KBBPPS

Knowledge Based Bio-based Products' Pre-Standardization

Work package 4, Biomass Content

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Thermal treatment study: Assessment study report on novel thermal treatments for biogenic measurement

Summary

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Summary

As established in the KBBPPS description of work, and reiterated on the project website (www.biobasedeconomy.eu/research/kbbpps), the project aims to increase the uptake of standard test methods and certification schemes for bio-based products. It is hoped that the development and application of standards for the bio-based product industry will have positive long-term effects on the development of a European bio-based economy. Higher quality and greater sustainability of bio-based products should increase to the satisfaction of end-users at all levels, and improve the economic viability of bio-based product utilisation. Finally, public acceptance of bio-based products can 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 (fossil fuel-based) products. These positive effects will indirectly result in faster growth of the bio-based product industry and increased share of bio-based in the total use of final (consumer) products and intermediates up to 2020 and beyond.

Currently, the state of the art in terms of direct bio-based content determination is restricted to biogenic carbon content. The methodology is based on accelerated mass spectrometry (AMS) or other techniques such as liquid scintillation counting (LSC) that can resolve the ratio of carbon isotopes ($^{14}C/^{12}C$) in a sample. Results based on the ^{14}C methodology are expressed as the fraction of the bio-based carbon relative to the total carbon content of the sample. The bio-based product must be combusted to carbon dioxide, and then converted to graphite (AMS), or benzene (LSC) in some methodologies.

The ubiquitous carbon dioxide production stage of sample preparation under **ASTM D6866** and related standards is laborious, involving several technically challenging processes that can involve extreme temperatures and the use of catalysis and other chemistries not amenable to automation. It is also not possible to monitor the combustion process *in situ* to ensure all the organic content is accounted for. In the case of incomplete combustion, thermogravimetric analysis (TGA) can record the proportion of residual material. Hyphenated detectors based on infra-red (IR) spectroscopy or mass spectrometry can help assign the combustion products of TGA, which may not necessarily be simply carbon dioxide and water. This information helps conclude whether a representative sample of the bio-based product has been taken.

Thermogravimetry (TG) experiments were conducted on lubricants, plastics, solvents, surfactants and some other formulated products. It was found that often carbon dioxide production was not clean, and partially oxidised products are observed in the volatiles of combustion. This means that it is not necessarily guaranteed that complete and representative combustion is always achieved, and any subsequent biogenic analysis may not give a true account of the bio-based product sample. Some issues were a result of the TG apparatus and are not problematic when a bomb calorimeter or a quartz combustion vial is used in-

stead. The volatility of solvents for instance meant that evaporation occurred before combustion. Because of the multitude of decomposition pathways available to bio-based products of all types, and the lack of clarity behind current combustion techniques, TGA offers the means to study the mode of decomposition and accurately calculate the amount of residual material and the chemical composition of the combustion products. In instances where bio-based content analysis has produced a result of dubious accuracy, the sample combustion stage of sample preparation can be scrutinised to a greater degree with TGA.

This report contains a brief overview of standard test methodologies relevant to the combustion of organic samples, some specifically in order to obtain bio-based content measurements. A description of TGA and its hyphenation to infra-red (IR) spectroscopy to give TG-IR, as demonstrated for a variety of bio-based products is covered. Experiments to compare TGA with bomb calorimetry as methods of carbon dioxide preparation are also reported within. Results are presented in the form of TG traces and 3D IR spectra (supplemented by a number of 2D cross-sections).

In summary it would seem prudent to only recommend TGA in instances where the conventional combustion practice (using sealed combustion apparatus) is providing a carbon dioxide sample producing biogenic analysis results of dubious accuracy. Then the combustion process can be carefully analysed. In this work that was achieved using a combination of the TG and IR (hyphenated to combined TG-IR analysis), but in some cases just the mass loss recorded in the TG trace would be sufficient to reveal the difference between complete combustion and incomplete or inaccurate sample preparation.

It is advisable to use freeze drying prior to thermal treatment as a method of enhancing the combustibility of samples, but also increases the quantity of organic carbon present relative to the sample size for clearer analysis. In some instances where samples were found to undergo incomplete combustion, various oxidation catalysts previously described in research articles were applied. Incomplete combustion was not resolved through the use of catalysis, this being attributed to volatility issues created in a flow system. Instead combustion efficiency was found to be strongly correlated to the proportion of oxygen in the apparatus atmosphere.