Publishable Summary for 19ENG09 BIOFMET
New metrological methods for biofuel materials analysis

Overview

Biofuels, originating from biomass, can be defined as fuels produced by means of technologically advanced biological processes, and are a key factor in supporting EU aims of reducing greenhouse gas emissions while diversifying the energy fuel supplies. Reliable information on the nature and quality of the biomass or biofuel used is important to support the optimisation of their combustion with respect to higher efficiencies and lower emissions in energy production. In this project, more accurate measurement methods were developed and advanced traceable measurement standards for the determination of biofuel calorific value and for determining impurities and ash content were established. Three new reference materials were developed and produced to make end-users able to calibrate their equipment. Significant improvements to the method applied for bomb calorimetry has been made. In addition, two new moisture transfer standards have been developed and calibration facilities are in place and ready for end users. Automatic sampling for solid biofuels has been researched and a new device made commercially available for safe and representative sampling. These results will aid enable a fair trade between biofuel suppliers and users and with that a reduction of disputes.

Need

United Nations has included efficient utilisation of renewable energy sources such as biomass in its sustainable development goals for ‘Affordable and Clean Energy’, ‘Industry, Innovation and Infrastructure’, ‘Sustainable Cities and Communities’, ‘Responsible Consumption and Production’ and ‘Climate Action’. The EU aims for biomass to increase to at least a 27% share of renewable energy consumption. Currently the total primary production of renewable energy based on biomass is about 130 kilotons of oil equivalent annually. One of the goals in the revision of the EU Energy Taxation Directive is that heat production taxes are calculated using estimated energy content of solid biofuels. This estimate is subject to errors caused by non-representable sampling and measurements based on non-ideal, slow, offline methods. This has major economic consequences.

The rapidly increasing use of biomass impacts international trade, whilst the need for optimal fuel utilisation, the minimisation of emissions and increased sustainability of the supply have increased the need for fast, reliable, traceable measurements and characterisation of biofuels as essential for this development and requires:

- Knowledge of the accurate content of water in solid biofuel materials such as wood pellets or wood chips is important for ensuring optimal combustion efficiency and fair payment of the fuel.
- Improved sampling methods for solid biofuels to reduce the significant associated errors in fuel quality control which can lead to error in moisture content measurement.
- Knowledge of the ash content for the accurate determination of its calorific value thereby establishing the energy content of the fuel.
- Knowledge and reliable methods for determination of the level of impurities in biofuels which are essential to limit precipitation of solids in the fuel transportation system and to establish the energy content of the fuel and regulate its combustion, as well as for fiscal billing of the fuel.

Achieving such measurements has been a significant challenge given the use of adapted and slow offline methods and documentary standards that originally was developed for measurement of coal and are unverified for biofuels and insufficient for understanding the contents of these fuels. Traceability will provide the legal and

financial regulatory means for “trackability” and determining the calorific value, as well as the bio-origin of the samples/blends and their carbon dioxide contribution.

Objectives

The overall objective of the project was to research online metrological methods for the analysis of solid and liquid biofuels, such as wood pellets and fatty acids methyl esters (FAME, a form of liquid biofuel), with the purpose of establishing traceable calorific values and ensuring optimal combustion. The end goal was to provide metrologically sound data sets for a larger fraction of biofuels, hence providing background information for their more efficient use.

The specific objectives were:

1. To develop traceable online measurements for water content in solid biofuels for the measurement ranges 5-12 % (wood pellets) and 20-75 % (wood chips) with a target uncertainty of 5 %.
2. To develop improved methods for the sampling of biofuels (i.e., in cases where online methods cannot be used). This should include using data-science techniques such as machine learning to optimise calibration curves and uncertainties.
3. To traceably determine the calorific value of the solid biofuels by developing validated methods for the online measurement of ash content. In addition, to develop accurate methods < 0.1 % absolute repeatability and < 0.2 % absolute reproducibility (as per EN ISO 18122) for determining the amount and composition of ash content in the measurement range 0-1.2 %.
4. To develop validated methods to determine the amount and nature of impurities in liquid biofuels, including quantifying and qualifying inorganic (i.e., Na, Ca, K, Mg, P) for a measurement range of 0.5 mg/kg to 2.5 mg/kg with a relative target uncertainty of 5-10 % (k=1) and organic by-products (i.e., total glycerol) < 5 % relative repeatability for 0.1-0.3 % range as per EN ISO 14105. In addition, to develop a traceable method for the online determination of the calorific value of liquid biofuels.
5. To disseminate and facilitate the take up of the technology and measurement infrastructure developed in the project by the measurement supply chain, standards developing organisations (CEN TC 335, CEN TC 19) and end users (e.g. the European Technology and Innovation Platform (ETIP) and European Biodiesel Board (EBB).

Progress beyond the state-of-the-art

Biofuel measurements are dominated by offline and slow laboratory analysis, regulated by standardisation. The project has therefore researched the potential of introducing new, fast, flexible, and traceable measurements.

The introduction of the new online methods and traceability schemes for moisture and ash content in biofuel power plants will allow continuous accurate measurements of the biofuels’ properties and will result in a high degree of digitalisation. This will lead to improved control, more efficient use of the fuel, lower consumption, and minimalised emissions. Two new transfer standards based on multiband electromagnetic radiation and acoustic principles have been developed and tested for calibration of online equipment. They are non-destructive, non-invasive and fast. Traceability of these transfer standards has been ensured by developing and establishing new calibration facilities. The developed calibration facilities can be utilised by end-users already now. An important step has been taken to move from current method-based standardised procedures, towards outcome-based verification of measurement results.

Until now the manual sampling procedures of standards ISO 18135 and ISO 14780 often cannot be applied in practice because they are time-consuming or require equipment and practices that are not possible to implement in the production line, and their sampling methodology lacks theoretical support. In this project, the aim was to ensure that proper and theoretically supported sampling techniques can be applied widely in the future. The consortium has researched the effect of sample handling and packaging on the homogeneity and stability of reference materials developed within the project. Advanced data science techniques such as machine learning and deep learning has been researched and demonstrated and have shown the potential to reduce the uncertainty of online measurements by optimising calibration curves. The measurement uncertainty is heavily affected by the extremely heterogenous nature of the biofuels and of the industrial environment. Using information from additional sensors located at the conveyer or sampling equipment combined with the new analysis techniques developed in this project, a method to uncover potential correlations between these

influencing factors and measurement uncertainties has been suggested. Implementing such techniques will significantly improve reproducibility and repeatability of online measurements such as those for moisture in wood chips.

A promising method for online traceable ash content measurements is X-ray fluorescence (XRF) for determining metal abundances and hence the ash content. The ash content is important as it is the part that has no calorific value. In the project traceability of portable XRF equipment has been established by using a wavelength dispersive XRF laboratory standard instrument. Traceability was achieved via the new reference materials developed in the project where defined amounts of ash, organic and inorganic impurities have been added.

A measurement and validation program for bomb calorimetry on solid and liquid biofuels has been developed and new reference materials have been produced to enable traceable calibration of measurement standards e.g. based on XRF, MW, NIR for accurately determining the biofuel's calorific value. The project partners have pursued different, complementary approaches to achieve the objectives. For instance, analytical procedures for the determination of organic and inorganic impurities in liquid biofuel have been developed and validated and a new transfer standard was developed for online measurement of impurities.

Results

The project produced a report (Deliverable 1) about the required parameters and metrological methodologies for measuring the calorific value, qualification and quantification of impurities, ash, and moisture content measurements. The report was based on a stakeholder survey with 58 participants. Most participants in the survey - around 45 % - were from research institutes. Adding to that, 22 % were from analysis laboratories and quality facilities, which confirmed the need for a profound metrological procedure and analysis under defined uncertainty budgets for the determination of the calorific value, moisture, and impurities of biofuels. Furthermore, around 31 % of the participants were from industry, divided between power plants and biofuel producers. The report included a literature review performed by the project members and has been made available to the public on the BIOFMET web-site.

Objective 1: Traceable online measurements for water content in solid biofuels

Two reference methods using different traceability routes to SI, were developed and validated by intercomparison. Two unique transfers standards were developed. One based on using electromagnetic wave propagation to determine water content, and one based on an acoustic measurement system. SI-Traceability of these transfer standards were obtained by comparison with the reference methods using wood pellets and wood chips. Uncertainties below the 5 % targeted was achieved. Finally, the calibration of an online measurement instrument was made at a CHP plant in Randers, Denmark demonstrating the applicability of the complete traceability chain.

Objective 1 has thereby been achieved.

Objective 2: Improved methods for the sampling of biofuels; exploiting data science techniques

A method for improving the sampling of biofuels was developed and validated. The method is based on a robot equipped with a 250 mm auger allowing class P100 biomass material to be sampled. Extensive testing at two Finnish powerplants showed that the automatic sampling gave similar results to when manually sampling is performed according to ISO 18135:2017, but in a much more efficient and safe manner. Input has been provided to European standardisation to encourage inclusion of automatic sampling in the next version of the standard based on the research made here. The device has already been commercialised.

The use of data-science techniques, in particular machine learning, for optimising calibration curves for water content to improve uncertainties has been researched and the developed method tested on data obtained at a CHP (combined heating and power) plant in Denmark, where an inline system for water-content measurements is employed at the conveyor belt feeding the boilers. The tests showed that applying machine learning has potential in improving the precision of calibration curves for in-line moisture measurement equipment. The work has provided essential input to the "Good Practice Guidelines on uncertainty assessment of biofuel measurements" (deliverable D7) that is made available to the public on the BIOFMET web site (https://doi.org/10.5281/zenodo.8180289).

Objective 2 has thereby been achieved.

Objective 3: Traceable determination of the calorific value of solid biofuels by measurement of the ash content

For solid biofuels, samples for testing and evaluating both ash and water content in a multi laboratory setup were prepared and sent to the participants (wood pellets and two qualities of wood chips). Measurements of ash content were performed, and less than 0.1 % repeatability was achieved. In case of wood chips, it was found that inhomogeneity strongly influences the reproducibility and the targeted reproducibility of less than 0.2% could only be achieved for high-quality wood chips. Calorific value measurements of solid and liquid biofuel were performed independently from three project partners. Based on the results, a unified uncertainty budget for bomb calorimetric measurements of biofuels and an improved measurement and sample handling strategy for the determination of the energy content of solid biofuels by bomb calorimetry were developed.

A protocol was developed for wave dispersive X-ray fluorescence (WD-XRF) method for the analysis of selected elements in pellet, wood chips and ash samples after milling and homogenisation. Evaluation of the partners' XRF measurement standards have been carried out.

Three new CRM (Certified Reference Material) candidates, two solid and one liquid, have been produced. The procedures for material preparation and handling as well as the methods of analysis, i.e., certification of parameters have been set up. The materials selected have been processed and subjected to the certification procedures (homogeneity and stability checks). Characterisation measurements, for calorific value and for ash/impurity content value, have been made and full characterisation measurements of the solid and liquid CRM are in place.

Objective 3 has thereby been achieved.

Objective 4: Methods to determine impurities and method for online calorific value of liquid biofuels

The metrological requirements for the certified reference material candidates and the impurity analysis were established (the report "D1: Report on required parameters and metrological methodologies for measuring calorific value of biofuels and qualifying impurities, moisture, and ash content" serving as input for defining the requirements, is available on the BIOFMET website). A liquid biofuel reference material was produced, certified for calorific value, density, viscosity and mass fractions of Ca, K, Mg, Na, P, S elements. The mass concentration was determined of total glycerol, free glycerol and residual mono-, di- and triglycerides contained by fatty acid methyl esters (FAME) resulting from the transesterification of vegetable oils. The targeted uncertainties were met and the work has provided essential input to the "Good Practice Guidelines on uncertainty assessment of biofuel measurements" (deliverable D7) that is made available to the public on the BIOFMET web site (https://doi.org/10.5281/zenodo.8180289). A prototype instrument for on-line measurement of impurities, such as ethanol in biodiesel or water content in bioliquids have been developed and tested. In the future this could be a promising tool for non-destructive fraud detection without chemical analysis or sampling.

Objective 4 has thereby been achieved.

Impact

Dissemination activities included:

a) A project website (www.biofmet.eu) as well as a LinkedIn page (https://www.linkedin.com/company/biofmet/) to promote the project to a user community as wide as possible. The first five project newsletters are available at the website, and a last newsletter will be published after concluding the project. All important documents and open access papers produced during the project, including the guideline "Good Practice Guidelines on uncertainty assessment of biofuel measurements" developed in the project, are also available via the website.
b) Formation of a formal stakeholders committee and collaborators joining the project. By the end of the project there were 18 stakeholders and collaborators from 11 countries. The stakeholder committee included representatives from national standardisation bodies, laboratories, regional metrology organisations, trade and industry associations, producers and traders of biofuels, operators of biofuel-fired powerplants, companies providing services and instrumentation for process automation and optimisation.

c) Two workshops where the first took place at IST, Lisbon in June 2022. This event had 34 participants and included ten presentations and six posters from the project's partners with details on the BIOFMET's activities. One additional presentation was carried out by a Portuguese company, manufacturer of thermal energy equipment powered by biomass fuels. The second Workshop was held at PTB, Braunschweig, Germany, in March 2023. This Workshop had 24 participants and included twelve presentations and five posters including an oral presentation from a company from the Republic of Türkiye regarding calorimetry. More details on the workshops as well as the presentations can be found on the project's website.

d) An online training course launched in May 2023 in the YouTube page: https://www.youtube.com/@biofmet. The training is divided into five modules, according to the different topics covered by the project. Each module is composed of a series of videos with presentations and laboratory equipment demonstrations.

e) Fourteen presentations about the project and its aims were given at EURAMET EMN Energy Gases, TC-T and TC-MC, to the CIPM CCT and CCQM meetings and to COOMET TC1.12 and 1.10. These are the leading metrology committees in this field.

f) The project was presented at meetings by ISO TC 193 WG 25, ISO TC 28 WG 24 and CEN-CLC/Eco-CG. Input in the form of a report with concrete suggestions for changes in EN-ISO 18135 and EN-ISO 18122 in connection with the next update has been made available for standardization groups (e.g. CEN/TC 19, CEN/TC 335, ISO/TC 238) via DS s358 (Biofuels).

g) 10 conference presentations at the: 29th European Biomass Conference (EUBCE 2021), 24th Kalorimetrietage, Biomass PowerON Conference 2021, International Conference on biomass (IConBM2022), XVIIIth International Symposium PRIOCHEM "Priorities of Chemistry for a Sustainable Development" (PRIOCHEM 2022), 9th International Conference on Materials Science and Technologies – RoMat 2022, 20th and 21st International Metrology Congress (CIM 2021 and 2023) and 789. WE-Heraeus-Seminar: Sustainable Aviation Fuels - Design, Production and Climate Impact.

h) 12 scientific papers have been submitted to open-access peer reviewed journals. At the time of writing 7 papers have been published and are available from the BIOFMET web-page.

Impact on industrial and other user communities

This project will have an impact on both producers of liquid and solid biofuels and users of these products in the power industry to whom accurate determinations of the fuel's energy content supported by product quality documentation underpinned by rigorous and traceable testing are of key importance.

The new rigorous calibration methods, reference materials and procedures developed in this project will enable improvement of the quality control of liquid and solid biofuels. The two reference standards developed for the calibration of the transfer standards are ready to facilitate industry with calibrations of measuring instruments for water content in biofuels. The technologies developed for on-line measurement of water-content and impurities is expected in the future to be taken up by instrument manufacturers. Three new reference materials are ready for the market.

Automated and representative sampling of the fuels by means of robots, has been implemented and commercialised by an industrial partner which supports improved quality control and support fair trade as well as a safer working environment. The published guideline on uncertainty and the use of machine learning to optimise calibration curves will assist the efficiency and digitalisation of the industry using solid and liquid biofuels.

When the suggestions for improvement of normative standards have been implemented greater measurement harmonisation across the biofuel sector is enabled, creating increased operator confidence in supplied calorific content of the fuels. This is important to ensure that the energy production meets the output expectations.

Impact on the metrology and scientific communities

New advanced measurement guidelines for accurate determination of the calorific value of solid and liquid biofuels has been established, and new reference materials for the determination of the calorific value, ash and impurities have been made available. This will in the short term enable the intercomparison of calorimetric facilities at NMI level with an accuracy not obtainable today. In the longer term, measurement uncertainties within this field will be improved at European biofuel supplier and operator facilities, where current differences in measurements of moisture content and calorific value are pronounced.

The project has produced 12 scientific peer-reviewed publications regarding bomb calorimetry, the new methods for impurity determination, new techniques for determining water content in solid and liquid materials. The published results and designs are expected to be used by the scientific research community.

At NMI/DI level, 3 organisations outside the consortium joined the project as collaborators.

Impact on relevant standards

The earliest impact of the project on standards will be at the level of sampling, determination of moisture, ash, impurities and calorific value. The project was presented at meetings by ISO TC 193 WG 25, ISO TC 28 WG 24 and CEN-CLC/Eco-CG. Input in the form of a report with concrete suggestions for changes in EN-ISO 18135 and EN-ISO 18122 in connection with the next update has been made available for standardization groups (e.g. CEN/TC 19, CEN/TC 335, ISO/TC 238) via DS s358 (Biofuels).

The project has developed reference materials for solid biofuels which will supply a quality control material for verification of methods for determining the calorific value of solid biofuels according to the ISO 18125 standard.

Long-term economic, social, and environmental impacts

The development of the new methods, technology and knowledge within this project will support greater uptake of sustainable biofuels enabling greater diversification in the energy supply and a reduction of reliance on fossil-fuelled electricity production. This will have an impact on climate and environmental protection. The EU aims for a 40 % reduction of greenhouse gas emissions compared to 1990 levels. The indicative target for an improvement in energy efficiency at EU level is at least 27 % (compared to projections), to be reviewed by 2020 (with an EU level of 30 % in mind).

Within 5-10 years, the introduction of new broad range liquid fuels will enter the market aimed at the land and sea transport sector. It is anticipated that these will be in the form of methanol, ethanol, biodiesel, diesel made from plastic, ammonia or other energy carrying liquids that can be used in combustion engines. These new liquid fuels will come from multiple sources and origin of feedstock which affect the impurities in the fuel. Accurate real time methods for identification of impurities on an industrial scale will be needed. This project has provided a step towards this.

Energy storage technologies are essential when the production of CO_2 neutral energy from e.g. wind power increases. Electro-fuels also known as Power-to-Liquid have a potential to replace fossil fuels in the future. Introducing new types of fuels for existing technologies (e.g. cars, ships, aviation) will require traceable measurements and documentation of the impurities in the fuel, not only after, but also during their production.

The outcome of the project will thus support the transition to clean CO_2 neutral energy and the independence from fossil fuels.

List of publications

- M. Shehab, C. Stratulat, K. Ozcan, A. Boztepe, A. Isleyen, E. Zondervan, K. Moshammer, A Comprehensive Analysis of the Risks Associated with the Determination of Biofuels' Calorific Value by Bomb Calorimetry, Energies. 15 (2022) 2771. https://doi.org/10.3390/en15082771

- M. Shehab, C. Stratulat, K. Ozcan, A. Boztepe, F. Coskun, F.S. Alper Isleyen, E. Zondervan, K. Moshammer, Improved Metrological Methodology to Address the Challenges Associated with the Determination of Biofuels Calorific Value by Bomb Calorimeter, Chemical Engineering Transactions. 92 (2022) 433-438. https://doi.org/10.3303/CET2292073

- F. Sparma, B. Tallawi, E. Georgen, and P. Sabouroux, Multi-Probe Sensor for Water Content Diagnosis of Liquid Biofuels, Progress In Electromagnetics Research Letters, Vol. 106, 1-6, 2022. https://doi.org/10.2528/PIERL22021104

- Floriane Sparma Sarah Sennoun Pierre Sabouroux , "Detection of Water Content in Honey by Electromagnetics Characterization Measurements," Progress In Electromagnetics Research Letters, Vol. 111, 1-7, 2023. https://doi.org/10.2528/PIERL23041205

- Bayan Tallawi Floriane Sparma Eric Georgin Pierre Sabouroux , "Towards Validating a Coaxial Transmission Cell for Dielectric Measurements on Liquids," Progress In Electromagnetics Research C, Vol. 134, 223-236, 2023. https://doi.org/10.2528/PIERC23013104

- Stratulat, C.; Ginghina, R.E.; Bratu, A.E.; Isleyen, A.; Tunc, M.; Hafner-Vuk, K.; Frey, A.M.; Kjeldsen, H.; Vogl, J. Development- and Validation-Improved Metrological Methods for the Determination of Inorganic Impurities and Ash Content from Biofuels. Energies 2023, 16, 5221. https://doi.org/10.3390/en16135221

- Shehab, M.; Moshammer, K.; Franke, M.; Zondervan, E. Analysis of the Potential of Meeting the EU's Sustainable Aviation Fuel Targets in 2030 and 2050. Sustainability 2023, 15, 9266. https://doi.org/10.3390/su15129266

This list is also available here: https://www.euramet.org/repository/research-publications-repository-link/

Project start date and duration:	1 June 2020, 36 months	
Coordinator: Jan Nielsen Tel: +45 7220 1236 E-mail: jnn@teknologisk.dk Project website address: http://www.biofmet.eu		
Internal Funded Partners: 1. DTI, Denmark 2. BRML, Romania 3. CETIAT, France 4. CMI, Czech Republic 5. IMBiH, Bosnia and Herzegovina 6. PTB, Germany 7. TUBITAK, Türkiye	External Funded Partners: 8. AMU, France 9. CTU, Czech Republic 10. IST, Portugal 11. PROMETEC, Finland 12. VERDO, Denmark	Unfunded Partners:
RMG: -		