KBBPPS

Knowledge Based Bio-based Products' Pre-Standardization

Work package 4
Biomass Content

Deliverable N° 4.2:
Assessment study report on fractionation of formulations pre-biogenic measurement

Summary

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Summary

As requested as part of the KBBPPS project the fractionation of bio-based products was explored for the purpose of assisting and clarifying complementary analyses of bio-based content. The origin of the research call was a Mandate by the European Commission addressed to the European Standardization bodies (CEN, CENELEC and ETSI) for the development of horizontal European standards and other standardisation deliverables for bio-based products. This Mandate M/429 was given in the context of the "Lead Market Initiative for Europe" of the European Commission and it was accepted and executed by CEN.

The project as a whole is targeting an increased uptake of standards and certification systems for bio-based products. The application of standards and certification systems in the European bio-based product industry is anticipated to have positive long-term effects on the overall development of bio-based product markets. Public acceptance of bio-based products will hopefully be increased through ensuring and verifying the sustainable sourcing of raw materials, the effective bio-content and clear indication of their (comparative) functionality in relation to the regular products. The programme will promote these positive effects by facilitating the development and improvement of standards and their related certification systems. The use of commonly agreed principles for the development of national and international methodologies for assessing the functionality and other qualities of bio-based products will ensure their consistency, credibility, and the efficient use of limited resources (for standardization), including data, knowledge and expertise. In establishing common principles with standards and related certification tools, industry and governments should develop and foster innovation, and boost trade in bio-based product markets.

There are very few products on the market that are a single chemical/material component and some contain a very large number of components (*i.e*. a formulation). Measurement of the biogenic content of formulated products was suspected as being possible of creating skewed results with both false positives and negatives depending on the precise formulation being measured. Fractionation of these formulations into simpler, ideally component, parts would facilitate measurement of biogenic content for the different formulation ingredients thus also enabling data to be used horizontally for other formulations using the same components in differing quantities. Values based on individual components pre-formulation can be compared to those obtained from measurements of components after deconstruction.

This report documents the results of fractionation procedures established in the literature and novel work focusing on the separation of formulated lubricants, plastics, solvents and surfactants. The outcomes varied in success rate from ineffective to satisfactory. Ultimately it was concluded that what is gained from even the most effective fractionation is not cost effective or viable pre-biomass content assessment, even given the greater detail in knowledge obtained concerning the origin of bio-based products. Not least the issue being

that no one fractionation methodology could be found that was suitable and applicable to the four product classes investigated (plastics, surfactants, solvents and lubricants) and therefore no horizontal method for all product types could be identified. Instead it is suggested that simple and rapid analytical techniques, that do not actually create any tangible fractionation, are worthy of application, for some knowledge of the composition of the sample can be obtained rather readily that may help decide whether the article in question can be considered bio-based or otherwise. For example, some of the methods demonstrated could be used as verification of a manufacturers claimed composition prior to submission for bio-based content.

Concerning the report, note that any errors in the identification of chemicals, or their relative composition within a formulation is indicative of the difficulties in analysing and fractionating bio-based products of unknown composition. An onus on the manufacturers and suppliers of bio-based products is suggested as the best way to clarify the composition and bio-based content of formulations, minimising errors and promoting transparency and uptake of bio-based products.

Fractionation of formulations and blended materials was applied to investigate whether the deconstruction of complex mixtures would aid the understanding of biogenic content analysis, chiefly bio-based carbon measurements. The usefulness of this would seem to be dependent on the class of product. For cleaning products, lubricants, and packing and building materials, half of these bio-based articles consist of at least 75% bio-based carbon content. The smaller solvent product set had a greater tendency for low bio-based content formulations. Because of the generally high bio-based content of bio-based product formulations, the need for fractionation is actually low for many of the more complex product classes to which successful fractionation would be the most rewarding. If the majority of components in a formulation are bio-based, then separating them will not reveal further significant details concerning their origin.

However, the potential size of the bio-based product market means that many products will have medium to low bio-based carbon content, and fractionation would clarify the nature of the composition and the origin of the components. Thus the fractionation of several consumer products and model formulations has been attempted, with limited success. It seems that the diversity of potential and present bio-based products, even when limited to just lubricants, plastics, solvents, and surfactants, demand a range of fractionation techniques, often multiple operations in sequence to create a separation of individual ingredients. Usually fractions consisted of multiple ingredients, and often ingredients could not be reclaimed. It was also found that ingredients consisting of mixtures of compounds (vegetable oils for one) were inadvertently separated into portions not representative of that original ingredient. Often solvents are required for analysis contaminating the sample. These problems were not resolved, and the principle of fractionation should not be incorporated into other tasks conducted within the KBBPPS project. Perhaps the only exception might be the freeze drying of samples for ease of handling and more efficient testing (providing higher concentrations of sample and less moisture to hinder

combustion when necessary). This can only be performed in certain circumstances, dependant on the volatility of other compounds in the sample. Any volatile components will be lost, such as aroma molecules and most solvents. Aqueous solutions of surfactants can be processed in this manner. It would be pertinent to analyse both the original article and a freeze dried portion if it is considered to be useful, and an acceptable margin of error between the results of any biogenic analysis established. A freeze-drying step could also be used as a means of determining water content and this is clearly of value when considering the issues relating to viewing water as bio-based or not and if it should simply be ignored. Otherwise, the fractionation process is time and money intensive and it seems an almost certainty they not horizontal fractionation methodology covering all product types will be achievable.

The elucidation of formulations by spectroscopic means and complimented through analytical chromatography might be a good exercise when ambiguity arises from a biomass content calculation. However these methods need to be developed before firm recommendations can be made. For this work, IR spectroscopy was useful because it is applicable to all phases of matter, and in turn, all bio-based products. Nuclear magnetic spectroscopy was even more useful but only when the sample was soluble in organic solvents. Volatile samples can be analysed by GC, or failing that HPLC along with other soluble samples as a matter of routine given the opportunity. More specialised chromatography is required for polymers and surfactants, which introduces a slight discontinuity into the horizontal analysis of all bio-based products. Again, solubility in solvents is required for chromatography and so possible recommended standard analytical test methods to assist biomass content claims will be fragmented according to product type, but undoubtedly useful nevertheless in an individual basis.