The Importance of Quality Standards to Providing Confidence in Biofuel Regulation and Analysis

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BIOFUEL
TESTING NEW ZEALAND

Background

- Career analytical chemist with 30 years experience in the chemical and petroleum industry.
- IANZ technical auditor and currently work for Biofuels Testing NZ, a division of IPL, a contract laboratory based at the Marsden Point Refinery

Aims of Presentation

- In this presentation I will attempt to:
  - Review the impact of biofuels on the NZ fuels regulations and test methods
  - Overview one regulated biofuel test methods in detail
  - Briefly review quality systems and quality assurance
- I hope you will all find something useful in this presentation

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What is Biofuel

- **Wikipedia Definition:**

  Biofuel is defined as solid, liquid or gaseous fuel derived from relatively recently dead biological material and is distinguished from fossil fuels, which are derived from long dead biological material. Theoretically, biofuels can be produced from any (biological) carbon source; although, the most common sources are photosynthetic plants. Various plants and plant-derived materials are used for biofuel manufacturing.

What is Biofuel

- **Biofuels International Conference (May 09 Holland) Definition:**

  Biofuel is the term applied to any solid, liquid, or gaseous fuel produced from organic (once-living) matter. The word biofuel covers a wide range of products, some of which are commercially available today, and some of which are still in research and development.

What is Biofuel

- **Encyclopedia Britannica Definition:**
  Biofuel is Mixture of volatile, flammable hydrocarbons derived from plant material or animal waste and used as fuel. Some long-exploited biofuels, such as wood, can be used directly as a raw material that is burned to produce heat. The heat in turn can be used to run generators in a power plant to produce electricity. Sugars and starches from sugarcane, corn, and high-cellulose plants (such as switchgrass) can be converted into ethanol, which is used directly in internal-combustion engines or is mixed with gasoline (gasohol). Oils from plants such as the soybean or oil palm can be chemically processed and blended with petroleum diesel fuel to make biodiesel.

What is Biofuel

- **Websters New World College Dictionary Definition:**

  Biofuel is any fuel derived from renewable biological sources, as plants or animal waste; esp., a liquid fuel for automotive engines made from corn or soybean oil

What is Biodiesel

- **Wikipedia Definition:**

  Biodiesel refers to a non-petroleum-based diesel fuel consisting of long chain alkyl (methyl, propyl or ethyl) esters, made by transesterification of vegetable oil or animal fat (tallow), which can be used (alone, or blended with conventional petrodiesel) in unmodified diesel-engine vehicles. Biodiesel is distinguished from the *straight vegetable oil* (SVO) (sometimes referred to as "waste vegetable oil", "WVO", "used vegetable oil", "UVO", "pure plant oil", "PPO") used (alone, or blended) as fuels in some *converted* diesel vehicles.

Regulation of Biofuels

- NZ Fuel Regulations have been designed to ensure fuels and biofuels conform to a minimum quality and therefore are fit for purpose.
- They define a number of physical and chemical properties the fuel shall possess and limit the amount of impurities. Thus maximum and minimum specification limits are adopted for each fuel type. In most cases the specification limits are regulated to a single analytical test method.
- Before we take a look at some the current diesel and biodiesel regulations it would be beneficial to consider the impact of biofuels on NZ fuel regulations.

Regulation of Biofuels

The three main impacts are:

- In NZ a fuel classified as 'diesel' may now contain up to 5% by volume of biodiesel.
- A fuel classified as gasoline may contain up to 10% by volume of bioethanol.
- Biodiesel (B100) has it own regulatory specifications as does E100.

Now let's take a look at the NZ Fuel regulations.

NZ Diesel Regulations

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Schedule 2
Requirements for diesel

rr 9, 15, 17(3)

Property	Limits	Test method
Fatty acid methyl esters (% volume)[1]	5 maximum	EN 14078
Density at 15C (kg/m^3)	820 minimum 850 maximum	ASTM D1298
Distillation—95% volume recovered at (C) (T95)	360 maximum	ASTM D86
Cetane	51 minimum cetane index, or 51 minimum cetane number and 47 minimum cetane index[2]	Cetane number: ASTM D613 or ASTM D6890 Cetane index: ASTM D976
Water content (mg/kg)	200 maximum	IP 438
Total contamination (mg/kg)	24 maximum	IP 440
Colour (ASTM colour)	3.0 maximum	ASTM D1500
Cloud point (C) and cold filter plugging point (C)[3]	Summer maxima: Auckland and Northland: +6 cloud point; rest of New Zealand: +4 cloud point. Winter maxima: +2 cloud point and –6 cold filter plugging point	Cloud point: ASTM D5773 cold filter plugging point: IP 309
Sulphur[4] (mg/kg)	50 maximum 10 maximum on and from 1 January 2009	IP 497 or ASTM D5453
Polycyclic aromatic hydrocarbons (% mass)	11 maximum	IP 391
Filter blocking tendency	2.5 maximum; fuel must be of acceptable filterability so that it is fit for common purposes	IP 387 or ASTM D2068
Lubricity—HFRR wear scar diameter at 60C (µm)	460 maximum	IP 450
Viscosity at 40C mm^2 per second	2.0 minimum 4.5 maximum	ASTM D445
Oxidation stability (g/m^3)	25 maximum	ASTM D2274
Carbon residue (on 10% distillation residue) (% mass)	0.2 maximum	ASTM D4530
Copper strip corrosion (3 hours at 50C)	Class 1 maximum	ASTM D130
Ash (% mass)	0.01 maximum	ASTM D482
Flash point (C)	61 minimum	ASTM D93

1 Regulation 10 provides that the fatty acid methyl esters (biodiesel) must comply with Schedule 3: Requirements for biodiesel. 2 The cetane index is not applicable for diesel blended with biodiesel.3 These are maximum criteria; cold flow properties of a fuel must be fit for common purposes in the region and the season in which it is sold. Diesel that complies with the previous season's quality, and that is stored in a filling station tank to which fewer than 3 deliveries of diesel have been made since 6 weeks before the beginning of the season, is regarded as complying with this specification. Sales for marine use may be summer grade at any time of the year.4 The limit for sulphur does not apply to sale for marine use.

NZ Biodiesel B100 Regs.

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Engine Fuel Specifications Regulations 2008 (SR 2008/138) – New Zealand Legis... Page 1 of 1

Schedule 3
Requirements for biodiesel

rr 10, 16, 17(2)

Property	Limits	Test method
Methyl ester content (% mass)	96.5 minimum	EN 14103
Density at 15C (kg/m³)	860 minimum 900 maximum	ASTM D1298
Viscosity at 40C mm² per second	2.0 minimum 5.0 maximum[1]	ASTM D445
Flash point (C)	100 minimum	ASTM D93
Sulphur (mg/kg)	10 maximum	IP 497 or ASTM D5453
Carbon residue (on 100% distillation residue) (% mass)	0.05 maximum	ASTM D4530
or		
Carbon residue (on 10% distillation residue)[2] (% mass)	0.30 maximum	ISO 10370
Cetane number	51 minimum[3]	ASTM D613 or ASTM D6890
Sulphated ash content (% mass)	0.020 maximum	ASTM D874
Water (mg/kg)	500 maximum	IP 438
Total contamination (mg/kg)	24 maximum	IP 440
Copper strip corrosion (3 hours at 50C)	Class 1 maximum	ASTM D130
Oxidation stability, 110C (hours)	6.0 minimum[4]	EN 14112
Acid value (mg KOH/g)	0.50 maximum	ASTM D664
Iodine value (g iodine/100 g)	140 maximum	EN 14111
Linolenic acid methyl ester (% mass)	12.0 maximum	EN 14103
Polyunsaturated (≥4 double bonds) methyl esters[5] (% mass)	1 maximum	—
Methanol (% mass)	0.20 maximum	EN 14110
Monoglycerides (% mass)	0.80 maximum	ASTM D6584
Diglycerides (% mass)	0.20 maximum	ASTM D6584
Triglycerides (% mass)	0.20 maximum	ASTM D6584
Free glycerol (% mass)	0.020 maximum	ASTM D6584
Total glycerol (% mass)	0.25 maximum	ASTM D6584
Group I metals (Na+K) (mg/kg)	5.0 maximum	EN 14108 and EN 14109 — AAS-1
Group II metals (Ca+Mg) (mg/kg)	5.0 maximum	EN 14538 — ICP no is
Phosphorus (mg/kg)	10.0 maximum	ASTM D4951 — ICP int STD.

1 Regulations 10(a) and 17(2)(a) provide that, in the case of the biodiesel component of any blend of diesel and biodiesel, the maximum viscosity at 40C is 6.0 mm2 per second. 2 ASTM D1160 must be used to obtain the 10% distillation residue. 3 Regulations 10(b) and 17(2)(b) provide that, in the case of the biodiesel component of any blend of diesel and biodiesel, the minimum cetane number is 47. 4 Regulation 10(c) provides that, in the case of the biodiesel component of any blend of diesel and biodiesel sold by retail sale, the minimum oxidation stability is 10.0 hours. 5 Suitable test method to be developed.

EN 14107 — ICP no int std *

Fuels and Biofuels Regulatory Methods

Biofuels & the Aviation Industry

- New generation biofuels are being developed from novel sources. Many of these compounds have dissimilar properties to traditional petroleum fuels due to the fact that they have a significantly different chemical compositions.
- Aviation fuels are manufactured to tightly controlled internationally approved (CAA) standards that have evolved over many years.
- These fuels have been manufactured to specifications that ensure the fuel's properties meet the requirements of both the engine manufacturers and the extremes of the application (e.g. low freeze point)

Biofuels Evolution & the Aviation Industry

Biofuels & the Aviation Industry

- The introduction of biofuels with significantly different chemical compositions would require extensive testing over many years before the aviation authorities would sanction their use in commercial aircraft. Indeed the new fuel composition may require engine redesign.
- Therefore the aviation industry is unlikely to adopt biofuels in the foreseeable future unless their matrix is virtually identical to the existing petroleum base fuels. Of course it is possible to produce biofuels of this composition however it does limits the options.
- Imagine if a biofuel with a new composition was adopted for aviation use the problems and associated dangers of handling two possibly incompatible fuels.

Fuels and Biofuels Regulatory Methods

Biofuels & Ground Fuels

- In the case of ground fuels there are less problems associated with introduction of new a fuel with a significantly different composition to petroleum based fuels due to the fact the specifications and applications have greater tolerance.
- However, it is easy to underestimate the ramifications of introducing a new or altered fuel composition to the automotive fuel arena.
- Later I will show you some examples of the impact of the effect of changing the fuel composition on the regulated methods employed to test the quality of ground fuels.

Fuels and Biofuels Regulatory Methods

- Lets first examine the impact of new biodiesel matrices on the existing diesel specifications.
- The majority the regulated test methods were written and validated before biofuel matrices were available in the marketplace.
- Thus the scope and precision of these methods were based on the analysis of petroleum based diesel fuels.
- However some of these test methods have been used as regulatory methods to define the properties of biofuel blends without the requirement to extend their scope and precision.

Fuels and Biofuels Regulatory Methods

- For example lets look at the regulatory test methods for the cold properties of diesel. The regulations define that cloud point and CFPP are measured by methods ASTM D5773 and IP309. These methods were originally developed and precision calculated for the analysis of petroleum fuels. They use defined cooling rates and sample preanalysis temperatures.
- Within the parameters of the method the cold properties of mineral fuels are typically independent of cooling rate and sample storage temperature prior to analysis.
- However the cold properties of some biofuels are not independent of cooling rate or preanalysis storage temperature.

Fuels and Biofuels Regulatory Methods

- Thus we need to heat some biofuel samples in order to break their thermal memory then store above 25C before we analyse them. This can be done by heating to about 40C followed by storage at 26C. Failure to do this will result in random results far outside the methods repeatability and reproducibility precision limits.
- Furthermore if we vary the rate of cooling, still within the method tolerance limits, we can obtain different results on biodiesel blends as the formation of cloud or crystals in the fuel is dependent on cooling rate. Again the results generated can be random and far outside the repeatability and reproducibility precision limits of the method as these precisions were measured on mineral fuels

Fuels and Biofuels Regulatory Methods

- Therefore it is obvious that we need to ensure that the test methods are scoped for the application before being adopted into the regulations.
- If new sample compositions are available in the marketplace then the test methods must be adapted to change codicils issued to make them applicable to the new sample composition

Determination of Ester in Biodiesel by EN14103

Now lets examine another test method that has been a problem due to application to a sample composition outside its scope.

- EN14103 is a GC method employed to determine the FAME content of biodiesel.
- The method was developed for the analysis of vegetable based biodiesel.
- The method employs an internal standard, methyl heptadecanoate to quantify the methyl ester and linolenic acid ME content of the biofuel.
- The method is unusual as it does not employ a calibration curve but relies on peak area normalisation and linear detector response.

Determination of Ester in Biodiesel by EN14103

- In NZ animal fats (tallow) have been used to produce biodiesel and this method has been regulated to determine the FAME content of biodiesel B100.
- Vegetable oil based biofuels do not contain the C17 internal standard methyl heptadecanoate. However animal based biodiesels have been found to contain naturally occurring C17 methyl ester with the result that erroneously low results are determined because the size of the internal standard peak is inflated by the natural C17 methyl ester

Determination of Ester in Biodiesel by EN14103

- In addition EN14103 determines FAME between C14 and C24. This can result in tallow based B100 samples with 98+% FAME being failed by the test due to the chain length of the FAME being outside the method tolerance.
- The European Committee for Standardisation (CEN) are working on a proposed revision of the method in order to correct for this deficiency however the industry currently has no alternative method available.
- In the meantime most analytical service providers are scanning sample for naturally occurring C17 ME and those samples that show evidence of these esters are analysed by the standard method and the method modified as per CEN recommendation.

Determination of Ester in Biodiesel by EN14103

- When we examine the EN14103 method we note that the scope does not exclude animal based biodiesels. This may be because when the method was written the animal based biofuel matrix were not considered as a source of biodiesel.
- Therefore this support the premise offered earlier that test methods are scoped for the application before being adopted into the regulations. If the matrix is not considered within the scope of the method then work must be completed by literature research and lab testing to fully understand the ramifications of the new sample matrix and amendments or codicils made to the methods.

Determination of Ester in Biodiesel by EN14103

- Thus we can conclude that if the regulated method is not correctly scoped to the application, method precision and or accuracy may be compromised.
- The first defence against this type of error is to ensure the samples are within the scope of the regulated method
- The second defence is to employ experienced analysts who understand the test methods and comparison accuracy data with other labs.

Quality Systems and Quality Assurance

- Quality control systems and standards have been around a long time. It is said that the friezes on the pyramids depicts an inspection procedure. In the middle ages Trade Guilds were established to ensure consistent quality from their members.
- Inspection departments were introduced into most factories at the beginning of the 20th century and the Second World War saw the development of military standards to which contractors had to comply. Inspectors were appointed and paid by the military to ensure the product was not compromised by the internal pressures of the manufacturers.

Quality Systems and Quality Assurance

- The next step was a quantum leap. Instead of inspecting the product, a set of standards was produced that defined the processes involved in running the company and therefore producing its products. The first of the modern standards had arrived.
- The evolvement of these quality standards can be traced from the MIL-Q-9858 US Military standards of 1963 to the DEFSTAN 05 UK Ministry of Defence studs of 1973 to the BS British Standards of 1979 the ISO9000 International Studs of 1987 to the ISO9000:2000 standards of 2000

Quality Systems and Quality Assurance

- There is widespread and growing adoption of ISO Quality standards worldwide and New Zealand has adopted some Australian additional guidelines/standards to supplement the ISO series.
- Individual companies have adopted production practices such as **Lean Manufacturing,** a production practice that considers the expenditure of resources for any goal other than the creation of value for the end customer to be wasteful, and thus a target for elimination.
- Other standards have been developed to apply to specific areas such as ISO17025 for testing organisations.

Quality Systems and Quality Assurance

NZS/ISO/IEC 17025

- This standard is applicable to any organisation performing tests and/or calibrations.
- In 1972 the Testing Laboratory Registration Council was established by Act of Parliament. This Council was established as the governing body for IANZ's (International accreditation NZ).
- In NZ IANZ is the technical accreditation body that verifies the competence of organisations to work to ISO 17025 standard.
- IANZ audits the technical, quality and administrative systems of the lab to ensure it meets the international criteria of the 17025 standard.
- ISO17025 has a requirement for ongoing improvement through the internal audit and other systems. This means that the organisation must be continually working to refine its systems and improve the competency of its operation.

Quality Systems and Quality Assurance

- It is important to remember that ISO9000-200 standards also have a requirement for ongoing improvement through the internal audit and other systems. This is a significant difference to the previous ISO9000 standards and means that companies certificated to this standard must demonstrate that their quality systems are adequate and being followed.
- This neatly leads us on the idea of quality assurance.

Quality Systems and Quality Assurance

Quality Assurance:

- This is a subject that in my opinion has not been given enough focus over the past few years.
- One can have the best, most encompassing quality systems but if they are not being followed then they are a waste of time.
- If the quality control systems and preventative maintenance procedures are not impacting on the quality of the data generated by a lab or the biofuel manufactured by a plant then they are a waste of time.
- Quality Assurance systems are designed to give the assurance that the systems are being followed and quality control is improving the quality of the product.

Quality Systems and Quality Assurance

Quality Assurance:

- The first system to monitor Quality Assurance is internal auditing.
- This is a requirement of most of the ISO standards and offers a structured way of checking if systems are being followed.

  However in my experience this needs to be backed up with a secondary system of assurance. In a lab situation may be best completed by training the most experienced analysts to mentor, train and monitor staff.
- Other organisations may set up quality assurance departments that are separate to the people who make the product. This ensures that the people who monitor the application of the quality systems are not under pressure to produce the product.
- Whichever way the Quality Assurance systems are organised the importance of this function is too easily underestimated and I ask you to consider how you organisation organises Quality Assurance

Summary

- We have defined biofuels and biodiesel
- We have identified that regulatory test methods must be scoped for the correct application
- We have identified that skilled analysts are crucial to an analytical laboratory
- We have briefly reviewed quality control and assurance and I ask that you consider assurance in your organisation.