006 of the European Parliament and of the Council of 18 December 2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), establishing a European Chemicals Agency, amending Directive 1999/45/EC and repealing Council Regulation (EEC) No 793/93 and Commission Regulation (EC) No 1488/94 as well as Council Directive 76/769/EEC and Commission Directives 91/155/EEC, 93/67/EEC, 93/105/EC and 2000/21/EC. *OJ L 396, 30.12.2006, p. 1–849*

[5] European Biodiesel Board, EBB, http://www.ebb-eu.org/biodiesel.php

[6] Biodiesel - A realistic Fuel Alternative for diesel Engines, A. Demirbas, Springer, London, 2008

[7] Biodiesel – Basics and beyond – A comprehensive Guide to Production and Use for the Home and Farm, W. H. Kemp, Aztext Press, Tamworth, Ontario, Canada, 2006

[8] UK REACH Competent Authority Information Leaflet Number 15 – REACH & Biodiesel, January 2009, http://www.hse.gov.uk/reach/resources/biodiesel.pdf

[9] EN 14214, Automotive fuels – Fatty acid methyl esters (FAME) for diesel engines – Requirements and test methods, CEN, 2009