ESTADOS UNIDOS MEXICANOS

GOBIERNO
FEDERAL

SENER

gtz

Recommendations for a mexican biodiesel standard and the infrastructure required for its handling

Vivir Mejor

Recommendations for a Mexican biodiesel standard and the infrastructure required for its handling

gtz

por encargo de
Ministerio Federal de
Cooperación Económica
y Desarrollo

COOPERACION
ESTADOS UNIDOS
MEXICANOS
REPUBLICA FEDERAL DE
ALEMANIA

The Ministry of Energy (SENER) thanks the Deutsche Gesellschaft für Technische Zusammenarbeit (GTZ) GmbH (German Technical Cooperation) for its collaboration and technical assistance in the preparation of this publication. Thanks also to the Mexican Petroleum Institute (IMP) for its participation. The collaboration of the GTZ was conducted in the framework of the technical cooperation between Mexico and Germany through the Program for Sustainable Energy in Mexico, which is commissioned to the GTZ by the German Federal Ministry for Economic Cooperation and Development (BMZ). The opinions expressed in this document are those of the author(s) and do not necessarily reflect the views of the SENER, GTZ and/ or BMZ.

SENER/GTZ
Recommendations for a Mexican biodiesel standard and the infrastructure required for its handling, Mexico, D.F., September, 2010.

Editors and Supervision: Roberto de la Maza, André Eckermann and Martin Amtmann
Authors: Dr. Jens Haupt and Dieter Bockey (AGQM), Dr. Thomas Wilharm (ASG Analytik Service GmbH)

Insurgentes Sur #890, Col. Del Valle, Del. Benito Juárez,
C.P. 03100, México, D.F.
www.energia.gob.mx

German Technical Cooperation
Dag-Hammerskjöld-Weg 1-5
65760 Eschborn/Alemania
www.gtz.de

Address in Mexico:
Torre Hemicor, Piso 11
Av. Insurgentes Sur No. 826
Col. Del Valle, Del. Benito Juarez
C.P. 03100, México, D.F.
T +52 55 55 36 23 44
F +52 55 55 36 23 44
E gtz-mexiko@gtz.de
I www.gtz.de/mexico

Table of Content

List of Tables

List of Figures

Abbreviations

AAS	Atomic absorption spectrometry
ABNT	Brazilian National Standards Organization
AGQM	Working group Quality Management Biodiesel reg. Ass. (Germany)
ANP	Brazilian National Agency of Petroleum, Natural Gas and Biofuels
ASTM	American Society for Testing and Materials
BEA	Berlin Energy Agency (GmbH)
CEN	European Committee for Standardization
CFPP	Cold filter plugging point
CoA	Certificate of Analysis
CRT	Continuously Regenerating Trap
EU	European Union
GC	Gas chromatographic
GC-FID	Gas Chromatography using Flame Ionization Detection
HFRR	High Frequency Reciprocating Rig
IBF	International Biofuels Forum
ICP-OES	Optical Emission Spectroscopy using Inductively Coupled Plasma
IMP	Mexican Petroleum Institute
m/m	Percentage per mass
NOx	Nitrogen oxides
RED	Renewable Energy Directive
SCR	Selective Catalytic Reduction
SENER	Federal Ministry of Energy of Mexico
UFOP	Union for the Promotion of Oil and Protein Plants reg. Ass. (Germany)
V/V	Percentage per volume

1 Introduction

With governments and societies becoming more and more aware of the geopolitical, economical and environmental risks of oil dependency biofuels are gaining a rising attention. In Mexico the use of biodiesel as an additive to improve the lubricity of Ultra Low Sulfur Diesel is considered. As biodiesel affects the properties of the final blended fuel agreeing on common standards for biodiesel properties is an important step towards the creation of a national biodiesel market. In consequence to its strong commitment to reduce greenhouse gas emissions the promotion of energy efficiency and renewable energy resources became a key task for the Mexican government in the process to make its energy sector become more sustainable. As one of the first steps in this process on the 2d of February 2008 the “Bill for the Promotion and Development for Biofuels” (Ley de Promoción y Desarrollo de los Bioenergéticos) was passed. The bill sets the basis for the promotion of biofuels in Mexico and initiates the development of instruments, actions, and regulations which allow a further sustainable development of the production and commercialization of biofuels.[1] In this context the report aims at supporting the progress towards the development of technical standards by actively incorporating international experience. The core objective of this report is to provide a coherent proposal for a Mexican technical standard for biodiesel and its blends based on the actual existing international experiences available in the field. For this purpose the report mentions the relevant quality properties of biodiesel making reference to the existing technical standards of Europe, United States and Brazil. From that basis an individual proposal for a Mexican technical standard as well as recommendations for a quality management system are derived. Concerning the former test methods and their respective equipment and operation costs as well as recommendations for the infrastructure required for the handling of biodiesel are given. The introduction to this report (Chapter 1) is followed by two Chapters providing background information on the market (Chapter 2) and some technical issues (Chapter 3). Chapter 4 gives an overview on the standardization of biodiesel at the international level preparing the basis for the derivation of a proposal for a Mexican biodiesel standard in Chapter 5. The next chapter (Chapter 6) gives information and recommendations for quality management in the production, transport and storage infrastructure. The study finalizes with a reflection on the necessary steps the report identified (Chapter 7).

---

[1] Ley de Promoción y Desarrollo de los Bioenergéticos

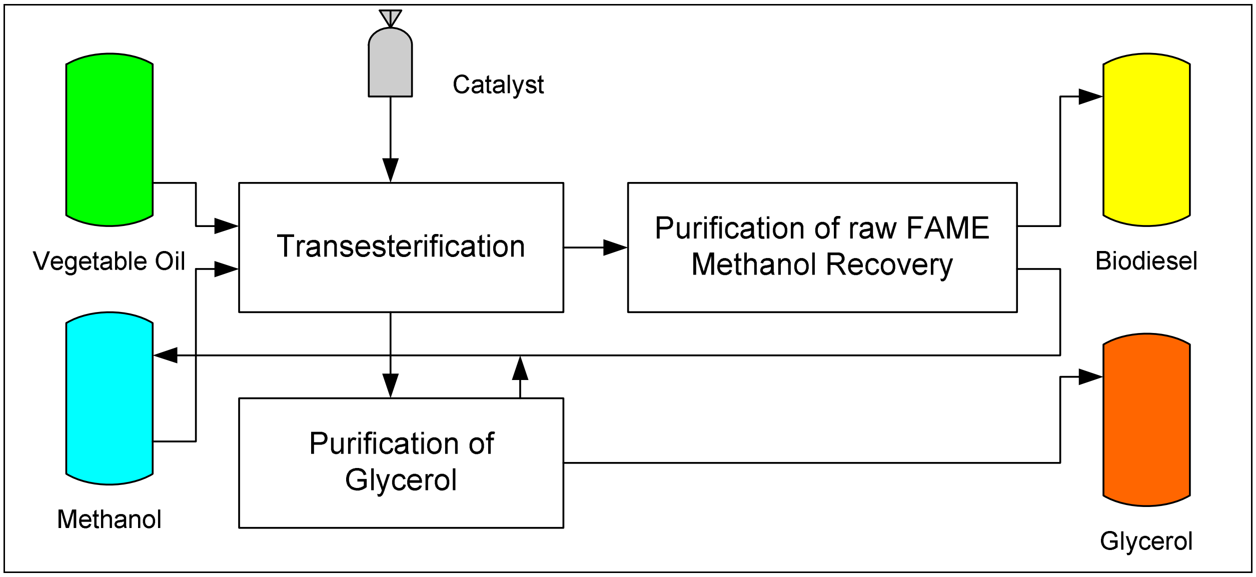
2 International markets and trends

2.1 Biodiesel production

Basically, the success story of biodiesel is based on the fact that vegetable oil as input material is converted into fuel by transesterification and that fuel has about the same energy density as diesel fuel and can be used as pure fuel or mixed with diesel fuel in practically all diesel engines under certain conditions. So biodiesel and its raw materials are as much eligible for transport as are fossil crude oil and fuels and - not least for this reason – have become internationally traded commodities. Biodiesel produced from rapeseed oil, soybean oil or palm oil is traded as a commodity all over the world.

Transesterification production process

Image 1: Basic process units of a biodiesel plant



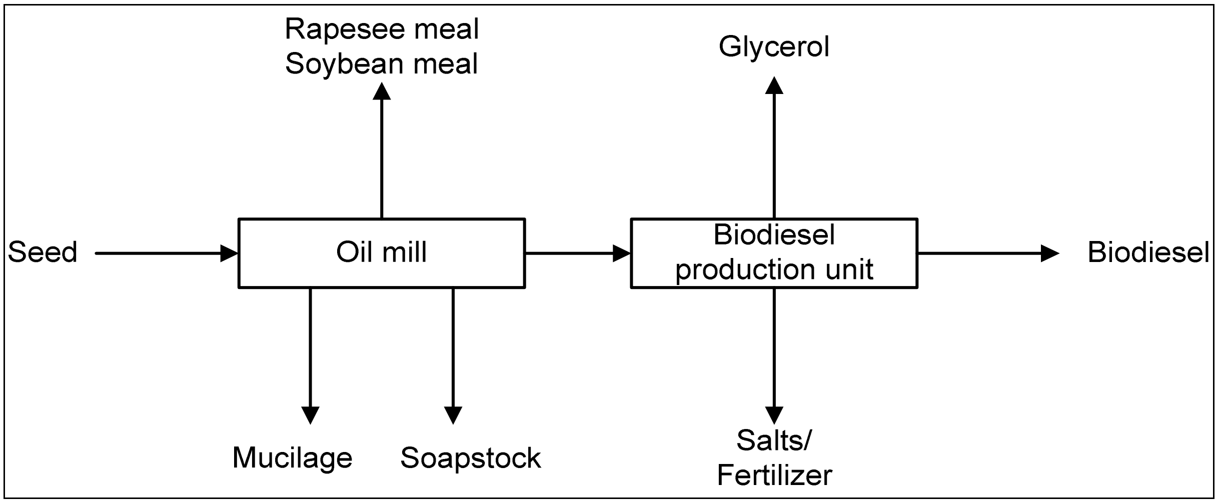
Source: AGQM

Biodiesel is produced by transesterification of glycerol esters in the presence of either acid or basic catalyst, e.g., KOH, NaOH or sodium/potassium methylate. Vegetable oil or other fatty (triglyceridic) raw material reacts with methanol in presence of the catalyst. This reaction leads to the exchange of the 3-bonding alcohol glycerol by the 1-bonding alcohol methanol. After the reaction the glycerol is a main part of the heavy phase which contains also the used catalyst and unreacted methanol. The upper phase (raw FAME) of the reaction mass contains the fatty acid methyl ester but also methanol and catalyst residues and must be purified in several steps. The process of transesterification has extensively been described in the literature.[2] The methods implemented in the production equipment vary from supplier to supplier and the crude biodiesel or crude glycerol is also treated in different ways. The processes are either batch processes using discrete portions of reactants and multiple repeat of each process step or continuous processes which are feeded permanently with the right portion of the reactants. Small plants have typically no equipment to purify the glycerol phase. Another typical plant design is to precipitate the catalyst using acids and to produce a raw glycerol (60 - 80%). For higher grades it is required to remove water and methanol by distillation. The production of technical or pharmaceutical grade glycerol requires an over-head vacuum distillation at very low pressures. Basically, transesterification is a simple chemical/technological process which can be mastered by personnel trained to operate the appropriate equipment. Compared with other processes for the production of alternative fuels (e.g. hydrogenation of vegetable oil, pyrolysis of biomass or gasification of biomass combined with Fischer Tropsch synthesis), transesterification is fairly cost effective and one of the main reasons why biodiesel plants have been built all over the world.

Value chain

The value-added chain of biodiesel production can comprise not only the production of biodiesel as such but also the processing of the raw materials and the rapeseed for extracting the rapeseed oil for the biodiesel process and rapeseed meal as by-product (see Image below).

Image 2: Substance flow diagram of an integrated biodiesel plant (oil mill plus transesterification)



Source: AGQM

---

[2] The Biodiesel Handbook, G. Knothe, J. Krahl, J. van Gerpen, AOCS Press, Champaign, Illinois, USA

The advantage of these so called integrated plants is that if market conditions change income can still be earned from relocating economic activities or selling the vegetable oil to food producers or as input material in oleo chemical processes. By-products, especially the combination product from rapeseed processing, or soybean meal from soybean processing, constitute major product flows (about 60% for rapeseed and approx. 80% for soybean). These by-products from raw material processing should be looked at individually (quantities obtained and nutritive value) as a function of the respective raw material and should be considered in a sensitivity analysis of different concepts in preparation of an investment decision. A by-product of transesterification is glycerol, which is upgraded to pharmaceutical level and can therefore generate high added-value.

The fact that a continuous supply of raw materials must be ensured if the available processing capacity followed by transesterification is to be utilized to the full needs particular attention. Therefore, the development of the concept as part of an investment decision process must also consider this aspect and include in the consideration domestic raw material sources and also the possibility of importing the raw materials as a risk compensating option (plant capacity utilization). On the request of the Union zur Förderung von Oel- und Proteinpflanzen e. V. (UFOP), the Institute for Economic Research of the University of Munich prepared an overall evaluation of the macro-economic performance of biodiesel production. The evaluation also included the effects on German agriculture as raw material supplier. Although the study already assumed rising imports of raw materials and also of biodiesel in view of the continuous growth of the need for these products, it was found that considering the available biodiesel production capacity of 4 million tons in 2009 about 22,400 jobs are secured, most of them in agriculture, and the prediction of the institute that the domestic rapeseed production from over one million hectares of land will ensure the safe supply of raw materials to the German biodiesel industry also in 2009 has actually come true.[3] [4] [5] However, looking at the sales prospects of biodiesel as pure fuel and also as admixture component, the proviso applies that the fatty acid composition of each raw material (rapeseed oil, soybean oil and palm oil) largely decides the potential use. For example, the fatty acid structure of rapeseed oil has a lower CFPP level (-12 ºC to -14 ºC) without flow improvers whereas biodiesel from palm oil has a comparatively high CFPP, which is explained by the high proportion of saturated fatty acids. On this background, the flexible use of certain raw materials and therefore also their potential export is restricted to certain times of the year, especially to markets with extended cold seasons (e.g. the European Union).

---

[3] www.ufop.de/downloads/Biodiesel_UFOP_report.pdf

[4] The Biodiesel Handbook, G. Knothe, J. Krahl, J. van Gerpen, AOCS Press, Champaign, Illinois, USA

[5] UFOP Annual Report 2008, Berlin, September 2008

2.2 Current biodiesel market in the EU and in Germany

Substantial investment has been made in the expansion of the biodiesel production capacity within the European Union since the year 2000. The present total capacity for biodiesel is estimated to be approximately 16 million tons. The table below shows the capacities of the individual countries of the European Union.

Table 1: Technical biodiesel production capacity and capacity use in EU-27

EU member state	Capacity in 1,000 t	Capacity use in %
Germany	5,100	53
France	1,980	92
Italy	1,566	38
Spain	1,267	16
UK	726	26
Belgium	665	42
Netherlands	571	18
Greek	565	19
Austria	485	44
Poland	450	61
Portugal	406	66
Bulgaria	215	5
Sweden	212	66
Slovakia	206	71
Czech Republic	203	51
Hungary	186	56
Finland *	170	50
Lithuania	147	0
Denmark	140	66
Estonia	135	0
Latvia	130	23
Romania	111	59
EU-27	15,800	48

Source: EBB, UFOP

In many cases, investments were made in the expectation of a constant growth of the market hoping that politics would stick to biofuels as the currently only fuel alternative of sizable quantity. This expectation was underlined by the first-ever adoption of quantity targets for biofuels in the European Union in 2003. However, the quantitative proportions of biofuels in the European directive on the promotion of the use of biofuels (directive 2003/30/EC) were so called indicative targets. i.e., they were not binding on the member states. The introduction of biofuels in the markets of the member states varied correspondingly. Whereas Germany promoted the introduction of biofuels in the market by granting total tax relief without limitation of the amount until July 2006 France, Austria and Italy encouraged the use of biodiesel admixed to mineral diesel fuel by fixing national minimum quotas. The vast majority of member states was slow in promoting the advent of biofuels in their markets. In 2005, the European Commission, in an analysis of the situation, came to the disappointing conclusion that only 1.4% of the fuels consumed in the EU were biofuels. This finding was utterly at variance with the indicative quantity targets of the European Union to gradually raise the consumption of biofuels from 2% in

2005 to 5.75% (energy based) by 2010. Besides, many member states failed to indicate that they were prepared to change their national promotion policies despite the unsatisfactory situation.

Not least with this in mind, the EU Commission, in January 2008, submitted a proposal as part of the EU’s climate protection and renewable energies package according to which the voluntary target was to be changed into a target obligatory for all member states:

1. National targets for the proportion of renewable energies in the total consumption as a function of the corresponding national energy mix (20% for all member states together).

2. Minimum target of 10% for the proportion of energy from renewable sources in the transport sector.

The „Directive on the promotion of the use of energy from renewable sources (2009/28/EC) published in the Official Journal of the EU in June 2009 had been preceded by a heated controversial debate between the European Parliament, the Council of Ministers and the European Commission. Therefore, as a result of that debate, the directive contains regulations and requirements on the demonstration of certain sustainability criteria for the origin, cultivation and greenhouse gas balance of biomass. The table below lists the biofuel need differentiated according to diesel and petrol markets provided the quantity targets fixed are met with biodiesel/bioethanol. However, the biodiesel sector needs to consider that the EU directive makes provision for a proportion of 10% (energy based) in the fuels market, not of 10% biofuels. This means that in addition to biofuels alternative drive energies such as electricity or biogas as fuel in natural gas powered vehicles can be included in the target calculation.

Table 2: EU-Action Plan Biofuels/EU-Summit June 2006/ Proposal of the EU-Commission 2020

	2005	2010	2015	2020
Target Quantity	2%	5,75%	8,0%	10%
Consumption of Diesel[6] [Mio. t]	158,6	165,0[7]	165,0[8]	178,0[8]
Biodiesel Demand[9] [Mio. t]	3,69	11,0	15,3	20,7
Area Demand[10] [Mio. ha]	2,63	7,88	11,92	14,7
Consumption of Gasoline[6] [Mio. t]	124,8	113,6[7]	105,0[8]	113,4[8]
Ethanol Demand[9] [Mio. t]	3,7	9,7	12,44	16,8
Area Demand[10] [Mio. ha]	1,85	4,84	6,2	8,4
Total Area [Mio. ha]	4,48	12,72	18,2	23,1

Source: D. Bockey, UFOP

After the tremendous rise of the oil prices and a biofuel friendly policy in some European countries a lot of investments had been set up. Subsidies in several forms had pushed this process. The expectation was to increase the biofuel quota in the market by price benefit and/or governmental regulations. Existing European regulations on the overcompensation of market disadvantage by subsidies, technical problems fuels containing higher biofuels blend ratios, the sustainability discussion and economical limitations led to a revision of the biofuels policy in several member states. As a result the present situation is dramatic for the biodiesel sector in the EU. According to information from the industry, only about 53% of the biodiesel production capacity was utilized in 2008 although the biodiesel is the biofuel with the biggest market share (see image below) with an increase of consumption from 5.9 million tons in 2007 onto 7.9 million tons 2008 (see table below).

---

[6] EUROSTAT (2002)

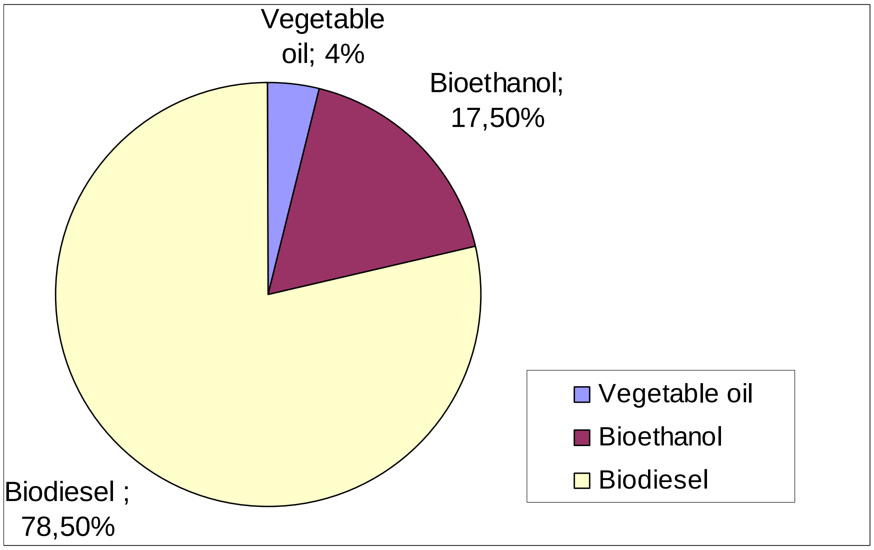
[7] Assumption: Reduction of consumption of gasoline 9 %, Growth for diesel 4 %

[8] Estimation

[9] Basis: Heating Value Diesel: 43 MJ/kg, Heating Value Biodiesel: 37 MJ/kg, Heating Value Gasoline 40 MJ/kg, Hearing Value Ethanol 27 MJ/kg

[10] Biodiesel yield 1,4 t/ha, bioethanol yield 2 t/ha

Image 3: Share of biodiesel and bioethanol of total biofuel consumption of the EU in energy content (2008)



Source: AGQM

Table 3: Biodiesel consumption in different EU member states

Country	Biodiesel consumption	
	2007	2008
Germany	2,906,266	2,477,983
France	1,214,200	2,020,690
Austria	189,674	186,645
Spain	259,000	519,000
UK	270,596	691,335
Sweden	102,762	129,888
Portugal	134,959	132,849
Italy	135,880	557,280
Bulgaria	2,000	29,412
Poland	25,000	340,560
Belgium	91,260	86,149
Greece	81,242	75,680
Lithuania	42,083	45,764
Luxembourg	41,575	41,447
Czech Republic	28,088	75,783
Slovenia	13,006	22,255
Slovakia	77,000	53,070
Hungary	2,000	81,000
The Netherlands	220,000	202,000
Ireland	17,300	40,000
Denmark	0	0
Latvia	1,710	1,927
Malta	1,780	964
Finland	115	11,441
Cyprus	750	14,180
Estonia	498	2,777
Romania	40,000	60,200
Total EU-27	5,898,744	7,900,279

Source: EU-Observer, UFOP

Due to the competition in the European biodiesel market, some plants were running at full capacity whereas others were forced into bankruptcy. The situation facing in the European Union at present is that of a shakeout. It remains to be seen to what extent the available overcapacity will disappear in the years to come. Another aspect which is not receiving the attention of the biodiesel sector it deserves is the fact that the tax relief granted to biofuels is subject to a yearly check for overcompensation which must be submitted to the EU Commission. Besides, it should also be noted that it is a precondition for the blending market that higher blending percentages can only be marketed if the automotive industry gives the go-ahead for them. According to information from the automotive industry, the present 7% (V/V) admixture represent the currently highest possible rate of biodiesel addition which the engines can tolerate. Measured against the total European sales of diesel fuel the total biodiesel market amounts to about max. 10-11 million tons at present. On this background it is a fact that the available production capacity of European biodiesel plants can only be utilized fully in the near future if substantial quantities of biodiesel can be sold to countries outside the European Union. This, however, is not a realistic scenario considering the biofuels policy of countries such as Argentina, the United States, Malaysia or Indonesia. On the contrary, countries such as the United States or also Argentina subsidize the export of biodiesel. For example, the subsidies paid by the United States government have been instrumental to substantial distortions of the market in the European Union. Payment of 1 $ per gallon as subsidy for so called B99 exports started a not insignificant predatory competition in the European Union with the result that even biodiesel producers were forced to import sizable quantities of B99 to survive the price battle. The different penalties which many industry associations demanded from the EU Commission to curb the United States policy of subsidies resulted in the EU Commission deciding, in June 2009, to levy punitive duties on imports of B99. In 2007 alone, some 700,000 tons of biodiesel were imported in the European Union from the United States. Basically, it should be stated that although member states are promoting the market launch of biodiesel and biofuels - generally primarily as blending components – there remains a gap to meet the overall EU targets. In this context the fact that not all member states follow the example of Germany, France or Austria in making full use of the possibility of adding up to 7% (V/V) of biodiesel to conventional diesel fuel as permitted by the European standard for diesel fuel (EN 590:2009) remains a problem.

Considering the total production capacity of about 5.1 million tons in Germany, the German biodiesel industry, in particular, is affected by any change of the national promotion policy. The coalition government agreed to gradually phase out – until 2013 - the complete tax exemption which had been limited in time to the year 2006 and to compensate the expected slump in biodiesel sale for use as pure fuel by fixing blending quotas instead. However, insufficient account was taken to the fact that the price of biodiesel is directly linked to the development of the diesel price and therefore, if the diesel price falls, the competitiveness of marketing the pure fuel would be reduced. As a result of diesel price reduction and energy tax increase the sales of pure biodiesel (B100) dropped from 1.84 million tons in 2007 to 1.16 million tons in 2008. The decline could not be compensated by the higher admixture to diesel fuel from 1.42 million tons in 2007 to 1.64 million tons in 2008. On the contrary, not only fleet operators but especially filling station operators have stopped using or selling biodiesel as pure fuel. In 2007, the service stations network selling pure biodiesel shrank from about 1,900 stations to a mere 200 stations at the beginning of 2009. The network which took years to build is practically non-existing today. This trend will continue as a consequence of the tax rates rising further in the next few years and is already reflected in the domestic consumption statistics. For example, the use of biodiesel as component in blended fuel increased from 510,000 tons in the period from January to April 2008 to 678,000 tons in the same period in 2009. This is the result of increasing the rate of admixture from 5% to 7% (V/V) to diesel fuel. However, the sale of pure biodiesel dropped from 260,000 tons to only 106,000 tons in the same period. Here it has to be considered that most of the pure fuel quantity is sold under contracts concluded last year and as such had to be accepted by the buyers.

The prospects of the pure fuel market this year depend on the degree to which the raw material prices for vegetable oils and therefore the selling prices of diesel fuel develop as competition products. As it is, as a result of the debate in connection with the amendment of the biofuels quota act the increase of the taxation was reduced from 0.06€ to 0.03€ with retroactive effect of January 1, 2009. If the diesel price should go up in the wake of the recovery of the economy, selling biodiesel as pure fuel may temporarily be again economically. Finally, however, the German and the European biodiesel industry are hopeful that the vehicle manufacturers will agree on raising the rate of biodiesel admixed to diesel fuel from maximum 7% today to 10%

(V/V). This corresponds, in Germany, to an increase from 2.1 to approximately 3 million tons of biodiesel. Considering the total capacity of 5.1 million tons, however, German biodiesel producers, in particular, will be forced to develop exports into the neighboring EU member countries and also to countries outside the European Union.

2.3 Sustainable production of biomass – the political framework in the European Union and in Germany

2.3.1 European Energy Directive – RED (part biofuels)

In January 2008 the European Commission presented the draft of a directive for the promotion of the use of energy from renewable sources (Renewable Energy Directive, 2009/28/EU)[11]. This draft has been extensively discussed at least in the so called Trilog, which consists of the European Council, the EU-Commission and the European Parliament. One of the key issues was the discussion about the requirements and corresponding regulations to ensure a sustainable biomass production, because during this time period not only the market price of crude oil but also for biomass food increased. The result was a comprehensive public discussion about the available sustainable biomass potential to produce biomass for energy purposes. The debate “food versus fuel” determined the public discussion. The European Parliament decided on a comprehensive directive which includes specific regulations with the aim to ensure a sustainable biomass production not only within the European Union (EU) but also in third countries exporting biofuels or biomass to the European Union with the purpose to produce biofuels. After publishing the directive (2009/28/EU) in the official papers of the Commission in June 2009, the member states are committed to introduce the directive into national law within the next eighteen months. With the adaption of the renewable energy directive the member states have to fulfill the following aims:

Based on an EU directive by 2020 a 20% share of the overall energy consumption within the EU has to be generated from renewable sources (in the transport sector a 10% share has to be achieved). To reach this target each member state must achieve by 2020 a specific national target of energy from renewable sources calculated as a share of its gross final consumption of energy. For example, while the United Kingdom must achieve a share of energy from renewable sources of 15% based on its gross final consumption of energy, Sweden must achieve a share of 49% and Germany of 18% (2009/28/EC). Additionally the directive particularly encourages the use of so called second and third generation biofuels. Concerning the calculation of the achievement of the 10% target, the contribution made by biofuels can also be produced from wastes, residues, non-food cellulosic material and lignol cellulosic material. The member states also must secure the availability and environmental benefits of the different sources of the renewable energies. In addition, if the percentage of biofuels (biodiesel or bioethanol) blended in mineral oil derivatives exceeds 10%, member states must ensure that this is indicated at the dispensing pump (e.g. labeling) or by flyers to inform the car owners. The directive prohibits the use of biofuels and bio-liquids to meet the directive’s renewable energy targets, national renewable energy obligations and their eligibility for financial support, if they do not meet specified sustainability criteria relating to greenhouse gas saving emissions and biodiversity. The directive introduces sustainability criteria for biofuels and bio-liquids Article 17), a model for

---

[11] eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2009:140:0016:0062:en:PDF

verification of compliance with those criteria (Article 18) and a calculation tool for establishing the greenhouse gas impact of biofuels (Article 19). Especially the calculation tool is rather complex and will cause problems to understand and/or to comply with. The sustainability criteria are the core of the biofuel part of the RED. Independently of whether the raw materials of biofuels or bio-liquids are produced in the EU or in third countries, biofuels and bio-liquids must meet specific greenhouse gas emission savings, must not be produced from raw material obtained from land with high biodiversity value, high carbon stocks, grass lands and in the case of agricultural raw materials cultivated in the EU, their production must be in compliance with EU-environmental requirements on agricultural production which are summarized under the so called “Cross Compliance Regulations”. In particular the directive requires the use of biofuels and bio-liquids to achieve a greenhouse gas emission saving of 34% in the case of installations that were already in operation in January 2008. This threshold shall apply as of April 2013. The threshold increases to 50% by 2017. In addition, after 2017 the saving must be 60% for biofuels and bio-liquids produced in installations whose production started after 2017. EU member states must require economic operators to show that their biofuels or raw materials for biofuels meet the directive’s sustainability criteria. Operators must use a mass balance system ensuring that consignments of raw material or biofuels of differing sustainability characteristics can be mixed. Information about the sustainability characteristics and sizes of the consignments remains assigned to the mixture, and the sum of all consignments withdrawn from the mixture is described as having the same sustainability characteristics in the same quantities as the sum of all consignments added to the mixture. Information submitted by operators must be subject to independent auditing. For this purpose acknowledged certification systems have to be introduced. The directive also provides that the EU may conclude bilateral or multilateral agreements with third countries regulating the sustainability criteria of biofuels and bio-liquids.

2.3.2 The German “Biofuel Quota Act”

On 23 April 2009 the German parliament passed the federal government’s draft bill of 1 December 2008 for the “Amendment of the Promotion of Biofuel”. Apart from making changes in the legislation, such as the reduction of the total biofuel quota in the fuel market by 1% to 5.25% for 2009, parliament has also passed a resolution, in which it calls on the government to ensure that the sustainability standards applicable for the production, delivery and use of biofuel are observed. The Amendment Act stipulates grave changes in the promotion principles from 2015 onwards. The use of biofuel will no longer be based on the obligation to observe quotas but to reduce the emissions of greenhouse gas. The act will thus result in a slower expansion rate for the use of biofuel than expected so far. According to the official reasoning given, the act stipulates in particular to focus the increased use of biofuel on the commitment to reduce the greenhouse gas emissions in the fuel market.

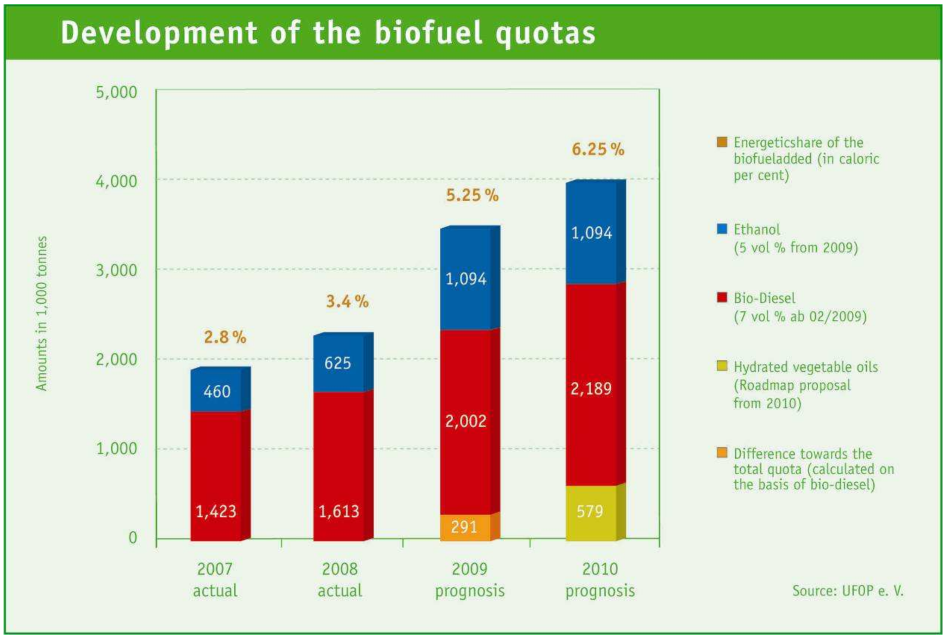
The German government lists a number of reasons for its decision:

- First of all, the sustainability criteria for the biomass production are to be documented and are to be effected not only at national or EU level, but also in non-EU countries.
- Biomass is to be gained from other sources, in order to avoid usage competition.
- The addition of 10% (V/V) of ethanol is not possible for a transitional period of time.
- Biofuel of the 2nd generation with a better climate footprint is not available yet.

The act mainly stipulates the following changes (see also image below):

1. The total quota valid from 2009 onwards will be reduced to the following minimum shares:
    - 5.25 caloric % in 2009 (instead of 6.25%) – with retrospective effect from Jan 1, 2009
    - 6.25 caloric % in 2010-2014 (instead of 6.75% - 8% in 2015)

Image 4: Development of the biofuel quotas in Germany (energetic share of the biofuel added in caloric percent)



Source: UFOP

2. The minimum quota for bio-ethanol in petrol will be 2.6 calorific % from 2010 on (instead of 3.6%)

3. The caloric minimum shares will be replaced from 2015 by a climate protection quota to reduce the greenhouse gas emissions from biofuel by (see also table below)
    - 3% from 2015
    - 4.5% from 2017
    - 7% from 2020.

    It had originally been planned in the draft bill of the 8th Amendment for the Federal Emissions Protection Act of 18 February 2008 to stipulate a reduction in greenhouse gas emissions by 5% in 2015 and a rise to 10% from 2020.

Table 4: Quota act and decarbonization strategy beginning from 2015

Year	Total Quota	Diesel Quota	Gasoline Quota	Co-refining	Greenhouse Gas Quota
2009	5.25%	4.4%	2.8%	-	
2010	6.25%	4.4%	2.8%	max. 3%	
2011	6.25%	4.4%	2.8%	max. 3%	
2012	6.25%	4.4%	2.8%	max. 3%	
2013	6.25%	4.4%	2.8%	max. 3%	
2014	6.25%	4.4%	2.8%	max. 3%	
2015	5.10%[12]			?	3.0%
2017	7.80%[12]			?	4.5%
2020	12.10%[12]			?	7.0%

Source: Gesetz zur Änderung der Förderung von Biokraftstoffen, April 2009, UFOP

Assuming a net contribution of 50% from biofuel for climate protection, a biofuel share of 6 caloric % would be required to meet the climate protection quota of 3% in 2015. It would have to be increased to 10 caloric % by 2020, if the net climate protection contribution was improved to an assumed 70%. The total quota, the diesel quota and the petrol quota will only be valid until the end of 2014.

---

[12] Example: GHG-Quota: 3%, Calculation basis: 58% net-GHG-reduction, corresponding to a quota of 5.1%

4. The minimum share of biofuel can be satisfied by
    - adding biofuel to diesel and petrol
    - pure biofuel (only if full tax rate is paid)
    - adding bio-methane to fuel made from natural gas (new).

5. Biofuel, for which direct state subsidies have already been made available and for which no countervailing or anti-dumping duties have been imposed, will be excluded. This concerns bio-diesel generated from soy from the United States (B 99), on which the European Union imposes already countervailing and anti-dumping duties.

6. The energy tax for pure biodiesel will be reduced for 2009 by 3 cent per liter with retrospective effect. The following tax rates will apply for the coming years (the corresponding tax for fossil diesel: 47.4 cent/l):
    - 18.29 cent per liter in 2009,
    - 24.50 cent per liter in 2010,
    - 30.41 cent per liter in 2011,
    - 42.22 cent per liter in 2012,
    - 45.03 cent per liter from 2013

2.3.3 The ordinance for sustainable production of biomass for biofuels

The coming into effect of the cause for the introduction of sustainability criteria as well as certification and verification systems fueled the intense public debate of „plate versus tank“ concerning the raw materials required for the production of biofuels. Therefore, the Renewable Energy Directive (2009/28/EC) and the EU directive on the quality of fuels (2009/30/EC)[13] contain sustainability requirements, from the cultivation of biomass to the processing and use of bio motor fuels and bio heating fuels. Both directives became effective in June 2009. With the national ordinance for sustainable production of „biofuels“, Germany is the first member state in the EU to apply the sustainability requirements of the European directives in national law. Even if the ordinance will become effective on January 1st 2010, the concrete application will – on the demand of the German Farmers’ Union and of UFOP - be postponed to the 2010 sowing period, i.e., the coming seed and harvest periods are still not affected by the new regulations (subject to the approval of the German parliament on 3 July 2009).

Basically, the sustainability ordinance provides that biomass for use as biofuel must not be cultivated on conservation areas. A precondition for offsetting against the quota obligation and the tax subsidy respectively is that the origin of the biomass, e.g., rapeseed, is documented or

---

[13] eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2009:140:0088:0113:EN:PDF

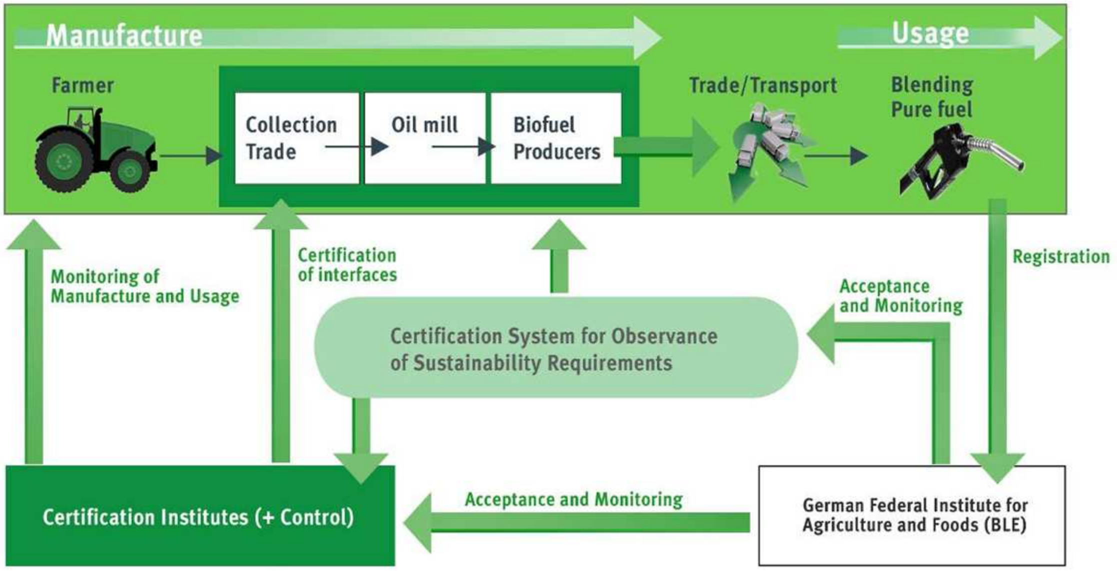
can otherwise be demonstrated. Of importance to farmers are the provisions of articles 4 to 7 of the sustainability ordinance which contain the following essential provisions:

- Protection of areas of high conservation value;
- Protection of areas with high carbon content, e.g., wetlands
- Protection of peat bog

Only biomass produced under these frame conditions can be accounted to fulfill the quota requirement. Regarding the cultivation of raw materials, the requirements of the sustainability ordinance are deemed met if the requirements of good professional practice for cross compliance are complied with. There is need for further clarification regarding the assignment of types of area of high conservation value. Another obligatory requirement is the demonstration that a certain minimum greenhouse gas reducing potential is obtained by the biofuel. The limit is 35% and will be obligatory for available oil mills and biodiesel plants from 1. April 2013. The required greenhouse gas reduction will go up to at least 50% on 1. January 2017. The minimum limit is 60% for new plants starting operation after 31. December 2016. The limit of 35% greenhouse gas reduction can already be demonstrated in the case of rapeseed from European cultivation. The target of 50% potential greenhouse gas reduction is a challenge which can be met in future only if the energy expenditure is optimized further at all steps, i.e., from the production of raw materials, raw material processing and the production of biodiesel.

Another obligation of documentation for which the sustainability ordinance makes provision is that the raw material producer should submit information on the following activities: The protection of soil, water and air, the restoration of degraded areas and the avoidance of excessive water consumption in areas in which water is scarce. The data will be collected - probably from the 2010 sowing period - by the agricultural trading companies, the first so called interface which must belong to a certification system. The ordinance remains the next months under discussion on the national level concerning the concrete requirements of the certification systems and control bodies. Looking at the international competition for raw materials it should be noted that similar requirements are also made for imports of raw materials or biodiesel to the European Union from states like Brazil, Argentina, Malaysia or Indonesia.

Image 5: Sustainable biofuels system for certification and verification



Sustainability verification is issued by biofuel manufacture as last interface, certified by a certification Institute in the course of certification system, both recognised by BLE.

Source: UFOP according to information from BLE

Source: UFOP

3 Technical background information: Technical requirements for the use of biodiesel in engines

3.1 Physical and chemical properties of biodiesel and their impacts

Unlike pure vegetable oil types, biodiesel can be burned in diesel engines in principle without the need of fundamental technical changes. This is because in the production of biodiesel, the high viscosity of the vegetable oil is reduced to a level approximately equal to that of mineral diesel. Thus, after some smaller adaptations, the available facilities for storage, transport and fuelling can be used for biodiesel. The requirements and preconditions of changing a vehicle from mineral diesel to biodiesel as only fuel is described in the product bulletins of AGQM.[14] In the following the most important aspects concerning the suitability of infrastructure for biodiesel are mentioned:

- Basically, before pure biodiesel is used, the vehicle maker should be asked whether the vehicle in question is suitable for the fuel. The written information from the vehicle maker contains certain maintenance requirements (e.g., halving the engine oil change interval for commercial vehicles running on B100 and strict compliance with the driving distance limit of cars running on B7) as precondition of the continued availability of the warranty under biodiesel fuel. Besides, the use of norm-complying biodiesel according to EN 14214, including biodiesel as blend component, is a standard requirement in Europe.
- If biodiesel is used as only fuel or used for blends, the compatibility of the metal in contact with the fuel must be considered. This refers, in particular, to alloys in injection pumps, sealing materials and fuel hoses. Biodiesel can cause corrosion and – because it is a solvent – also cause swelling of unsuitable plastic materials.
- The combustion processes of biodiesel and diesel are different from each other due to differences in their composition as motor fuel and the resulting fuel properties. To remain safely within the statutory emission limits, the engine and the exhaust treatment systems should be adjusted optimally to the fuel. If alternately biodiesel (B100) or diesel fuel is used it is considered good practice to have a sensor to identify the quality or composition of the fuel in the tank. This information helps the engine management system adapt the fuel injection control as required.
- A decisive parameter is the boiling curve of biodiesel, which is clearly higher than that of mineral diesel fuel. Diesel boils in the temperature range of approx. 200-340℃, biodiesel starts at the upper limit of that range and has a narrower boiling range (approx. 330-340℃). The boiling behavior of biodiesel is due to the chain length of the fatty acid methyl ester. The state of engine development (common-rail high-pressure injection) compensates any significantly poorer combustion. But as a result of the high-boiling behavior of biodiesel, biodiesel can enter the engine oil. This happens especially when the vehicle runs only short distances or on low-load modes (e.g., city traffic, stop-and-go) because the engine does reach sufficiently high temperatures under these conditions. What happens is that like with other fuels, non-combusted biodiesel enters the engine oil due to the so called blow-by effect (escape of combustion gases at the piston rings) and the condensation of fuel droplets at the cold cylinder wall. Whereas fossil fuels in general

---

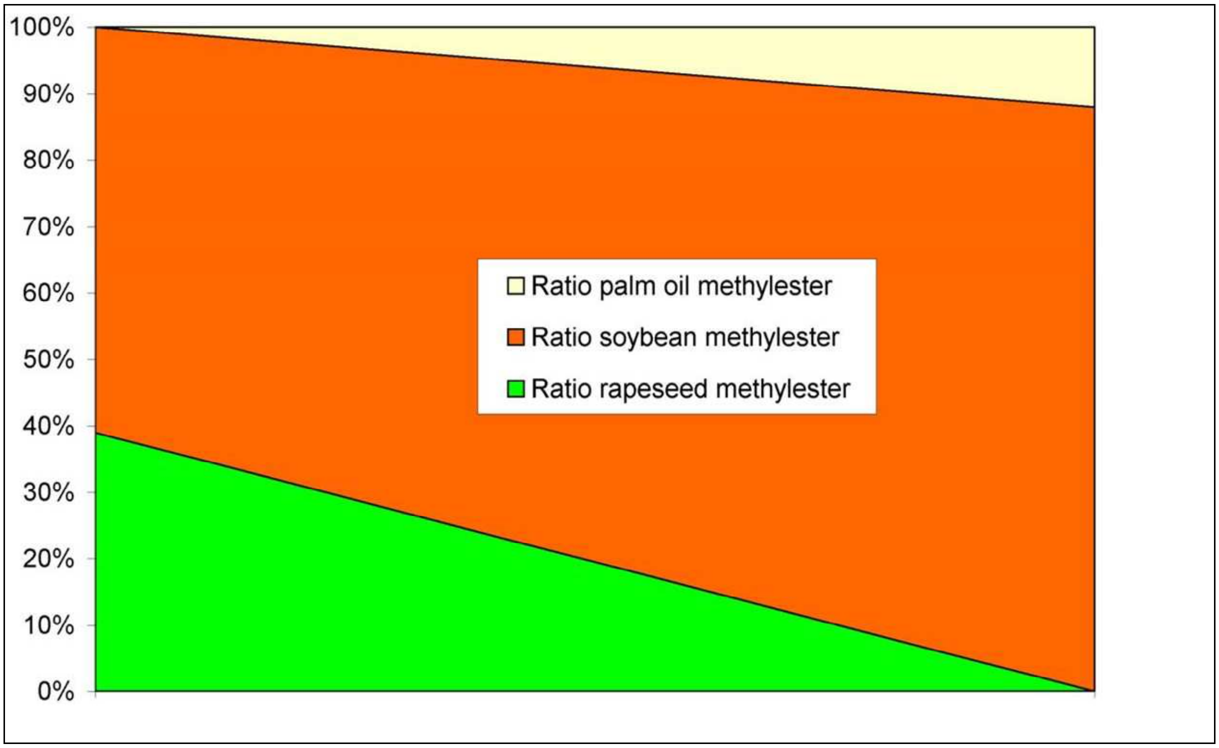
[14] www.ufop.de/downloads/Vehicles_Biodiesel.pdf

evaporate at high engine oil temperatures from the oil, biodiesel remains in the engine oil. The rising concentration of fuel in the engine oil results in a significant dilution of the engine oil which reduces the lubricating function of the oil (in addition to creating the risk of polymerization of fuel/engine oil components). To control the risk of the lubricating film breaking away and the destruction of the sliding surfaces of the piston and the cylinder, the intervals in which the oil is changed should generally be shorter if biodiesel (B100) is used in commercial vehicles. The oil change intervals specified by car makers should be strictly followed if biodiesel blends (B7) are used. Biodiesel also enters the fuel combustion space in mixed fuels (B5, B7 or B10). The entry of biodiesel in the engine oil is caused by the post-injection of fuel into the engine, such as is generally common for the regeneration of closed diesel particulate filters in modern cars and light commercial vehicles (exhaust levels Euro-4, -5 and -6). The particulate filters of these vehicles must be regenerated in regular intervals to reduce the carbon load. For this reason, the carbon is burnt at high temperatures. As the required exhaust temperatures are often not reached during normal driving, the exhaust is heated by post-injection of fuel in the engine. For this, fuel in the engine is injected at a late combustion cycle. The pressure conditions in the cylinder are such that the fuel is not combusted but evaporates. The fuel vapor reaches the oxidation catalyst, where it burns. In the particulate filter, the hot exhaust then burns the carbon. For this reason, vehicles using the regeneration strategy are licensed today only up to B7. This, in fact, precludes – at present - the use of higher biodiesel blends and B100 in new cars and light-duty vehicles. Heavy commercial vehicles, such as trucks and busses using different principles of exhaust cleaning, are not affected. Certain types of cars in which the particulate filters regenerate by the post-injection of fuel downstream the engine do also not have this dilution effect. However, the regeneration strategies are subject to improvement to ensure that as little fuel as possible is needed for the regeneration of the particulate filter. These developments also mitigate the problem of engine oil dilution by biodiesel as blending components in diesel fuel.

- If a vehicle is fuelled up with biodiesel (B100) after an extended period of running on mineral diesel, deposits in the tank and the fuel system can come lose. To prevent the lose material from clogging the fuel filter, the fuel filter should be changed after 2 or 3 tank fillings of biodiesel even if the regular service interval is different.
- Biodiesel is exposed to stronger degradation by oxidation than mineral diesel. Therefore, biodiesel (B100) should only be used if it is certain that the vehicle is used regularly without interruptions of several weeks or months. Aging of the fuel, which tends to be stronger due to heat (high temperature) or strong temperature fluctuation, can result in a critical reduction of the oxidation stability, in addition to polymerization and deposits in the tank. Vehicles with long periods of non-use or which operate on biodiesel and only for a few months in a year, should be parked with the tank and the fuel system full of diesel.

Some chemical and physical properties of biodiesel are similar to those of diesel (e.g., viscosity and cetane number). The chemical structure of the product is different due to the biological origin and the production method. Whereas mineral diesel consists mainly of alkanes and aromatic hydrocarbons, biodiesel essentially contains fatty acid methyl esters of C16 to C18 chain lengths. The fatty acid composition has a substantial impact on the properties of the fuel, especially on the oxidation and cold stability: The higher the number of unsaturated bonds of the fatty acid residue (= the higher the iodine number), the lower the oxidation stability of the fuel. Conversely, the higher the number of saturated bonds, the lower the stability at low temperatures (= the higher the CFPP). The figure below illustrates possible mixing ratios of rapeseed, soybean and palm oil methyl ester which reliably obtain the iodine number of 120 which is considered as a reliable value to prevent accelerated oxidation processes and the formation of sludge. However no direct correlation is given between iodine number and oxidation stability it becomes more difficult to reach good oxidation stability in case of high iodine numbers.

Image 6: Possible biodiesel raw material compositions to achieve an iodine number of 120



Source: AGQM

The fuel properties of biodiesel depend both on the input materials (e.g., rapeseed, soybean or palm oil) and the production method. The table below lists a number of important parameters influenced by the raw material or/and the reaction.

Table 5: Factors influencing the characteristics of biodiesel

Characteristic	Influenced by raw material	Influenced by reaction/technology	Possible cause for deviations
Acid number		X	Reaction turnover, degree of conversion
Iodine number	X		Fatty acid profile
Methanol content		X	Quality of the removal of methanol
CFPP	X		Fatty acid profile
Viscosity	X	(X)	Fatty acid profile
Density	X		Fatty acid profile
(Remaining) glycerides and glycerol		X	Reaction turnover, degree of conversion, phase separation, purification efficiency
Total contamination	X	x	Phase separation/ quality of the raw material
Flash point		X	Methanol residues in the FAME
Carbon residue	X	(X)	Fatty acid profile
Ash	(X)	X	Quality of the raw material
Phosphorus content	X		Quality of the raw material
Cetane number	X		Fatty acid profile
Oxidation stability	X	(X)	Fatty-acid profile and the content of tocopherols, e.g., and additives (oxidation stabilizers)

Source: AGQM

Norm EN 14214 defines the value ranges of the main fuel components which must be complied with if biodiesel is to be used in motor vehicle engines running on biodiesel (B100/B7). The following table lists selected examples of what the consequences can be if the limits are ignored:

Table 6: Impact of violation of standard parameters

Property (EN 14214)	Consequence/comment
Kinematic viscosity at 40 ℃	Fuel delivery problems (fuel pump, injection pump)
Flash point	If the flash point is lower than 100 ℃ , the product is classified as hazardous material/substance (!)
Cold filter plugging point (CFPP)	Engine stops due to crystallization of the fuel in pipelines and in the fuel filter in case of low temperatures
Carbon residue	Cooking in the area of the injection pump and the piston rings (often a problem in case of FAME with high proportion of multiple bonds or glycerol/glycerides)
Ash	Damages exhaust after-treatment systems
Water content	Corrosion problems with diesel/FAME mixtures: Turbidity (in extreme cases even separation of the aqueous phase) and microbial infestation (sludge, filter clogging and possible corrosion)
Total contamination	Engine stops due to clogged filter, possible consequential damage to the injection pump due to poor lubrication/cooling by the circulating fuel
Oxidation stability (induction time)	Filter clogging, precipitation of polymers forming in blends Diesel/biodiesel in the entire fuel system
Acid number	Corrosion problems
Glycerol and glycerides	Carbonization in the area of the injection pump and the piston rings, can be the cause of increased carbon residue
Iodine number	Indicates a poor fatty acid profile, deviations can have a negative consequence for the oxidation stability and the CFPP
Alkali (Na + K) Alkaline earth (Ca + Mg)	Engine stops due to clogged filter (saponification reaction with fatty acids), can also cause the increase of ash

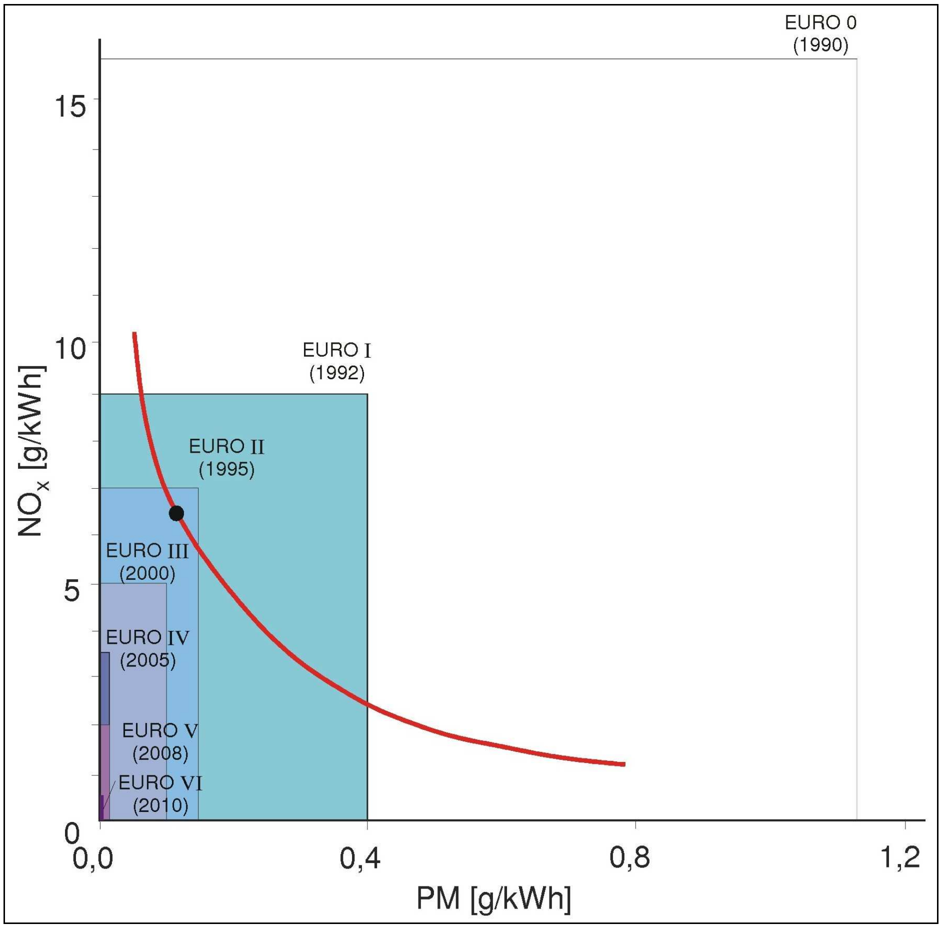
Source: AGQM

Typically of biodiesel is also the content of chemically bonded oxygen (11% m/m) which, on the one hand, is responsible for the slightly lower energy content of biodiesel and, on the other hand, facilitates complete combustion with less carbon forming than in case of mineral diesel.

3.2 Requirements to fulfill the emission demands today and in the future - adjustments of the engine and exhaust after-treatment/ biodiesel quality

With biodiesel as pure biofuel or bio-component in fossil diesel, the requirements of modern engines and of exhaust after-treatment should be observed. Even if biodiesel is similar to conventional diesel (especially the viscosity), they are different in compressibility, spraying, evaporation, ignition, combustion and emission. The emission of nitrogen oxides (NOx) is a critical issue. Biodiesel (B100) causes slightly higher emission than conventional diesel. Rising reaction temperatures cause more NOx to form whereas fewer particles (carbon) are produced at higher temperatures. This opposing effect between NOx and particulate is referred to as trade-off. The phenomena is illustrated in the image below.

Image 7: Trade-off phenomena of internal combustion engines



Source: AGQM

To safely remain within the statutory emission limits the exact control of combustion in the engine (engine management) is essential. As most vehicle diesel engines operate on conventional diesel fuel the engine control is set for conventional diesel fuel in the factory. To optimize the engine operation and exhaust emission for biodiesel, it may therefore be reasonable to set the engine management (most of all, the timing and volume of injection) for that fuel. However, it should be considered that owners may fill their vehicles with conventional diesel fuel or with biodiesel (depending on the availability and the prices of the fuel). To flexibly adapt the engine control to changing fuels, a so called biodiesel sensor was developed by the Institute of Agricultural Technology and Biosystems Engineering in Braunschweig, supported by the Volkswagen AG. The biodiesel sensor has not been used serially either in cars nor in commercial vehicles. Whereas commercial vehicles in the Euro-5 category are still licensed to use biodiesel (B100) pure biodiesel and higher biodiesel blends (> B7) are forbidden in cars of emission level Euro-4 and higher. As explained above, these vehicles have self-regenerating particulate filter systems. Actions to improving the situation inside the engine alone are no longer sufficient to comply with ever stricter emission limits. So a combination of optimizing engine and the exhaust after-treatment is needed. Several different technical solutions of exhaust after-treatments are available for reducing the remaining emission by the engine. The most common are:

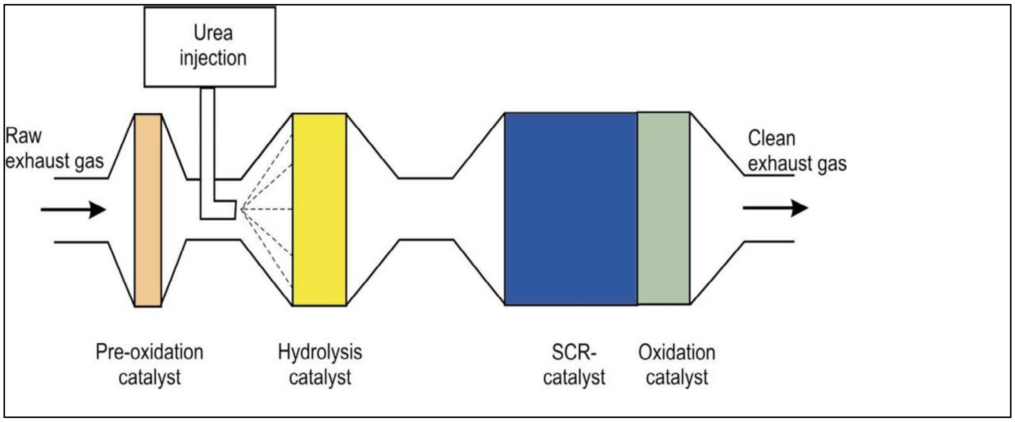
- <u>Oxidation catalysts:</u> Unburned or partially burned fuel, characterized by the so called “soluble organic fraction (SOF)”, consisting of carbon and hydrocarbons (HC), are oxidized to CO2 in upstream by means of oxidation catalysts. Besides, NO is converted to NO2. Oxidation catalysts consist of a ceramic or metal substrate with reactive coating crossed by fine ducts. Gas molecules react while passing through the oxidation catalyst, particles are not separated.

- <u>Particulate filters:</u> They reduce the carbon in the exhaust. There are different versions of surface and band filters whose separation action is mainly due to steric principles (size exclusion). As the load of the particulate filter increases, the exhaust pressure rises. To regenerate the particulate filter, the separated carbon is burned to CO2. Carbon oxidizes at temperature between 550-600℃. This temperature is usually not reached during regular operation of cars. In German cars and light-duty vehicles, the exhaust temperature is mostly raised by post-injection of fuel in the engine. This strategy is referred to as active regeneration. Passive regeneration, on the other hand, does not increase the exhaust temperature but fuel borne catalysts reduce the reaction temperature or the NO2 in the exhaust is used as oxidant. For example, fuel borne catalysts are used in French cars - in combination with reduced post-injection in the engine. Some heavy-duty vehicles are equipped with a so called Continuously Regenerating Trap (CRT) as particulate filter with a passive regeneration strategy: An upstream oxidation catalyst converts NO to NO2, which provides the oxidant for burning the carbon in the CRT. Regeneration is an almost continuous process. NO2 acts as catalyst so that carbon oxidizes already at 200-250℃. NO2 is converted to NO in this process. Hence, there is almost no reduction of NOx by CRTs. CRTs can only be used with ultra-low sulfur diesel because sulfur content over 10 ppm poisons the active catalytic surface of the filter due to the formation of SO2. In view of the very low sulfur content, CRTs are useful in combination with biodiesel.

Concerning the reduction of NOx emissions there are also two common exhaust after-treatment methods available:

- NOx storage catalysts: During „lean” combustion ($\lambda > 1$), so called NOx storage catalysts at first store nitrogen oxides as nitrate. The engine operates in „rich” mode ($\lambda < 0$) in the regeneration cycles, during which the stored NO3 can be converted to N2 (denitrification) by unburned hydrocarbon (HC) and carbon monoxide (CO). A NOx sensor indicates the saturation of the storage material.
- Selective Catalytic Reduction (SCR) system: The image below shows the schematic of an SCR system of the type used for Euro-5 and Euro-6 applications in heady duty vehicles and high-power cars.

Image 8: Principle of actual after treatment systems



Source: AGQM

In the SCR process, nitrogen oxides in oxygen-containing exhaust can be reduced by ammonia in a catalytic converter. Urea is the reducing agent which is injected and which releases ammonia at a hydrolysis catalyst. Unlike ammonia, urea is not toxic and is a water pollution category 1 product (non-polluting). An SCR system typically consists of the following components:

- Pre-oxidation catalyst: To establish an optimal (equimolar) ratio between NO and NO2 for the reduction of nitrogen, some NO is converted to NO2 in the oxidation catalyst.
- Production of ammonia: The urea solution is injected in the exhaust line. The energy of the exhaust causes the hydrolysis/thermolysis of the aqueous urea at the hydrolysis catalyst to form ammonia gas.
- SCR catalyst: Here, ammonia selectively reduces the nitrogen oxides to elemental nitrogen (N2) and water.
- Post-oxidation catalyst: Like with a sealing catalyst, ammonia exiting the SRC catalyst is oxidized to elemental nitrogen.

Generally, there is a risk that the functionality of the after-treatment of exhaust may be affected by trace elements (alkali metals: Na, K; alkaline earth metals: Ca, Mg) and phosphorus: The presence of metals in biodiesel leads to more ash which reduces the permeability and consequently the life time of the filters and catalysts. This requires more maintenance of the exhaust after-treatment system because of the higher specific fuel consumption in comparison with cars and the considerably higher mileage of the engine. Phosphorus is a catalyst poison which reduces the conversion rate at the reactive surface and thereby acts as life limiter. For this reasons, the contents of alkali and alkaline earth metals as well as of phosphorus are limited by EN 14214, whose further reduction is an urgent demand of the automotive industry (the automotive industry demands a zero level).

4 Standardization of biodiesel at the international level

4.1 Description of relevant properties

Biodiesel has to comply with a lot of very different requirements mostly derived from engine based demands. Additionally a fuel standard contains also identification parameters/test which are not directly related to the fuel properties (for example, a typical identification parameter is the density). The Table below gives the most important parameters/tests and explains their relevance.

Table 7: Overview of biodiesel parameters and tests

Property	Unit	Definition	Relevance
Appearance	-	The appearance of FAME should be "clear" which means: No visible turbidity or sediments. Also a colored but homogeneous FAME can be accepted if the said condition is matched.	Easy to check and can help to identify unclean handling conditions or critical behavior due to unexpected components. Should be tested for each batch.
Acid value	mg KOH/g	The acid value of oils gives an indication of the quantity of fatty acids present in the sample.	High fuel acidity is linked with corrosion and engine deposits. Should be tested for each batch.
Carbon Residue	%	Carbon Residue is the percent of coked material remaining after a sample has been exposed to high temperatures. Results are reported as a percentage of the weight of the original sample.	The diesel carbon residue property is a measure of the tendency of diesel to form carbonaceous deposits in engines which can lead to stress, corrosion or cracking of components. The deposits of most concern are those which build up in the nozzles of fuel injectors. The amount of carbon in the fuel can be correlated with a tendency to form deposits, hence the use of a carbon residue test.
Cetane number		Cetane number is actually a measure of a fuel's ignition delay; the time period between the start of injection and start of combustion (ignition) of the fuel.	Serves as a measure of ignition quality. Fuels with low cetane numbers show an increase in emissions due to incomplete combustion. Palm Oil and Tallow derived biodiesels have the best cetane numbers.
Cold Filter Plugging Point (CFPP)	℃	CFPP measures the temperature at which paraffin or, in the case of biodiesel, ester structures, crystallize before injection, thereby blocking the filter.	With regard to the blending of small amounts of biodiesel (e.g., 5 to 10 %) with mineral diesel the CFPP level does not play a role.

Property	Unit	Definition	Relevance
Copper Strip Corrosion		Polished copper strips are immersed in the biodiesel sample and placed in a sample tube in a heated bath for several hours. The sample test strip is then compared to a standard test strip to determine the effect of the biodiesel on the copper.	Acids and sulfur containing compounds have the potential to cause corrosion in an engine system. The Copper Strip Corrosion test indicates the potential of the biodiesel to affect copper and brass fuel system parts.
Density at 15℃	kg/m³	The density of a material is defined as its mass per unit volume.	Biodiesel generally have higher densities than mineral diesel. Density increases with a decrease in chain length and with unsaturation. This can impact on fuel consumption as fuel introduced into the combustion chamber is determined volumetrically. Density as a quality parameter is easy to check and can help to identify high contents of not accepted components like hydrocarbons or solvents <u>Should be tested for each batch.</u>
Diglycerides	% (m/m)	Is a glyceride consisting of two fatty acid chains covalently bonded to a glycerol molecule through ester linkages.	Risk of carbon deposition in injection systems. Diglycerides (like Monoglycerides) aggregate with sterols forming a precipitate that falls out of solution and which ends up clogging filters. Diglycerides stem from incomplete esterification reactions and cannot be washed out of the biodiesel as they are not water-soluble. <u>Should be tested for each batch.</u>
Ester content	% (m/m)	Esters are chemical compounds derived by reacting an oxoacid (one containing an oxo group, X=O) with a hydroxyl compound such as an alcohol or phenol.	Linolenic and polyunsaturated esters have shown to display a disproportionately strong effect on oxidative stability.
Flash point	℃	Flash point of a volatile liquid is the lowest temperature at which it can vaporize to form an ignitable mixture in air.	The flash point is a very significant indicator of methanol residues or of contamination by hydrocarbons. <u>Should be tested for each batch.</u>

Property	Unit	Definition	Relevance
Free glycerol	% (m/m)	Glycerol is an organic compound, also called glycerin or glycerin. Glycerol has three hydrophilic hydroxyl groups that are responsible for its solubility in water and its hygroscopic nature. The glycerol substructure is a central component of many lipids. Glycerol is of low toxicity.	The glycerol level in the oil is important as it can affect the running of an engine in a negative way (such as injector and valve deposits or filter clogging). Generally, a high free glycerol content points to incomplete separation of the ester and glycerol phase. Because of the high water solubility of the triol free glycerol can be readily extracted from biodiesel or biodiesel blends. Should be tested for each batch.
Group I metals	mg/kg	Sodium (Na) and Potassium (K)	Cause high ash levels in the engine. Should be tested for each batch.
Group II metals	mg/kg	Calcium (Ca) and Magnesium (Mg)	Calcium and Magnesium soaps have been related to injector pump sticking. Should be tested for each batch.
Iodine Value (IV)		Iodine number is a measure of total unsaturation (double bonds) within the FAME product.	High Iodine value is related to polymerization of fuels, leading to injector fouling. It is also linked to poor storage stability. The parameter is used to compare the chemical stability properties of different biodiesel fuels. The IV does not necessarily make the best measurement for stability as it does not take into account the positions of the double bonds available for oxidation. In some cases this can lead to IV values that are misleading. High Iodine value is related to polymerization of fuels, leading to injector fouling. It is also linked to poor storage stability.
Linolenic acid methyl ester	% (m/m)	A polyunsaturated fatty acid found in biodiesel (18 carbon atoms, two of which have double bond). It is abundant in many vegetable oils, especially poppy seed, safflower and sunflower oils.	The fatty acid composition is of substantial impact on the properties of the fuel, especially on the oxidation and cold stability: Unsaturated fatty acids have lower melting points than saturated fatty compounds. Thus biodiesel fuels derived from fats or oils with significant amounts of unsaturated fatty compounds will display poorer cold flow properties resulting in lower cloud points and pour points. The higher the number of unsaturated bonds of the fatty acid residue, the lower the oxidation stability of the fuel.

Property	Unit	Definition	Relevance
Methanol content	% (m/m)	-	Methanol can be removed from FAME by washing or distillation. High methanol contents pose safety risks due to the very low flash point of methanol.
Monoglycerides	% (m/m)	Is a glyceride consisting of one fatty acid chain covalently bonded to a glycerol molecule through an ester linkage.	Risk of carbon deposition in injection systems. Monoglycerides aggregate with sterols forming a precipitate that falls out of solution and which ends up clogging filters. Monoglycerides stem from incomplete esterification reactions and cannot be washed out of the biodiesel as they are not water-soluble. Should be tested for each batch.
Oxidation stability, 110℃	h	The Oxidative stability specification is defined as a minimum Rancimat induction period of six hours. Essentially a fuel is heated at 110℃ in a constant air stream and the formation of volatile organic acids is detected. This property relates to the overall storage stability of the fuel and the higher the degree of unsaturation (double bonds) within the FAME molecules gives a decrease is oxidative stability. This can be improved with the addition of antioxidant additives.	High oxidation stability is the key issue to secure a long term function of the injection equipment. Should be tested for each batch.
Phosphorus content	mg/kg	-	Phosphorus is a exhaust gas catalyst poison. The interaction with the catalyst is stronger compared to sulfur. Poisoning with phosphorus is irreversible. Should be tested for each batch.
Polyunsaturated methyl esters (>= 4 double bonds) [PUFA]	% (m/m)	Polyunsaturated fatty acids containing two or more double bonds, occurring in vegetable and seed oils.	This parameter should prevent the use of remarkable amounts of fish oil as raw material. Fish oil contains high amounts of PUFAs which lead to a rapid decrease in oxidation stability.

Property	Unit	Definition	Relevance
Sulfated ash content	% (m/m)	A sample is ignited and burned until only ash and carbon remain. After cooling, the residue is treated with sulfuric acid and heated until the oxidation of carbon is complete. The ash is then cooled, re-treated with sulfuric acid, and heated to constant weight. When phosphorus is absent, barium, calcium, magnesium, sodium and potassium are converted to their sulfates and tin (stannic) and zinc to their oxides. Sulfur and chlorine do not interfere, but when phosphorus is present with metals, it remains partially or wholly in the sulfated ash as metal phosphates.	The biodiesel may contain materials that are in the form of abrasive solids, soluble metallic soaps, and unremoved reaction catalysts. The Sulfated Ash determination indicates gross levels of ash-forming compounds in the biodiesel. The primary ash-forming materials that may be present in biodiesel are calcium, magnesium, sodium, and potassium. Abrasive solids and un-removed catalysts contribute to injector, fuel pump, piston and ring wear, and also to engine deposits. Soluble metallic soaps have little effect on wear but can contribute to filter plugging and engine deposits.
Sulfur content	mg/kg	-	Sulphur emissions are harmful to human health and high sulphur fuels cause greater engine wear and in particular shorten the life of the catalyst. Cecking the value is therefore important to lower the car emissions. A critical point is the entry of sulphur by acidic esterifications. Such products must be processed very carefully (several intensive washing steps are required). Biodiesel derived from pure Rapeseed oil will contain virtually no sulfur, however FAME derived from animal sources may contain significant quantities.
Total contamination	mg/kg	Total contamination is defined as the insoluble material retained after the filtration of a heated sample over a standardized 0.8m filter.	FAME samples with high quantities of insoluble materials tend to cause fuel filter and injector blockages. High concentrations of soap stock are normally associated with high total contamination. Very important value. Should be tested for each batch.
Total glycerol	% (m/m)	Total glycerol is the sum of free and bound glycerol. The latter is the sum of residual mono-, di- and triglycerides.	Failing to meet certain limits implies deposit formation on injectors and valves. Should be tested for each batch.

Property	Unit	Definition	Relevance
Triglycerides	% (m/m)	Is a glyceride in which the glycerol is esterified with three fatty acids. It is the main constituent of vegetable oil and animal fats.	Risk of carbon deposition in injection systems. Triglycerides stem from incomplete esterification reactions. They cannot be washed out of the biodiesel as they are not water-soluble. Should be tested for each batch.
Viscosity at 40℃	mm²/s	Viscosity is a measure of the resistance of a fluid which is being deformed by either shear stress or tensional stress.	Biodiesel has a higher viscosity than mineral diesel. High viscosity results in poor atomization and incomplete combustion which leads to coking of injector tips. This results in engine power loss. Viscosity decreases with unsaturation but increases markedly with contamination by mono-, di- or triglycerides or by fuel ageing.
Water content	mg/kg	-	Biodiesel can uptake up to 1200 mg H2O/kg Biodiesel. High water concentrations can lead to rapid growing micro organisms in blend fuels; this effect can be enforced by the use of ultra low sulfur diesel fuel. The only realistic chance to prevent such occurrences is the lowering of the water content over the whole supply chain. Should be tested for each batch.

Source: AGQM

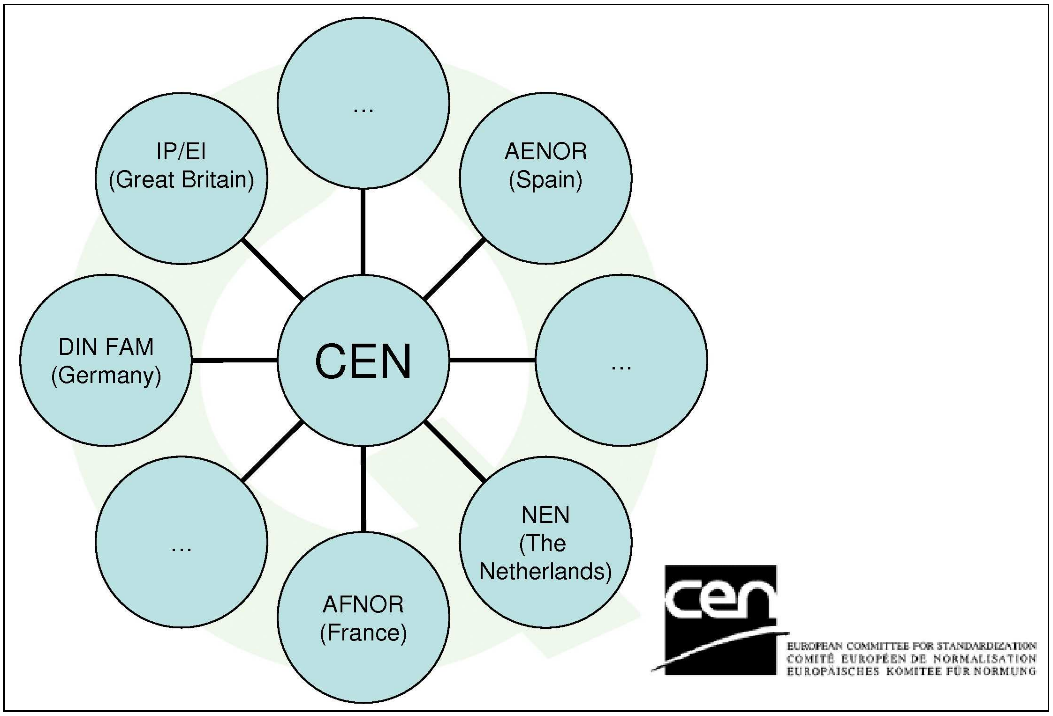
4.2 Standards for biodiesel and diesel/biodiesel blends in key countries

The most important biodiesel standards are the EN 14214 (available in the national derivates of all European Committee for Standardization (CEN) member states), the ASTM D 6751 and a Brazilian standard, whereas the Brazilian standard contains no own test methods and refers therefore to ASTM, ISO or CEN. Many other national standards which are not assigned to any of these standards under a standardization agreement resemble at least one of them very strongly. Special standards for blended fuels were developed more recently. For blends with a volumetric content of up to 5% of biodiesel (B5), the known mineral oil diesel standards were merely modified in the way that they now contain a passage stating the percentage up to which FAME can be used for mixing and what standard requirements FAME must satisfy. As a conclusion it can be stated that there is no need to develop additional standards for blends of up to B5, however it is crucial to standardize the FAME component the conventional diesel is blended with.

European Union - EN 14214

Since a long time fuels standards within Europe are developed by the European standardization body CEN. However national and international standards are both in force. Member states may develop own standards if no corresponding European standard exists. Typically national standards exist for a transition period until a European specification for the same subject is developed. Based on the European Standardization Agreement CEN standards have to be adopted as national standards. When CEN initiates the process of a European standardization, national standardization processes on this subject have to cease.

Image 9: Organization schema of CEN



Source: CEN

The EU member states are also CEN members. The work is organized by means of Technical Committees and Working Groups. They consist of experts nominated by the members. The participation in standardization processes is restricted to invited people. The European biodiesel standard is available since 2003 in the form of national derivates in all CEN member states. Contemporaneously all previous existing national standards had been drawn back. The mention of the standard is to define the quality during handover to the final customer (and not only at the place of delivery). This causes additional user's security. The European commission has handed over a mandate to develop a European B10 standard but there are a lot of objections – especially from the car manufacturers and the original equipment manufacturers so an intermediate CEN work item for a more or less agreeable B7 standard has been inserted.

Meanwhile the EN 590 is revised to open it for up to B7. For this purpose the same additional parameters and limits have been included. The blend component FAME is defined by an also revised biodiesel specification. This European standard remains nearly unchanged since this initial step. The rules of European standardization require a re-check of all active standards after 5 years. This is done meanwhile and led to a new release in 2008 (published e.g. as DIN EN 14214:2009).

This new revision contains the following changes:

- Inclusion of the revised method for total contamination
- Permission of Pensky-Martens method for flash point
- New limits for flash point and phosphorus content
- Introduction of a new method for polyunsaturated fatty acids (the former revision did contain the parameter but without a method).

Meanwhile also improved methods to determine glycerol/glycerids and the ester content are in place. It can be expected that these revised test methods will be adopted (including an increase of oxidation stability to a minimum of 8 h) in a next revision of EN 14214. The parameters of EN 14214 and their respective values can be found in the table below.[15]

United States - ASTM D 6751

ASTM D 6751 – 08 describes a "B100" but covers biodiesel according grades S15 and S500 (concerning the sulfur concentration) **only for use as a blend component** with middle distillate fuels. The required properties of the diesel fuel blend component are defined at the time and place of delivery.

ASTM D 7467 – 08 describes a blend fuel "B6 to B20" and covers fuel blend grades of 6 to 20% (V/V) of biodiesel with the remainder being a light middle or middle distillate diesel fuel. The biodiesel component of the blend shall conform to the requirements of Specification D 6751. The remainder of the fuel shall be a light middle or middle distillate grade diesel fuel conforming to Specification D 975 grades No. 1-D and No. 2-D of any sulfur level specified with some exceptions. Acceptable sulfur levels are as follows (the number means always the max. sulfur concentration in mg/kg):

- Grade B6 to B20: S15
- Grade B6 to B20: S500
- Grade B6 to B20: S5000

The required properties of the final diesel fuel are defined at the time and place of delivery. The parameters of ASTM D 6751and their respective values can be found in the table below.

---

[15] Proceedings of 3rd International Conference for Biodiesel Producers 2008, AGQM, Berlin, 2008

Brazil – ANP Order 42/2004

The Brazilian standard for biodiesel is a conglomerate of ASTM and CEN concepts. The test methods are linked either to ASTM or, how it is more often the case, to EN test methods. Unfortunately in some cases no limits are defined (only report intended). This seems to be a compromise between the existing plant technology and the requirements of the car manufacturers. The Brazilian standard ANP Order 42/2004 is shown in the table below.

Comparison of biodiesel fuel standards

Especially the European and the ASTM standard are also applied outside of the formal area of validity to describe the properties of trading products anywhere in the world. The following table gives the parameters and their respective values of the three standards described above allowing an easy comparison of the biodiesel specifications. Additionally between ASTM and EN methods a sameness or similarity check is done and marked in the table.

Table 8: Comparison of European, American and Brazilian standards for FAME

#	Parameter	Unit	EN 14214	Test method	ASTM D 6751	Test method	E / S	Brazil*	Test method
1	Appearance				clear, bright & free of impurities			clear and w/o impurities	
2	Ester content	% m/m	≥ 96.5	EN 14103				record only	EN 14103
3	Density at 15℃	kg/m³	860-900	EN ISO 3675 / 12185					
4	Density at 20℃	kg/m³						record only	ASTM D 4052, ASTM D 1298
5	Density at 40℃	kg/m³							
6	Viscosity at 40℃	mm²/s	3.50-5.00	EN ISO 3104	1.9-6 .0	ASTM D 445	E	record only	ASTM D 445, ISO 3104
7	Flash point	℃	≥ 101	EN ISO 3679	≥ 93	ASTM D 93	E	≥ 100	ASTM D 93, ISO 3679
8	Sulfur content	mg/kg	≤ 10	EN ISO 20846	≤ 15 / ≤ 500	ASTM D 5453	S	record only	ASTM D 5453, ASTM D 4294, 14596
		mg/kg	≤ 10	EN ISO 20884					
9	Carbon residue (on 100% distillation)	% m/m			≤ 0.05	ASTM D 4530	S	≤ 0.1	ASTM D 189, ASTM D 4530, ISO 10370
10	Carbon residue (on 10% distillation residue)	% m/m	≤ 0.3	EN ISO 10370					
11	Cetane Index								
12	Cetane number		≥ 51	EN ISO 5165	≥ 47	ASTM D 613	E	record only	ISO 5165, ASTM D 613

#	Parameter	Unit	EN 14214	Test method	ASTM D 6751	Test method	E / S	Brazil*	Test method
13	Sulfated ash content	% m/m	≤ 0.02	ISO 3987	≤ 0.020	ASTM D 874	S	≤ 0.02	ISO 3987, ASTM D 874
14	Water content	mg/kg	≤ 500	EN ISO 12937					
15	Total contamination	mg/kg	≤ 24	EN 12662					
16	Water and Sediment	% vol/vol			≤ 0.050	ASTM D 2709		≤ 0.05	ASTM D 2709
17	Copper strip corrosion		≤ 1	EN ISO 2160	≤ 3	ASTM D 130	E	≤ 1	ASTM D 130, ISO 2160
18	Oxidation stability, 110℃	h	≥ 6	EN 14112/prEN 15751	≥ 3	EN 14112	E	≥ 6	EN 14112
19	Acid value	mg KOH/g	≤ 0.5	EN 14104	≤ 0.50	ASTM D 664	S	≤ 0.8	ASTM D 664, EN 14104
20	Iodine Value		≤ 120	EN 14111				≤ 120	EN 14111
21	Linolenic acid methyl ester	% m/m	≤ 12	EN 14103					
22	Polyunsaturated methyl esters (>= 4 double bonds)	% m/m	≤ 1	EN 15779					
23	Mono alcohols content	% m/m						≤ 0.5	EN 14110
24	Methanol content	% m/m	≤ 0.2	EN 14110		EN 14110	E		
25	Free glycerol	% m/m	≤ 0.02	EN 14105	≤ 0.02	ASTM D 6584	E	≤ 0.02	EN 14105, EN 14106, ASTM D 6584
		% m/m	≤ 0.02	EN 14106					
26	Monoglycerides	% m/m	≤ 0.8	EN 14105				record only	EN 14105

#	Parameter	Unit	EN 14214	Test method	ASTM D 6751	Test method	E / S	Brazil*	Test method
27	Diglycerides	% m/m	≤ 0.2	EN 14105				record only	EN 14105
28	Triglycerides	% m/m	≤ 0.2	EN 14105				record only	EN 14105
29	Total glycerol	% m/m	≤ 0.25	EN 14105	≤ 0.240	ASTM D 6584	E	≤ 0.38	EN 14105, ASTM D 6584
30	Group I metals (Na+K)	mg/kg	≤ 5	EN 14538	≤ 5	EN 14538	E	≤ 10	EN 14108 / EN 14109
31	Group II metals (Ca+Mg)	mg/kg	≤ 5	EN 14538	≤ 5	EN 14538	E	record only	EN 14538
32	Phosphorus content	mg/kg	≤ 4	EN 14107	≤ 10	ASTM D 4951	S	record only	EN 14107
33	CFPP	℃	(nat.req.)	EN 116					
34	Cold soak filterability	s			≤ 360	ASTM D 6217			
35	Cloud Point	℃			report	ASTM D 2500			
36	Distillation Temperature, 90% recovered	℃			360	ASTM D 1160		360	ASTM D 1160

Legend:
E: ASTM method is equivalent to EN method
S: ASTM method is similar to EN method
* No actual proven data available

Source: AGQM

4.3 Test methods

The test methods for biodiesel are based on classical methods used for a long time in the petrochemical industry completed by tests developed for fat chemistry purposes or food industry. Nevertheless a further development was needed to adapt the methods to the biodiesel specifics. The test methods included in the requirement standards themselves are the object of standardization. Despite differences in names, several methods are virtually identical or similar (see table above). Recently, some European methods were included in ASTM standards directly without any changes.

4.3.1 Technical description of test methods

All present test methods for FAME are described in national or regional standards and fall under copyright regulations. European standards are available in all CEN member states, e.g. via Beuth Verlag[16] (a DIN division). The webpage is available also in English. All European standardization bodies are responsible to supply also the documents from other CEN member states. The Spanish derivates start with the code UNE EN. Electronic order is possible. ASTM standards are sold by the ASTM offices within United States, but are also available via online shop.[17] Brazilian standards concerning petroleum/fuels can also be obtained via internet.[18]

Precision data and in-house testing

The benefit of the EN methods is to come with a complete set of precision data, gathered from large round robin tests. Due to this fact the methods have the power to give clear decisions in case of claims. Similar or identical ASTM methods or special in-house tests can be accepted as a substitute for internal testing. In case of arbitration the EN methods should be used including their normative precision data.

---

[16] www.beuth.de

[17] www.astm.com

[18] www.anp.gov.br

The parameters which are most often tested using special in-house tests are:

- Total and free glycerol: For instance the determination of glycerides/free glycerol is intended by gas chromatography. A substitute method could be the use of an enzymatic test. This test gives only the concentration of total glycerol and free glycerol. However it is well known that this test principle can be disturbed by other components like alkaline, acids, complexing agents, oxidizing components and others. Thus, the test can give a mere indication but there is no chance to trace back to the real situation.
- Phosphorus content: Another simplification is the use of a photometric test to determine the phosphorus content instead of Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). The photometric test can fail in presence of unusual substances, e.g. occurring in waste fats or recovered oils from restaurants.
- Iodine number: The iodine number can be tested (according to the EN specification) by titration but the alternative use of the data set coming from the determination of the ester content (gas chromatographic method) for this purpose by a post-calculation is also possible and seems to have better precision data compared to the original method. Germany has started an initiative to accelerate this test to the same level as the traditional iodine number test.
- Cetane number: A Near Infrared Spectrometer Test as a substitute for a test engine to determine the cetane number is very common in the mineral oil refinery industry. In case of a good calibration using engine data the method is applicable for this testing field. But the method collapses for biodiesel – also in case of large training data sets. Unfortunately the test equipment is sold manifold also to biodiesel labs.

4.3.2 Equipment costs and specific operating costs of test facilities

The following table gives an indication of the equipment cost for the most important test methods. A prediction of the operating costs is not possible due to the special labor costs and the more or less optimal usage of reference materials. An orientation for the costs per analysis can give the price lists of international acting laboratories which are available on request. The operating costs depend remarkably from the throughput of analytics. From this position a concentration of the analytic work is desirable but on the other hand a minimum of independent labs is necessary to handle complaints and arbitrations.

Table 9: Lab equipment costs and commercial prices for analytical work

Parameter	Method	Testing Equipment	Equipment cost in 1000 EUR	Commercial price per analysis in EUR
Ester content	EN 14103	GC-FID	30.0	40-60
Density at 15 ℃	EN ISO 12185	Density Meter (U-Tube)	2.0	10-20
Kinematic viscosity at 40 ℃	EN ISO 3104	Viscosimeter	3.0	20-40
Flashpoint	EN ISO 3679*	Pensky-Martens-Flashpoint-Tester	12.0	25-50
CFPP	EN 116	CFPP-Tester	24.0	35-70
Sulfur content	EN ISO 20884	RFA	70.0	45-90
Carbon residue CCR (from 10% distillation residue)	EN ISO 10370	Vacuum-Distillation + Conradson Tester	50.0 + 15.0	45-90
Cetane number	EN ISO 5165	Test Engine	120.0	120-200
Sulfated ash	ISO 3987	Muffle Furnace	1.50	15-30
Water content	EN ISO 12937	Karl-Fischer-Titrator	6.5	35-70
Total contamination	EN 12662	Suction Filter and Glass Ware	1.5	45-90
Corrosivity to copper	EN ISO 2160	Tempering Bath + Test Vessels	2.0	25-50
Oxidation stability	EN 14112	“Rancimat” test equipment	15.0	45-90
Acid number	EN 14104	Color Titration	0.5	30-60
Iodine number	EN 14111	Color Titration	0.5	30-60
Linolenic acid methyl ester content	EN 14103	GC-FID (same like ester content)	-	see ester content
Methanol content	EN 14110	GC-FID (same like ester content)	-	40-80
Free Glycerin, Monoglycerides, Diglycerides, Triglycerides, Total Glycerin	EN 14105	GC-FID	30.0	110-200
Phosphorus content	EN 14107	ICP-OES	70.0	45-90

Parameter	Method	Testing Equipment	Equipment cost in 1000 EUR	Commercial price per analysis in EUR
Metals I (Na, K)	EN 14108	AAS	30.0	40-80
Metals I (Na, K)	EN 14538	ICP-OES (same like P-content)	-	40-80
Metals II (Ca, Mg)	EN 14538[19]	ICP-OES (same like P-content)	-	40-80
Laboratory Balances	-	-	3.5	
Drying Cupboard	-	-	1.0	
Total			350.0 - 400.0	880-1680

Source: AGQM

4.4 Lessons learned

Creating a standard and to set up a way to check the quality of the FAME should be implemented as parallel activities. At the end the same group which finds a joint decision for a parameter set and the limits should be engaged to find methods to make it true. Risky raw materials like waste fat, fish oils, recovery fat from restaurant require a very good analytical basis to prevent the introduction of a non suitable fuel or fuel component to the market. As a result of different levels in quality check one can also find different pictures of field problems. Germany has (meanwhile) very strong regulations and implemented checks by the government, the industry and quality control organizations (like AGQM), and so there is also a very low level of field problems or complaints. Compared to that the quality requirements and the control system are comparatively weak in the UK, and subsequently a lot of problems are reported which are still not solved. There seems to be an overlay between missing cold stability properties, “simple” quality violations and other very specific issues (e.g. microbiological contamination). Problems with blend fuels have also been reported in the United States. The most problems seem to be linked with a poor quality but also with minor components like sterol glucosides, which are not restricted in standards up to now. To prevent such a situation in Mexico from the very beginning it is strongly recommended to implement a quality assurance system carried both by biodiesel producers and biodiesel customers. To reduce the lab costs it could be a good solution to implement an independent full featured lab acting nationwide for all market participants. The best way would be if the same actors developing the Mexican standard were those implementing the quality assurance system or at least are the ones giving the guidelines for this process. Standards are living documents. There is a key regulation in CEN but also for the national standardization bodies to revise standards after a well defined period. As a result of the progress in engine technology and additional emission requirements fuel standards had been revised quite regularly in Europe leading to a more stringent criteria and additional or

---

[19] Applicable since revision EN 14214:2008

improved test methods. Standards for FAME became the most complex specifications among other fuels. This is linked as well with the origin of the FAME but also to prevent unsuitable impacts in case of higher blend rates.

4.5 Initiatives for an international standardization of biodiesel

4.5.1 Tripartite-process and ISO activities

The tripartite process was a trial for a global biodiesel standardization process. On initiative of EU, United States and Brazil a group was formed with the aim to gather the present biodiesel standardization situation in the world and to find a way to come to a joint worldwide standard.

History:

- 2006 Trilateral discussion between Brazil, EU, and the United States
- 02/2007 Conference in Brussels on global standardization
- 03/2007 Launch of the International Biofuels Forum (IBF)
- 04/2007 Development of Biofuels Standard Roadmap (Brazil, EU, United States)
- 06/2007 Appointment of BR, EU and United States representatives for the revision of existing Biofuels' standards (ABNT, ANP, CEN and ASTM International)
- 07/2007 Start of the technical work
- 12/2008 Final report including a compilation of identified compatible requirements and incompatibility issues
- 03/2009 Termination of the tripartite process at the Biofuels Standardization Conference in Brussels

It resulted that positions were too different for a possible unification of biodiesel requirements in the future. The main factors for these differences are the special national and regional frame conditions, different raw materials and different strategic concepts how to use the biodiesel. The published Tripartite Whitepaper[20] shows the present differences in biodiesel standardization worldwide (see table below).

---

[20] ec.europa.eu/energy/res/biofuels_standards/doc/white_paper_icbs_final.pdf

Table 10: Differences in biodiesel standardization

Category A parameters	Category B parameters	Category C parameters
Sulfated ash	Total glycerol content	Sulfur content
Alkaline & alkaline earth metals	Phosphorus	Cold climate operability
Free glycerol	Carbon residue	Cetane number
Copper strip corrosion	Ester content	Oxidation stability
Methanol & ethanol content	Distillation temperature	Mono, di-, tri-acylglycerides
Acid number	Flash point	Density
	Total contamination	Kinematic viscosity
	Water content & sediment	Iodine number
		Linolenic acid
		Polyunsaturated methyl ester

Source: White Paper on International Compatible Biofuel Standards

Classification of standard parameters and limits:

- Category A: Specifications that are already similar.
- Category B: Specifications with significant differences between parameters and methods but which might be aligned by work on documentary standards and measurement standards.
- Category C: Specifications with fundamental differences, perhaps due to emission or environmental regulations within one or more regions, which are not deemed bridgeable in the foreseeable future.

Unfortunately most parameters fall in Category C.

4.5.2 World Wide Fuel Charter, Biodiesel Guideline

Summer 2008 the three largest automotive industry associations in the world had published a so called “World Wide Fuel Charter, Biodiesel Guideline” as a supplement to the annual issued “World Wide Fuel Charter” related to the conventional fuels. This document contains normative and non-normative description of the situation „around“ biodiesel and can be considered as a list of car manufacturer‘s wishes. Unfortunately the paper contains a lot of misunderstandings and heavy faults and is not suitable as a guideline for the quality development of biodiesel.

5 Towards a technical standard for biodiesel in Mexico (max. B5)

The main reason to introduce biodiesel in Mexico is the improvement of the lubricity of a high desulfurized Diesel fuel by a small portion of FAME instead of using lubricity additives. Studies performed by the Mexican Petroleum Institute (IMP) showed that for that purpose a blend containing 0.5-1.0% (V/V) of biodiesel (B0.5-B1) is required in order to achieve a lubricity below 520 microns.[21] This fits well with international experiences which show that, using biodiesel of good quality, blends with up to 5% (V/V) biodiesel (B5) are no critical issue for existing car fleets. Thus, to define the required quality of the biodiesel a FAME standard is needed.

5.1 Proposal for a standard of FAME components

The idea of the proposed standard for the FAME used as blend component is to make sure that the biodiesel component doesn't become a critical component of the blended diesel fuel related to all classical fuel parameters but especially to oxidation stability. AGQM proposes to remove the following parameters, which are used in a similar way in different biodiesel standards (The experience shows that these parameters are always met if the others comply with the rules):

- <u>Sulfated ash content:</u> The actual standardization discussion tends to substitute the ash content by determining different ash forming elements like heavy metals and others in a very low range. The existing limitation based on ash content is no help for the injection equipment manufacturers and exhaust gas treatment system producers.
- <u>Carbon residue (on 10% distillation residue):</u> See sulfated ash content
- <u>Copper strip corrosion:</u> In case of biodiesel copper strip corrosion test will give always an “OK” due to the fact of dissolving the potential surface compounds by the FAME itself.

Another actual issue is the oxidation stability. As a result of new demands from the car industry and the original equipment manufacturers AGQM expects an increase of the required minimum oxidation stability from the actual six hours to eight hours in the next revision of EN 14214. Using suitable raw materials and no-harm proven antioxidants it is no problem to reach or secure this limit. The following proposal for a FAME standard presented in the table below contains comments and advices on the respective test method. Additionally, parameters which should be checked for each batch individually are marked with bold letters. It should be noted that it is not a part of the standard but part of a further quality management system to define special regulations, how often and for which purposes the “other” parameters should be checked. The proposal is the result of a discussion of a draft proposal by a group of Mexican stakeholders invited by the Ministry of Energy of Mexico (SENER).

---

[21] Programa de Introducción de Bioenergéticos, SENER, 2009. Page 34

Table 11: Proposal for a Mexican FAME standard

#	Parameter	Unit	Value	X	Method	Comments/advices
1	**Appearance**		Clear & bright	x	Based on the following description: "Clear at 15 ℃ and free from water and visible impurities"	Easy to check and can help to identify unclean handling conditions or critical behavior due to unexpected components. "Clear" means: No visible turbidity or sediments. Also a colored but homogeneous FAME can be accepted if the mentioned condition is matched. The test can be run very effectively using a beam-lamp. There should be no visible light-scattering effect. Very dark samples could absorb so much light that detection becomes impossible.
2	Ester content	% m/m	≥ 96.5		EN 14103	The value can fail in case of methyl esters prepared from sources with short chain fatty acids like coconut oil or animal fats containing C17 components. An improvement of the method is coming soon but will not cover all reported problems. The method is helpful to identify non-FAME components (e.g. fatty alcohols. hydrocarbons). Unfortunately the method has bad precision data. Nevertheless it is the only possible method. A substitution by other methods (e.g. distillation curve) leads to wrong or indistinguishable results due to the fact, that nearly all FAME components evaporate at the same temperature.
3	**Density at 15℃**	kg/m³	860-900		EN ISO 3675/12185	Easy to check and can help to identify high contents of not accepted components like hydrocarbons or solvents. The density reference temperature in the most trading conditions is 15 ℃. This can be a problem for warmer countries. A particular density measured at higher temperatures can be recalculated to 15 ℃ by the following equation: *Density (15℃) = Density (T) + 0,723* (T-15 ℃)* with: Density (15 ℃) and Density (T) are given in kg/m³ and T is the temperature in ℃. The equation above is part of the EN 14214. Newer tests are under evaluation and will be available soon. For a test temperature of 25 ℃ the equivalent density range would be from 853 to 993 kg/m³. But it is not recommended to set up the specification to another temperature instead of recalculation (reason: Typical international supply specifications are based on 15 ℃ reference temperature).

#	Parameter	Unit	Value	X	Method	Comments/advices
4	Viscosity at 40°C	mm²/s	3.50 -5.00		EN ISO 3104	By using "normal" vegetable oils (like rapeseed, soybean, sunflower, palm) as raw material this range is matched. Polymerized esters (e.g. in case of restaurant fasts as raw materials) can lead to an increase of this value. Problems can be considered as inevitable for a viscosity > 7 mm²/s The range of the ASTM specification (1.9 - 6.0 mm²/s) is also applicable for this parameter. The lower limit of ASTM does not correspond to any realistic FAME raw material. The value for Jatropha based FAME is expected in the same range as for soy or rapeseed based esters. An exemption is a castor-oil based FAME. The viscosity is 20 mm²/s and higher and can be used only in small concentrations in FAME blends with FAMEs derived from other raw materials.
5	**Flash point**	°C	≥ 101		EN ISO 2719/ EN ISO 3679	Chemicals safety, Pensky-Martens method preferred as a worldwide accepted test for flash points for a wide range of substances, could be considered as a pre-test to meet the methanol specification. The former flash point in EN 14214:2003 was 120 °C. This was only caused by the property of a special test method (not the Pensky-Martens method!) which seems to have an offset. Recently run round robin tests have shown that this effect is not true. The flash point is a very significant indicator of methanol residues or a contamination by hydrocarbons. The value “101 °C” is linked to other legal requirements (safety of chemicals) so a higher value (like 120 °C) can be accepted easily by both, producer and user.
6	Sulfur content	mg/kg	≤ 15	x	EN ISO 20846 / 20884	The value is important to lower the car emissions. A value of 10 mg/kg is reachable also by FAME producers using fats of low quality.
7	Cetane number		Report	x	EN ISO 5165	By using "normal" vegetable oils (like rapeseed, soybean, sunflower, palm) as raw material this limit is matched. Also for Jatropha a suitable value is expected. The value varies only in a small range. Saturated FAMEs lead to better results, unsaturated to worse results but even at a suitable level. “Report” is useful for new productions but later on the value can be omitted.
8	**Water content**	mg/kg	≤ 300	x	EN ISO 12937	To be determined at point of sale. At point of real handover 500 mg/kg must not be exceeded (also normative). For a producer there is no problem to meet a specification of 300 mg/kg and better. The limit should be significant lower than 500 mg/kg

#	Parameter	Unit	Value	X	Method	Comments/advices
9	**Total contamination**	mg/kg	≤ 24		EN 12662	Very important value – but unfortunately bad precision data. Currently it is the only opportunity to find particles, rust and sediments. A new method is under evaluation (CEN TC 19/TC 307 WG 31).
10	**Oxidation stability, 110℃**	h	≥ 8	x	EN 14112 or prEN 15751	A change of EN 14214 specification to 8 h oxidation stability is expected. A lot of additional supply specifications of the European mineral oil industry contain already the accelerated value and a mandatory use of stabilizers equivalent to 200 mg/kg BHT (min. dosage), a max. dosage of 500 mg/kg must not be exceeded. The additive shall be no-harm proven. ASTM uses the same test method but requires only 3 h induction period. This limit was related to the use of soy bean oil as raw material. High oxidation stability is the key issue to secure a long term function of the injection equipment. Using stabilizers allows reaching 8 h also in case of soy and other raw material. Caution: The method is not able to find already existing polymers coming from pre-treated (aged) oils and fats.
11	**Acid value**	mg KOH/g	≤ 0.5		EN 14104	Simple method, pre-warning in some cases of wrong process run
12	Iodine Value		≤ 120		EN 14111 or EN 14214 (Annex)	Calculation from fatty acid profile shall have the same priority as titration according to Wijs. The parameter is a simple indicator, but the oxidation stability gives (if tested properly) more evident results.
13	Linolenic acid methyl ester	% m/m	≤ 12		EN 14103	Complete fatty acid profile as output of the analysis is strongly recommended. This parameter is a part of determining the ester content and does not cause any additional costs.
14	Polyunsaturated methyl esters (>= 4 double bonds) [PUFA]	% m/m	≤ 1		EN 15779	Important in case of processing fish oil containing raw materials. GC method (equipment similar to ester content).

#	Parameter	Unit	Value	X	Method	Comments/advices
15	Methanol content	% m/m	≤ 0.2		EN 14110	If flash point is “Ok” a reasonable value can be assumed. The method is simple but requires a special headspace GC. The substitution by flash point is possible but prevents a detailed detection of the cause.
16	**Free glycerol**	% m/m	≤ 0.02		EN 14105/ 14106	
17	**Monoglycerides**	% m/m	≤ 0.8		EN 14105	Monoglycerides of saturated fatty acids should be limited to at least 0.4% as a known cause for precipitations (for cold climates a value of 0.1% is under discussion). Currently a special test method does not exist, but the value can be calculated from the total monoglycerid content using the fatty acid profile.
18	**Diglycerides**	% m/m	≤ 0.2		EN 14105	
19	**Triglycerides**	% m/m	≤ 0.2		EN 14105	
20	**Total glycerol**	% m/m	≤ 0.25		EN 14105	The set of parameters (glycerol and glycerides) is very important but is the most challenging GC method in the standard. An enzymatic test (only evaluation of total glycerol and free glycerol) cannot be recommended because a) the test fails in some cases, b) without knowing the concentration of tri- and partial glycerids it is impossible to detect production problems directly.

#	Parameter	Unit	Value	X	Method	Comments/advices
21	**Group I metals (Na+K)**	mg/kg	≤ 5		EN 14538	This is an ICP-OES method. The AAS method according to EN 14108/EN14109 can be used alternatively but has no benefit and additional devices are required. Actual methods allow only securing a specification limit of 5 mg/kg. Ash residuals as a substance contaminating and blocking the exhaust gas treatment system are discussed by the car manufacturers. The tendency goes toward lowering this limit.
22	**Group II metals (Ca+Mg)**	mg/kg	≤ 5		EN 14538	Some vegetable raw materials can contain remarkable amounts of Ca, partially also of Mg. Typical process technologies for transesterification cannot remove enough of Ca. Ca can also be introduced by use of unsuitable washing water.
23	**Phosphorus content**	mg/kg	≤ 4		EN 14107	The origin of the phosphorus is the plant (respectively the oil mill process). The equipment (ICP-OES) is expensive but can be used also for the determination of Na, K, Ca and Mg. A method for S is under preparation. The parameter cannot be substituted by another one. Proposal for the determination of all element concentrations: One well equipped central lab which runs the test for all parties.
24	CFPP	℃	Report	x	EN 116	Up to 2% FAME in mineral oil based diesel fuel there is no correlation between cold stability parameters of the final fuel and the CFPP of the blend component. In the range above interferences can occur in case of cold climate fuel applications. The parameter is important for B100. Nevertheless there is the tendency to re-integrate this (and other cold stability) parameter in EN 14214 to prevent a critical behavior of the blend. “Report” is the chance to get the information without sanction or exclusion. Besides the low temperature properties of FAME and diesel fuel the general filterability becomes a big issue. It can be expected that filterability criteria (above Cloud Point) will be a part of the biodiesel specification in the near future.
Legend: “x” refers to deviation from EN 14214:2008						

Source: AGQM

A precondition for implementing a FAME standard on the basis of the presented proposal is to set up all required test methods.

5.2 Proposal for the amendment of the Mexican diesel fuel standard for up to B5

Consideration on a special standard for blended final fuel

The following remarks link to the suggestion to introduce FAME as blend component in lower concentrations, typically up to 1.5% (V/V) but in max. to 5% (V/V). It is proven that a concentration of up to 5% (V/V) biodiesel of a reliable quality does not change the existing fuel properties (exempted the expected improvement of the lubricity according to the High Frequency Reciprocating Rig[22] method) of the conventional diesel. The properties of the blend are determined by the base fuel. There is no chance to link any measurable parameter directly to the biodiesel properties. As an example the recent DIN EN 590 Diesel standard which is in fact an “up to B5 standard” does not contain any special parameter to check the impact of the blend component. It is only said that the used blend component must comply with EN 14214 and shall be admixed not higher than 5% (V/V). Biodiesel in higher portions can change the oxidation stability of the final fuel, but up to now AGQM has no data based on actual methods on stability of the existing FAME free fuel in the Mexican market. The risk to define such a parameter without the knowledge of a broad quality survey is to set limits which can already not be fulfilled by the existing base mineral oil fuel. Conventional oxidation stability test methods for mineral oil based Diesel fuels determine often the formation of sludge (containing the polymers). It is meanwhile well accepted that this kind of test principle has no power to find fine differentiations or tendencies between the fuels, as their expressiveness hardly goes beyond “Ok” or “Fail”. In the case that “Fail” is reported the fuel is of really very bad quality. For B7 or higher blend rates the sludge testing methods fail completely due to the fact that biodiesel is a very good solvent for organic polymers and depresses the precipitation of the sludge. Based on this fact for higher blend rates (B7 and higher) a new test method for oxidation stability is needed. One of the candidates for such a method is a modified Rancimate test (similar to EN 14112, but using longer tubes and a higher weighted sample amount). This method is already used in the new German and Austrian standard for B7 and will be adopted also in the future European standard. Another possible solution is the so called PetroOXY method. The principle is known from a former stability test for gasoline based on pressure loss in a reaction chamber during the oxidation process. This test is comparatively fast and has the analytical power to describe the behavior of a FAME blended fuel in a right way.

---

[22] The High Frequency Reciprocating Rig (HFRR) test method is widely used as a wearing test method in the mineral oil and car industry. The core principle is to evaluate the wearing of a standardized plate after interaction with four spheres.

Conclusion

Concerning the Mexican frame conditions and the use of biodiesel of up to 5% (V/V) AGQM proposes to simply add a statement like the following to the existing Mexican Diesel fuel standard instead of defining a new specification:

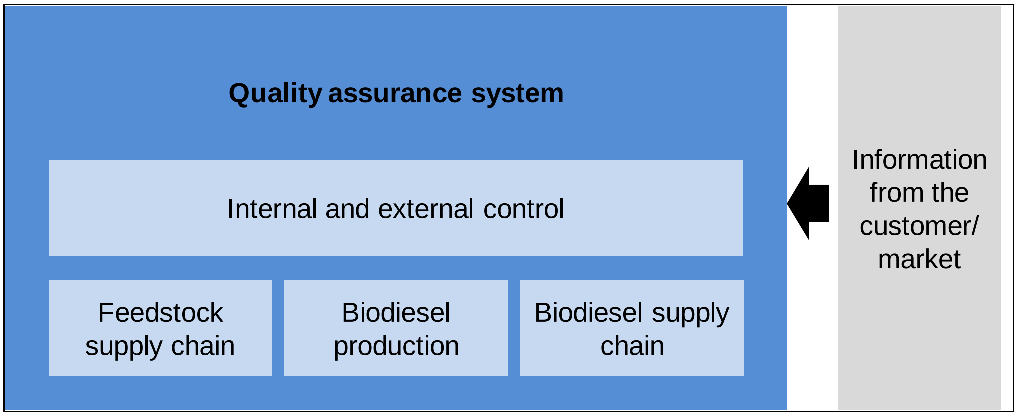
"*The fuel according to this specification can contain up to x% biodiesel as blend component. This component shall comply with the specification [Mexican standard on biodiesel/ FAME/ B100].*"

Of course the standard for the blended fuel could contain a link to a method to determine the concentration of FAME. Such a method exists (EN 14078), but AGQM does not know of any real standard in the world which includes such a parameter as a mandatory part. The reason for that are the precision data of this method in the lower concentration range. It is in any case more precise to make sure the volumetric dosage (or per mass - depending from technical solutions and regulations) of FAME by recording at the blend terminal level instead to measure it later on by analytical means (e.g. the German Biofuel Quota Act is based <u>only</u> on the recording of the dosage under supervision of customs control, supplemented by a check of the quality of the FAME which has been used as blend component).

6 Quality assurance regarding production, transport and storage infrastructure

The quality of biodiesel is influenced by a large amount of factors across the whole process chain. Resulting from that fact a quality assurance system has to take into account the various process steps which is expressed by the image below.

Image 10: Areas of a quality assurance system



Source: AGQM

For a better understanding the chapter is structured along the line of the process in three sections:

- Feedstock supply chain
- Biodiesel production
- Biodiesel supply chain

For each section the most important aspects of a quality assurance system are presented. In general it should be noted that a quality assurance system includes technical and organizational aspects.

Technical aspects:

- Short term decision about delivered raw materials
- Process: Stability
- Process: Known control data set
- Impact of supplies and additives
- Raw material: Known relation to properties of the final product
- Raw material: Side components and their behavior
- Interval and equipment for internal control
- Clean and suitable transportation units

Organizational aspects:

- Knowledge and open information about main principles of the quality policy
- Sensitivity for customer problems
- Knowledge about raw material and final product requirements
- Clear information paths and responsibilities
- Defined product release policy
- Documentation and traceability
- Quality of the internal control
- Check of the transportation units

A good control system consists further of internal and external control. Internal control means to perform tests within the own plant by an internal laboratory. External control can be realized by contracting external labs or quality assurance organizations. This also supports the work of the internal laboratory as it helps to prevent biased test results. Only with a combination of internal and external control the quality assurance system has the power to prevent failures and to win disputes in case of deviations.

Another very important issue is the description of the own final product by a significant certificate of analysis. Such a certificate should contain at least the following statements:

- Headline: “Certificate of Analysis” (CoA)
- Producer’s address (complete address, phone and fax numbers)
- Product description
- Commodity compliance with standard (e.g. EN 14214 or others)
- Definite and clear distinguishing feature (e.g. batch number, date, number of delivery note, dispatch number, number plate of truck, if possible in connection with tank number)
- Date of sampling
- Exact labeling of retain samples, which mirror the quality of the sent goods and give the opportunity to run checks in case of complaints or disputes
- Analysis: Specific parameter, test method, test result with correct measuring unit, limits of the standard
- Indication must be given if specific types of additives (e.g. oxidation stabilizers) are used for certain application fields
- Name and position of person in charge for issuing the CoA
- Signature of person in charge

Besides these general aspects biodiesel producers should be aware of the fact that a very important quality feedback comes from the market. In most of all cases possible future quality problems send pre-signals before really complaints come in. For instance if tested parameters show a long term tendency to grow in the direction towards the limit or show a very strong variation this should be considered as a pre-signal before a real problem occurs. This is a chance for a good quality assurance system to react in advance.[23]

---

[23] Proceedings of 2nd International Conference for Biodiesel Producers 2007, AGQM, Berlin 2007

6.1 Feedstock supply chain

Basically the supply chain of the biodiesel feedstock can be considered to consist of the steps harvesting, seed storage and oil mill. All of these steps have impacts on the properties of the feedstock and thus affect the properties of the biodiesel. Changes which, for example, can increase the concentration of free fatty acids in the oil mill process may already occur during storage of the seed. If these free fatty acids are not removed by suitable cleaning (at least neutralization), negative effects on the transesterification can be expected which can be the reason for poor conversion in the reactor and therefore a high residual content of triglycerides and partial glycerides, respectively.

Irrespective of this, the oil mill process itself has a major impact. For example, if rapeseed oil is obtained only by pressing (not followed by extraction of the oilseed cake), poor settings of the press (if no extraction follows, the press conditions determine the oil yield) can cause the transfer of substantial amounts of calcium and phosphorus compounds in the oil. High pressures and high temperatures lead to a good oil yield but also to increased phosphorus und calcium concentrations. By experience, the phosphorus content can be reduced by downstream degumming to an acceptable level, making the oil suitable for the biodiesel process as far as this parameter is concerned. On the other hand, it is extremely difficult to eliminate calcium. It was found on several occasions that even intensive scrubbing of the biodiesel failed to reduce calcium compounds to a tolerable degree. There seems to be a chance for the use of ion exchangers after the oil production but this technology is not very common and under evaluation (research is running not for biodiesel raw material but for the use of pure rapeseed oil as fuel).

The quality of the vegetable oil produced in the oil mill depends largely on the different cleaning steps (degumming, neutralization, bleaching). Even if biodiesel is a technical product, the requirements on the input materials are very much like those made on foodstuff oils. No limits are designed, for example, for the color of biodiesel, but bleaching may still be required to remove certain unwanted components. Typical distinguishing features of raw materials are listed below:

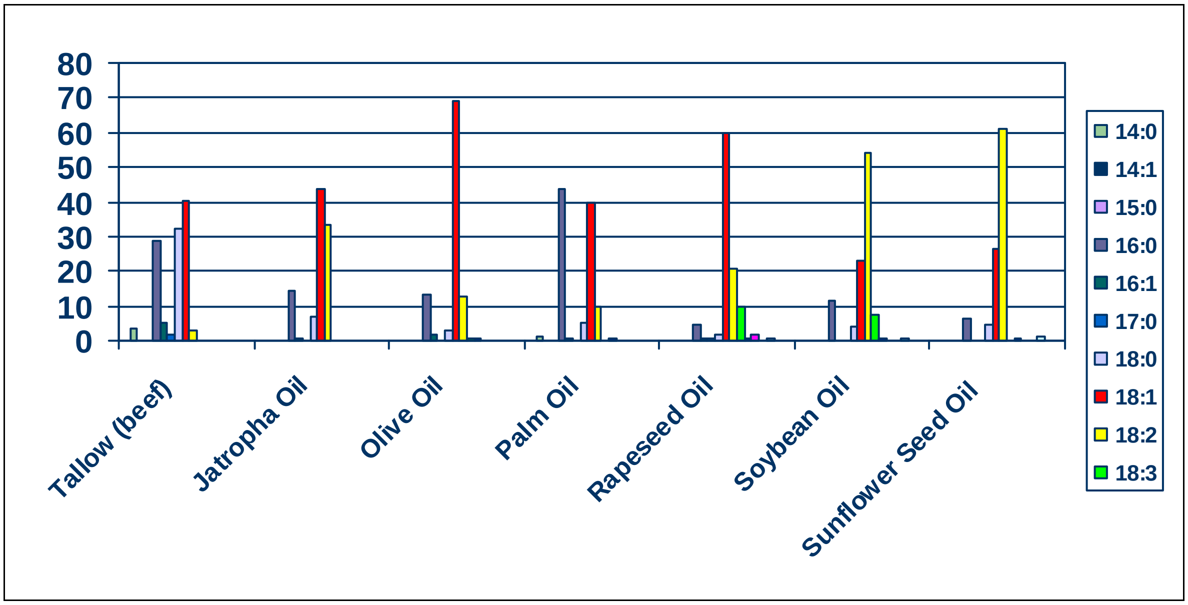
- Vegetable oils
- Animal fats
- Collected waste fats
- Fatty acids from soapstock hydrolysis

- (more) saturated
- (more) unsaturated

- Oils/Fats, raw
- Degummed
- Degummed and bleached

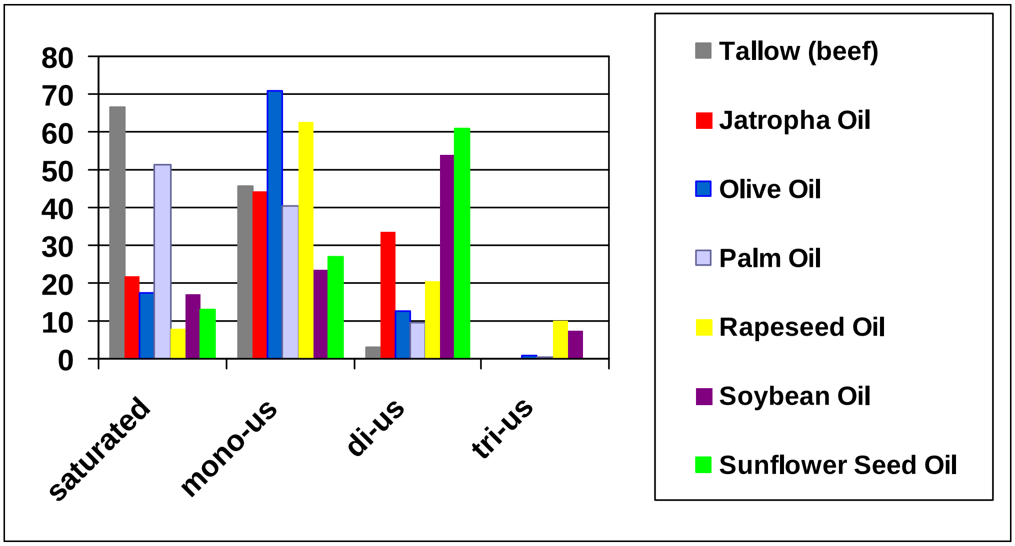
The fatty acid profile is very important for assessing the suitability of feedstock. Fatty acid methyl esters from oil with high proportions of unsaturated fatty acids have unfavorable properties at low temperature. On the other hand, high proportions of unsaturated fatty acids – polyunsaturated acids, in particular - are responsible for low oxidation stability. A possible compromise is the mono-unsaturated oil acid which reacts fairly slow to atmospheric oxygen. FAMEs with a high concentration of oil acid methyl ester are usually stable at low temperatures and also have good oxidation stability. The following figures show typical fatty acid profiles of frequently cultivated oilseed crops and of animal origin, respectively.

Image 11: Fatty acid profile of different fats and oils



Source: AGQM

Image 12: Degree of saturation of different oils [%]



Source: AGQM

Special comments on Jatropha as a potential raw material

In addition to the traditional feedstock materials, alternative oilseed plants which can be expected to be grown on large areas and which are not potential food crops are becoming more and more important. Recent findings show that these crops are far from fulfilling the ideal expectations placed in them. Despite this, Jatropha will be discussed in some detail here as an example. The table below contains typical quantifiable parameters of Jatropha methyl esters in comparison with FAMEs from conventional oilseeds and the requirements of DIN EN 14214. The table includes only parameters which relate directly to the chemical structure of the methyl esters. Parameters which are essentially determined by the process are ignored.

Table 12: Comparison of Jatropha methyl ester with most important FAMEs

	DIN EN 14214	**Raps-ME**	**Soja-ME**	**Palm-ME**	**Jatropha-ME**
Density [g/cm³]	0.8750-0.0900	0.883	0.885	0.876	0.882
Viscosity (40℃) [mm²/s]	3.5 – 5,0	4.45	4.5	4.4	4.3
CFPP [℃]	0/-10/-20	-13	-4	+8	-3
Pour Point [℃]		-9	-1	+12	+3
Cloud Point [℃]		-5	+1	+13	+4
Iodine number	120	115	129	52	97
Cetane number	51	54	47	66	64

Source: AGQM

It can be seen that the properties of a Jatropha methyl ester are similar to those of a mixture of soybean methyl ester and palm oil methyl ester. The plant and the fruit of Jatropha can be characterized as follows:

- Vegetable from the spurge family
- Nearly 190 different varieties
- Most important variety: Jatropha Curcas
- Oil content of the seed: Approximately 30-35%
- Yield: 0,6-4,1 metric tons of seed/ha
- Oil and press cake cannot used for feed or food purposes due to toxic components like lectin and diterpenes

The Jatropha plant is said to have quite a variety of ideal properties which, however, do not match reality. Some facts about the properties of Jatropha are listed below:

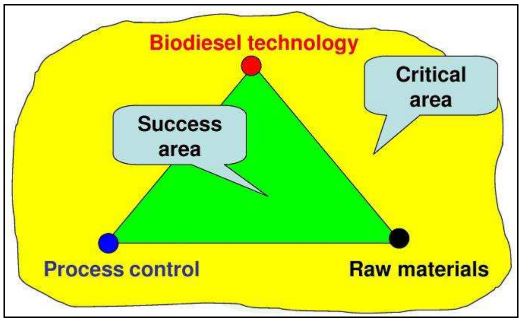
- Jatropha is a frugal plant, which grows also at nutrient-poor and dry soils.
- Jatropha is no „weed“ and is not self-distributing.
- Jatropha is no desert plant and needs at least a minimum of rainfall.
- Jatropha resists long dry periods.
- The yield depends from the growing conditions.
- Jatropha is not frost-resistant.
- Jatropha is up to now a non cultivated wild plant and needs breeding activities.

Despite the obvious limitations, Jatropha remains an interesting alternative as input material for bio-based fuels and should remain in focus. However, it will be a long way before Jatropha can produce the yields we know from the traditional oilseed crops.

6.2 Biodiesel production

The production of biodiesel can be considered as a normal chemical production process. Insofar the same well known principles for quality assurance are also valid for biodiesel production. The precondition to meet required product properties is often described by the so called “magic triangle” (see image below): Technology, raw materials and process control always form one unit. Only with a fine tuning of these factors the production remains in a safe quality area. Outside of this symbolic triangle the quality becomes critical. If one of the factors does not harmonize with the others the risk to produce failing products rises remarkably.

Image 13: The Magic Triangle of Quality



Source: AGQM

So it is in no way sufficient, for example, to just select a progressive technology if the input materials do not meet the requirements. On the other hand, professional monitoring of the process is a fundamental condition for exploiting the potential of the applied technology. A good choice is to produce always not “border line” to make sure to have under several less optimal conditions a suitable product. Such a built-in „quality reserve“ requires a technology and quality environment which is able to produce not only at the specification limits. This refers above all to parameters such as the residual content of mono-, di- and triglycerides, alkali and alkaline earth metals, and phosphorus. A production with such a positive gap to the minimum is also a support for the whole supply chain.

The production of biodiesel is subject to a large number of factors which cannot be discussed in detail here. Instead, some fundamental remarks should suffice. Continuous systems can rarely control feedstock whose composition changes frequently. Batch processes are clearly better in this respect. This impact is also valid for the size of a plant: Large plants are limited in the possibility of a quick adaptation. On the other hand, processes in large plants are very stable, as a rule. Agitated reactors have shown to be fairly non-critical in connection with unfavorable feedstock. Reactors working on the principle of counter-current columns, reactive distillation or membrane processes can convert high-quality feedstock best. Similar observations can be made for the process pressure, the choice of the reaction medium/solvent and the catalyst. Other distinguishing criteria for process technologies are:

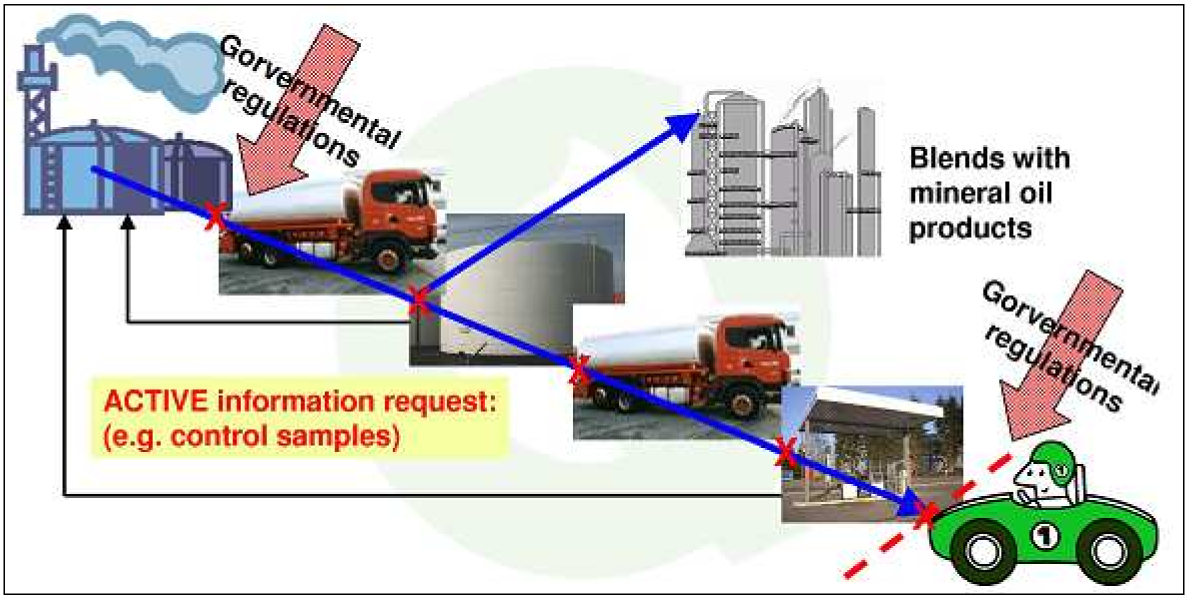
- Pressure (normal, increased, high)
- Solvent (two-phase fluid system, overcritical, additional third solvent)
- Catalyst (NaOH, KOH, methylates, solid state, acids, enzymes)

There is no basically bad or good technology, but generally the process technology should be appropriate to the raw materials.

6.3 Biodiesel supply chain

Basically the supply chain of the biodiesel feedstock consists of the steps transport, storage, blending and filling station (see image below). The influence of the supply chain is considerable and every step can systematically impair the quality of the product which is why the assessment of the quality situation should not be limited to shipments from the factory.

Image 14: Biodiesel supply chain



Source: AGQM

Loading and unloading processes should be done carefully. Tank cars must be always clean. They could be cleaned by special operations but the easiest way is to secure a usage for always only one and the same product. Some kinds of preloading like vegetable oil, acids, alkalines, particle containing fluids and gasoline should be excluded generally. Improper loading and unloading can be also a reason for water entry or a decrease of oxidation stability. Also a long term storage or improper storage conditions in the intermediate warehouse can cause a quality deterioration of the biodiesel. As improper conditions are considered the presence of water in the tank, plastic tanks, use of pipes and fittings containing copper or some other heavy metals. A general recommendation is to use paired retain samples for both sides in a business at any point where the individual trace of the product can be lost. In some extra critical case there should be taken three retain samples (one additional for a neutral arbitration). Such extended controls require good cooperation among all market players but is extremely efficient in an overall system.

6.4 Recommendations for quality assurance in Mexico

First of all the market participants from both sides should find a general accepted guideline how to come forward. The experience is to install a strong control system which can be established by a voluntary body of the FAME producers' side but also by very rigid control systems built up by the mineral oil industry. The best choice would be to find a joint conclusion of the minimum requirements for such a quality control system. To initiate such a national process it could be very helpful to join an international technical based certification system (like AGQM's "Biodiesel Production AGQM Certified (BPAC)"). By means of such a certification a biodiesel plant participates in the more than 10 years experience in quality assurance for FAME and gets special support to improve or stabilize the product quality. Round robin tests and training for quality assurance staff are important and also a part of this system. Another possibility is to create a national quality control group. The problem is to install powerful instruments to recognize and to punish deviations from the set frame requirements. The experience shows, that a control system without sanctions only relying on self-commitment does not work.

The work of the Mexican biodiesel test labs is in the very beginning. There is no lab available which has a complete or nearly complete equipment to run the most important test methods. Some of the existing equipment is not suitable or seems to be out of date. A very large lack is related to missing possibilities to test element contents (like Na. K, Ca, Mg) and GC based parameters (ester content, concentration of glycerids/free glycerol). To overcome this situation – and to prevent a manifold investment - it is proposed to install the required equipment at one central independent lab which can be used by all market partners including the mineral oil industry. To improve the test quality it is suggested to participate in large international round robin tests. The anonymous data generated by such tests can help to identify and to solve problems of a laboratory and/or to get information about the precision data of a test method. Some internationally available quality assurance systems provide such round robin tests.

7 Conclusions

The development of a Mexican biodiesel standard should be achieved by an agreement of all national stakeholders. The standard could be a compromise between the consequences of the intended low blend target (up to B5) and new demands deduced from actual market and research results on biodiesel application and impacts. The blend fuel should not get a special standard but only a remark in the existing mineral oil standard about the permitted maximum FAME concentration and the standard which describes the minimum FAME requirements for the blend component.

Bibliography

- Ley de Promoción y Desarrollo de los Bioenergéticos
- Programa de Introducción de Bioenergéticos, SENER, 2009. Page 34
- The Biodiesel Handbook, G. Knothe, J. Krahl, J. van Gerpen, AOCS Press, Champaign, Illinois, USA
- UFOP Annual Report 2008, Berlin, September 2008
- UFOP Annual Report 2009, Berlin, September 2009
- Proceedings of 3rd International Conference for Biodiesel Producers 2008, AGQM, Berlin, 2008
- Proceedings of 2nd International Conference for Biodiesel Producers 2007, AGQM, Berlin, 2007

Vivir Mejor