Measurement and Standards in the Biofuels Sector

A workshop hosted by Chemistry Innovation and Bioscience for Business Knowledge Transfer Networks, London, 17 September 2008

Report and recommendations

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1. Introduction and Background

Biofuels are fuels derived from biomass and biowaste and provide an important and increasing contribution to the renewable energy sector. The adoption of biofuels presents an opportunity to reduce the contribution of emissions from fossil-based transport fuels to climate change. By offering near carbon neutrality (biofuels only release the carbon dioxide that their biological source has absorbed during plant growth, although some carbon is released during processing and distribution) and, by virtue of usually being a liquid, biofuels are ideally suited to replace fossil fuels in transport applications. In addition to transport, biofuels can also be used in power generation and to produce chemicals.

The biofuels sector has been characterised by rapid growth over the past five years. This emerging sector has seen strong expansion in both the European biodiesel market and the US bioethanol market. An established bioethanol market in Brazil has been operating for some time and significant interest worldwide is being shown in emerging technology for production of biobutanol. Despite this growth in activity, there remain many challenges to overcome whether these relate to technical, regulatory or socio-economic issues. Further key considerations concern the quality, reliability and safe use of biofuel products. It cannot be assumed that measurements and standards developed for fossil-based fuels, and their associated infrastructure, are suitable for bio-based fuels. To support fully the growth in the sector, it is critical that appropriate and validated measurement techniques and associated standards are available to ensure the quality, safety and performance of biofuel products and the processing methods that have been used in their production.

To address some of these measurement challenges, a workshop entitled "Measurement and Standards in the Biofuels Sector" hosted by the Chemistry Innovation and Bioscience for Business Knowledge Transfer Networks was held in London on 17 September 2008. The objectives of the workshop were to review and discuss current measurement provision for the biofuels sector and to identify future needs for new measurement techniques, protocols and standards. Based on the outputs of this workshop, this report provides some recommendations on the developments necessary to ensure that measurement technology and standards fully meet the needs of this emerging sector.

2. Workshop objectives

The workshop focused on the application of measurement and standards to the production and distribution of biofuels and brought together industrialists representing production activities across the biofuels value chain alongside other experts and interested parties from research institutions and public sector organisations.

Key objectives were:

- To identify knowledge and technology gaps in measurement provision for both product compliance and process control and optimisation across production activities in the biofuels value chain.
- To demonstrate the potential of new analytical tools, sensors and diagnostics to improve processing methods and to reduce the costs and risks involved with biofuels production.

- To highlight where there are requirements for new or revised standards.
- To indicate where research and development activity should focus to generate the new measurement and analytical tools needed for this sector.
- To determine whether the biofuels sector has the right mix of skills available for providing measurement support and, where there are skills gaps, to identify training needs.

Speakers from BP, Innospec, Green Biologics, TMO Renewables, LGC and The Energy Institute presented to the meeting. Attendees were then invited to join parallel workshop discussions based around the following themes:

- Manufacture and production of biofuels
- Product specification and distribution
- The development of new methods to meet future needs

The combined outputs from these workshop discussions are presented and analysed in this report.

A copy of the Workshop Programme is given in Appendix 1 and copies of available presentations can be accessed through either the Chemistry Innovation or Bioscience for Business websites (www.chemistryinnovation.co.uk or www.biosciencektn.com)

3. Key issues

3.1 Biofuels are not simple hydrocarbons

Biofuels offer an attractive route to replacing transport fuels obtained from the refining of crude oil. However, although marketed as being functionally equivalent alternative to hydrocarbon-based petrol or diesel, biofuels are in fact chemically distinct substances that are produced from biomass-derived oxygenated feedstocks (starches, sugars, and plant oils). As a consequence, the physical and chemical properties of biofuels differ in a number of important ways from those exhibited by conventional hydrocarbon-based fuels.

This chemical distinction raises a number of issues regarding the properties, function and performance of biofuels that impact on the analytical protocols, quality control methods and the standards that are needed to examine and certify this new family of fuels. Policy-makers in government need to be made aware of the technical and quality issues, and related measurement and analysis challenges, that the different chemistries of biofuels present to the industry and that the biofuels sector needs time to address fully these new measurement challenges. The current situation has been likened to trying to build the railway tracks while the trains are running. It should be remembered that the petrochemical industry has achieved its current state of sophistication, in which large volumes of fuel are produced, blended and distributed to exacting customer specifications, after a century of development. However, the test methods underpinning the assurance of performance that have been developed for fossil-based fuels are not directly transferable to biofuels. Technologists need to examine the 'chemographies' of biofuels – to understand the physiochemical properties of these fuels and to define the 'chemical space' that the molecules in biofuels occupy (whether as fuel or impurities).

Only with such understanding can the impact of composition on performance, and hence reliable standards and analytical protocols, be established.

3.2 Standards: fitness for purpose

There is concern within the industry about the fitness for purpose of existing standards, particularly those originally developed for the petrochemical industry and simply transposed to the biofuels sector. Reports from the sector indicate that at present the existing standards process is not working adequately: protocols are unevenly applied and are in some cases inappropriate. Experiences in the field show that the current standards are easy to apply but can fail, in the sense that the product can nominally comply with the standard (as defined by analytical/measurement protocols) but fall short of performance requirements in use. This suggests there is a requirement for bespoke standards, tailored specifically for biofuel chemistries, and that a realistic timeline needs to be agreed for the delivery of these new standards.

Currently, the EN14214:2003 is the European standard for biodiesel (automotive fuel) which has been developed by CEN (European Committee for Standardisation) in partnership with national bodies. Some of the methods and potential issues associated with the current EN 14214 standard are summarized in Appendix 2. This information has been compiled by the Government Chemist at LGC as part of development of a biodiesel route map. The CEN technical committee CEN/TC 19 is addressing automotive fuels including ethanol as a blending component for petrol and E85 ethanol automotive fuel; CEN/TC 307 is working on oils and fats. Standards are also being applied and developed in the US and Brazil amongst other countries. Two Tripartite Task Forces comprising representatives for the EU, US and Brazil, for biodiesel and ethanol respectively, were set up in 2007 to classify biofuels specifications *. The remit of these task forces, nominated by the respective standards agencies of each region (CEN, NIST and ABNT) was to comment upon the extent and relative impact of work required to bring closer alignment between specifications as a basis for defining next steps. Agreement was found that International Standards are needed to facilitate and promote global trade in biofuels. It was also concluded that the ISO procedure was too lengthy and sometimes inconclusive.

The Government Chemist's expertise in biofuel measurement issues stems from an authorised analyst function under the Hydrocarbon Oil Duties Act 1979, and is complemented by a diversity of specialised R&D undertaken by LGC. As part of the National Measurement System (NMS), LGC is also UKAS-accredited to ISO Guide 34: 2000 for the production of reference materials, and is a founder member of the European Reference Material (ERM®) collaboration[1], which provides an additional level of peer review. Currently, LGC has ERMs for sulfur in petrol and diesel, and a flexible expertise in the development of complex matrix-based reference standards[2], and on this footing is open to views on the need for specific biofuel-related materials. NMS programmes provide regular (often annual) opportunities to develop proposals for certified standards, and for other measurement tools needed to advance biofuels, such as proficiency testing schemes. Projects that win NMS funding are usually robust collaborations with clear outcomes, e.g. meeting sustainability goals, advancing science and innovation, and supporting regulatory compliance.

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* White paper on internationally compatible biofuel standards: Tripartite task force Brazil, European Union & United States of America, December 31 2007

[1] http://www.erm-crm.org/html/homepage.htm

[2] http://www.lgc.co.uk/our_science/reference_materials.aspx

3.3 Specifications and feedstock variability

Principal requirements are:

- identification of the key chemical and physical properties of biofuels that require specification

- accurate measurement of biofuel variability

Clearly, the analysis of biofuels presents a complex analytical challenge. Central to any initiative to produce new standards for biofuels is to take account of bio-feedstock variability. To meet this challenge, more resource in terms of analytical expertise and facilities is required to examine the underlying chemistry of biofuels and to understand how this relates to feedstock type and origin. Many of the current standards for biodiesel have been developed with reference to rapeseed.

Finding resource for the development of measurement and analytical techniques is often a difficult task within the manufacturing and process industries. Often measurement is viewed as a cost with a lack of appreciation of the added value provided by investing in necessary equipment etc. Added to this generic problem of accessing funding for equipment and facilities, the biofuels sector is experiencing a situation where customer demand and government policy to promote use are running ahead of the specialised technical knowledge and expertise necessary to ensure fully adequate performance in application. Knowledge exchange with other sectors making use of sensing and process control technologies may help to bridge these gaps.

3.4 Manufacturing

There is a lack of know-how on how optimally to design and build biorefineries, how to fine tune and control production processes and how to make best use of by-products (e.g. glycerol from the production of biodiesel) generated by the manufacturing process. Economies of scale should be achievable through the adoption of a process-based approach. Industrialists indicate that there is little automation installed in production processes at present and that SDPs are need for standards and plant operations.

Under these circumstances, there is a need both for further development and application of measurement technologies appropriate to an R&D environment, where process understanding and design optimization are major concerns, and for robust and highly cost-effective on-line process monitoring technologies to enable product quality assurance and process control for large scale manufacturing. The detailed requirements will not only be quite different from those for petrochemical plant and will potentially be quite different for different biofuel manufacturing processes (fermentation to produce an alcohol-based fuel is quite different from biodiesel production from plant oils, for example).

3.5 Links with the automotive sector

It is important that biofuel manufacturers fully engage with the automotive OEMs. The development of both petrol-driven and diesel-driven engines to their current (high) performance levels has been a synergistic process over a long period that has required heavy investment in R & D. Ideally, given the heavy investment involved, the automotive

industry would like biofuels to be identical to (or exhibit complete fungibility towards) the petrochemically derived products they are intended to be substitutes for. However, this is probably an unrealistic goal and the adoption of biofuels across a broad range of transport applications will likely require development through partnership between (bio) fuel manufacturers and engine designers over an inevitably significant period of time. An effective forum for constructive interaction between the relevant parties is essential, as is recognition of the significant investment that will be required.

4. Current measurement needs

As stated in the introduction, whether in the form of biodiesel, bioethanol or other fuels derived from biomass, biofuels are chemically distinct systems from fossil-based fuels since they are derived from the oxygenated compounds in plant-based feedstocks (e.g. sugars, starches and plant oils). As such, biofuels are characterized by complex chemical compositions and contain a wide range of impurities including trace elements (these tend to be nature-dependent). For example, biodiesel is known to contain 3-5% of largely unspecified impurities. New methods are required to analyse this degree of chemical complexity and to determine the effect of feedstock variability on biofuel properties and performance.

The biofuels sector needs to develop a fundamental understanding of how the molecules in biofuels (both fuel and impurities) pass through the value chain. The 'fitness for purpose' for current tests to specify FAME in biodiesel, under EN14214, is currently a subject of some debate within the industry. The original test was designed for a narrow feedstock range (e.g. rapeseed) but problems have been reported in the field such as deposition for biodiesel formulations that were within specification but derived from alternative feedstocks. More work is needed to understand fully this behaviour and to establish predictive tests that could be part of a standard.

Oxidative stability is one of the most pressing measurement challenges in the biodiesel sector and new test methods are required. Water take-up is also a recognized problem in biodiesel and ethanol. As FAME can act as an emulsifier, water in biodiesel can become emulsified resulting in increases in viscosity thus initiating blockages in filters and valves. The presence of water can also affect the solubility of additives for both biodiesel and ethanol. Ethanol is also susceptible to the development of acidity causing corrosion problems in storage and distribution systems. Methods are needed to measure pH in non-aqueous systems.

Research is needed to understand the fundamentals of biofuels chemistry and specifically to determine the roles of oxidative stability, water content, acidity, bacterial growth, feedstock dependence and viscosity on fuel performance. Resultant operational problems related to these properties include poor cold flow properties, blockages from fuel emulsification and deposition and corrosion (e.g. pipelines, pumps). A key research target is to understand the mechanisms underpinning oxidation in biofuels and to identify anti-oxidants that would be effective in bestowing oxidative stability.

5. Future Developments

As the biofuels sector moves forward, a better understanding of the relationships between fuel properties and performance needs to be developed across all points of the value chain, including the impacts of feedstock heterogeneity. The relationships between chemical entities and physical properties of biofuels will be of fundamental importance.

Improved measurement technologies are needed to monitor and control the production and distribution processes. These will be technologies that can be applied *in situ* and that provide a fast response. At present, techniques and instruments are required for batch processing and to operate at a small-scale. Off-line measurement is currently acceptable but these must be robust, user-friendly and simple to apply. As the sector grows, however, analysers will need to operate at a larger scale and on-line. Developments are needed that are relevant to product quality and performance and that integrate different types of measurements, with some statistical correlation, in order to improve the basic understanding of the underlying science. Suggestions from the workshop participants included fast and detailed compositional analysis, the identification of a manageable number of critical impurity parameters and on-line monitors for the product as well as the process.

Experience to date with 'first generation' biofuels suggests the need for their 'smarter specification' going forward. In essence, this means that readily measurable parameters, which are reliable surrogates for key performance criteria, need to be established. These will be required in all the different parts of the value chain: from manufacture, through storage and distribution, to combustion in engines or power plant. For example, it will be necessary to address product corrosivity, viscosity and cold-flow characteristics, stability (over time and under a range of environmental conditions), and performance through the combustion process (including effect on engine life and exhaust emissions profile).

These areas are all currently adequately addressed by well-established methodologies for petrochemically derived fuels, but as already discussed, measurements that provide reliable surrogates for performance criteria for conventional fuels may not do so for the chemically quite different biofuels.

There is a further area with short – medium-term requirements that is additional and specific to biofuels relating to sustainability criteria. The whole thrust towards biofuels stems from the twin drivers of carbon footprint reduction and security of supply against a global background of ever-increasing carbon dioxide emissions and depleting oil reserves. To address these concerns biofuels need to come from genuinely renewable resources with demonstrably lower net emissions impact than current fossil reserves-based fuels. Protocols to establish renewable content are therefore required. This is a broad-ranging issue going significantly beyond the domain of analytical measurement techniques and will require consideration of Life Cycle Analysis methodologies and audit trail protocols.

As in the most of Europe, biofuels production in the UK is predominantly focused on the manufacture of biodiesel with some emerging activity in the production of bioethanol. A significant proportion of this manufacture and development activity is occurring in smaller companies who have limited access to measurement facilities or expertise. To

support these smaller enterprises in having access to measurement technology and expertise, mechanisms need to be found at a pre-competitive level that make available some of the expertise based in larger companies and RTOs to these smaller, less well-resourced companies. There are roles that the government through the Technology Strategy Board and National Measurement System could play in assisting such support either in-kind or through direct funding (such as the R&D grant scheme or some of the new voucher schemes being pioneered by several regional development agencies).

6. Conclusions

- Research is required to better understand the fundamental chemistry of biofuels, particularly with regard to oxidative stability, water take-up, acidity and the nature and levels of biofuel impurities. Developments in measurement technology will be essential to address and resolve these technical issues.

- Policymakers need to be made aware of the measurement challenges facing the biofuels sector and to gain a better awareness of the significant implications of the different chemical make-up of biofuels compared with fossil-based fuels.

- Realistic timelines need to be set for developing the new measurement technologies and standards that are required to accommodate the chemically distinct nature of biofuels. Collective effort across the relevant standards bodies will be a critical factor for success in developing international standards and promoting global trade in biofuels.

- Direct participation of the automotive manufacturers to help define specifications for advanced biofuels compatible with evolving engine design would help achieve longer tern broad uptake of biofuels.

- Methods need to be developed that can assess how feedstock type and feedstock heterogeneity can effect biofuels performance. This is essential for designing robust specifications for biofuels.

- Measurement is a necessity for successful innovation in the biofuels sector.

7.Recommended Actions

(where possible, to be pursued by the Knowledge Transfer Networks)

- Generate funding and industry support for a biofuels routemap as guide to the role of measurement in the biofuels sector. The biodiesel route map under development by the Government Chemist at LGC may provide a platform for this type of activity.
- Discuss with the Technology Strategy Board and other relevant funding bodies potential initiatives to address the issues listed in Appendix 2, one possible route being the National Measurement System.
- Create measurement and standards communications fora with a biofuels focus. The government-backed Knowledge Transfer Networks (KTNs) could assist in realizing this recommendation through the creation of a Special Interest Group.

- Create a biofuels centre of excellence to pool expertise relevant to measurement in the biofuels arena. New methods are needed to improve the basic understanding of biofuel systems as well as to monitor and control the manufacturing process.
- Generate funding for demonstrator projects at scale. The Knowledge Transfer Networks can advise on potential funding sources.
- Create mechanisms for the provision of 'big company' support in measurement practice and know-how to smaller companies and university groups. Funding mechanisms provided The Technology Strategy Board and National Measurement System may provide some opportunities. Targeted proof-of-concept funding to enable collaboration between sensors manufacturers and biofuels producers should be encouraged.
- Create validated reference materials.
- Policymakers in government need to be better informed of the measurement challenges facing the biofuels sector. This should be achieved through the publication of a position paper validated by industry practitioners and through fora already in place to support the biofuels sector (e.g. the Energy Institute) or through the networking platforms provided by the Knowledge Transfer Networks.

Appendix 1

Measurement and Standards in the Biofuels Sector

17 September 2008

Kingsway Hall Hotel, 66 Great Queen St, London WC2B 5BX

Final Programme

10.00 – 10.30 Registration and coffee

10.30 Opening remarks
Julie McDonald, Chemistry Innovation KTN and Dave Woodwark, Bioscience for Business KTN

10.40 "Analytical Challenges from the Distribution and Use of Automotive Biofuels"
Tom Lynch, BP.

11.05 "Difficulties in the Analysis of Biodiesel and Bx Blends"
Tony Cooney, Innospec.

11.30 Coffee

11.45 "Re-commercialisation of the Clostridial Acetone-Butanol Fermentation - Analytical and Measurement Challenges"
Preben Krabben, Green Biologics Ltd.

12.10 "Analytical Methodologies for a Second Generation Bioethanol Process"
Elliot Firth, TMO Renewables.

12.35 "Analytical Measurement for Energy Sector Innovation"
Neil Harris and John Francis, LGC.

13.05 Lunch

14.05 Breakout sessions

15.10 Presentation of outcomes

15.45 Closing remarks

16.00 Workshop ends

Appendix 2

Potential measurement issues for biodiesel

Standard measurement techniques are defined under BS EN 14214:2003

These tables have been reproduced from the initial consultation version of the biodiesel route map under development by the Government Chemist (http://www.governmentchemist.org.uk/Publications.aspx?m=77&amid=679 – feedback welcome)

Physical properties of biodiesel – measurement issues

Property	Examples of potential measurement issues
Density	Sampling technique that preserves volatiles; temperature control. BS EN 14214:2003 specifies a referee method
Viscosity	High results, which can be due to glycerides, may inform decisions on chemical testing
Flash point	Highly dependent on standardised procedure and apparatus
Cetane number	For novel blends, modelling fails - need direct measurement
Cold filter plug point	Temperature control; interpretation of anomalies

Inorganic chemistry of biodiesel – measurement issues

Analyte	Examples of potential analytical issues
Sulfur content	Strategy for best use of independent UV and X-ray fluorescence tests
Carbon residue	Analyte is not chemically well-defined, so additives invalidate the test
Sulfated ash content	Formation of pyrophosphates or MgO may add to uncertainty
Water content	If sampling directly, need to validate for any product/process change
Total contamination	Precision (but updated method now current as BS EN 12662:2008)
Copper strip corrosion	Qualitative; in future, imaging software may objectivise the test results
Acid value	The measured value includes mineral acids as well as free fatty acids
Group I metals	Atomic absorption spectrometry is routine
Group II metals	ICP optical emission spectrometry is routine
Phosphorus content	ICP optical emission spectrometry is routine

May need inductively coupled plasma mass spectrometry (ICP-MS) as referee method

Organic chemistry of biodiesel – measurement issues

Analyte	Examples of potential analytical issues
Ester content	Validation needed for feedstocks other than rapeseed & sunflower
with linolenic acid methyl ester	Depends on ester content accuracy & choice of standard compound
Oxidation stability	Temperature control; relevance of accelerated protocols to end use
Iodine value	Measure of unsaturation (double bonds), but relevance under review
Polyunsaturated methyl esters	(≥ 4 double bonds) Development of suitable standard method
Methanol content	Volatile components in novel sample types may interfere
Mono/di/triglyceride	Method suitable for rapeseed, sunflower & soybean may not resolve all peaks from coconut or palm kernel feedstocks
with free glycerol	Referee method incorporates chemical pre-reaction - requires expertise, skill and training
& total glycerol	Measured indirectly by summation from glycerides & free glycerol