

Captured carbon vs. biobased

Can products made from captured/recycled CO₂ be called biobased?

B iobased carbon content and captured or recycled carbon content are two separate metrics, though not always exclusive of each other. Biobased content is based upon the source of the raw material and is thus a 'beginning of life' concept. On the other hand, recycled or captured carbon content is based upon an 'end of life' action of e.g. incineration. As such, it is important to understand the differences between the two carbon content types and why each needs to be treated differently when developing standards for measurement or determination.

Defining biobased

The term biobased is used to describe materials (products and/or chemicals) derived in whole or in part from biomass resources; organic materials available on a continuous basis (i.e. renewable) from terrestrial and marine agricultural, plant, animal, and fungal sources living in a natural environment in equilibrium with the atmosphere (ref D6866, USDA, Farm Bill, EU). The phrase "living in a natural environment in equilibrium with the atmosphere" in the definition is critical because it provides for the absolute measurement of the biobased carbon content of a product using radiocarbon (carbon-14) analysis, and validates the amount of carbons originating from plant-biomass resources.

There are three naturally occurring isotopes of carbon: ¹²C, ¹³C, ¹⁴C and all are present in living organisms. Carbon-14 (¹⁴C), however, is radioactive. The living systems maintain their C-14 content in equilibrium with atmospheric C-14. In other words, all plant-biomass feedstocks will contain the same level of C-14 as the atmosphere does. When a living plant or animal dies, it ceases to take up C-14, and thus no longer maintains an equilibrium level of C-14 with atmospheric C-14. The amount of C-14 in the carbon from this material will then decay exponentially from the equilibrium level with a half-life of 5730 years. Products made from biomass feedstocks like agricultural, plant, animal, marine, and forestry materials will still retain 100% of C-14 radioactivity for a long period of time (only 1% of radioactivity is lost after 100 years). Fossil carbons in products will have zero radioactivity as they are formed over millions of years. The ASTM & ISO test methods use the above radiocarbon concept to quantify the biobased carbons originating from the biomass feedstocks. The amount of biobased carbon in a given sample can be determined using radiocarbon dating, which measures the amount of carbon-14 present.

Because carbon present in biobased materials is recently captured from the atmosphere, the combustion and release of carbon dioxide (CO₂) from biobased material results in a net zero carbon footprint: if this carbon dioxide is captured or recycled, then this is also biobased captured or recycled carbon dioxide. In contrast, fossil fuel-derived material is formed over millions of years (devoid of carbon-14) and thus combustion of fossil fuels adds to the atmospheric levels of carbon dioxide. But, as will be discussed later, the use of

captured or recycled CO₂ partially mitigates this addition of greenhouse gases into the atmosphere.

Test standards for biobased testing

Carbon-14 testing is performed according to widely accepted test standards such as ASTM D6866 and ISO 16620-2. ASTM D6866 is a standard test method used for determining the biobased content of solid, liquid and gaseous samples using radiocarbon dating [3]. Likewise, ISO 16620-2 is an international standard test method for determining the biobased content of solid, liquid and gaseous samples using carbon-14 analysis [4].

After analyzing a sample, the result is cited as percent modern carbon (pMC) and reported as percent biobased carbon content (or simply percent biobased content). A result of zero pMC indicates a sample is wholly derived from fossil carbon and does not contain any measurable carbon-14. In contrast, one hundred pMC represents a sample comprised entirely of biobased carbons from plant-biomass resources. If the pMC value is between 0 and 100, the content is a mixture of fossil carbon and biobased carbon. Under ASTM D6866, this percentage is a measure of the amount of biomass-derived carbon in a product compared to its total organic carbon (TOC) content. ISO 16620-2 uses this terminology as well [3, 4].

Certifying biobased products

Carbon-14 testing has been used for over a decade to validate biobased claims and often to receive product eligibility for third-party certifications and eco-labels. ISO-17025 accredited laboratory Beta Analytic has tested the percent biobased content of over a thousand samples within a wide range of product types. The biobased approach has qualified over 2,500 biobased products in the marketplace today [5].

Globally, there are several biobased certification programs. The United States Department of Agriculture (USDA) BioPreferred® Program requires the measurement of the biobased content of products according to the ASTM D6866 standard. This program includes two parts: a mandatory federal purchasing requirement and a voluntary labeling program for biobased products. The USDA has identified over 100 product categories with a minimum biobased content established per category for which federal agencies have purchasing requirements. Furthermore, the voluntary labeling initiative allows companies to receive the USDA Certified Biobased Product certification label on products that exceed the minimum threshold of biobased content required for the specific product category. This has certified over 2,500 products [6]. Several of these products may also be certified by other programs such as TÜV AUSTRIA's OK biobased (using a star system: one-star is for products with biobased content between 20% and 40% while a four-star certified product contains over 80%



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biobased content [7] and DIN CERTCO's DIN-Geprüft (with three quality divisions: Biobased 20-50%, Biobased 50-85%, and Biobased >85%) [8] in Europe.

Beyond those mentioned above, biobased testing has been incorporated into many other eco-labeling programs and biobased product initiatives. These include but are not limited to Japan BioPlastics Association's BiomassPla certification, Canada's EcoLogo Program, French Decree 2016-379 on Single-Use Plastic Bags, and Italy's EU Directive 2015/720 on Biobased Plastic Bags.

Products manufactured from captured/recycled CO₂

To reiterate, in order to be called 'biobased' a product or chemical needs to be manufactured from renewable, plant-biomass living systems that exist in a natural environment in equilibrium with atmospheric CO₂. Products obtained from converting smokestack CO₂ from coal, natural gas or other fossil fuel burning systems do not fall under the 'biobased' definition and do not lend themselves to quantitative analysis by radiocarbon measurement (ASTM D6866) since these products do not contain any carbon-14 content.

Therefore, PHAs and algae-based products, polymers, or chemicals produced from only petroleum-based smokestack CO₂ are not "biobased."

However, these products are beneficial to the environment by removing CO₂ during production that would otherwise be emitted back into the atmosphere.

By using recycled CO₂ the product manufacturing process also does not require the burning of additional fossil fuels. Again, this reduces the emissions of carbon dioxide into the atmosphere.

There are, however, fuel combustion sources that burn municipal solid waste (MSW) or mixed fuels (biomass-derived and fossil fuel). Any captured or recycled CO₂ from these sources will have a radiocarbon signal. The US EPA Greenhouse Gas (GHG) reporting rule requires the determination of the biogenic (biomass-derived) CO₂ contribution from these sources using the ASTM D6866 standard. Thus, products made from these sources of captured CO₂ may have biobased content.

Conclusion

While products derived from recycled CO₂ may provide environmental benefits, they do not always meet the requirements to be considered as biobased products. There are over 2,500 products certified under the USDA BioPreferred Program based on testing per ASTM D6866 and countless products in Europe and Asia that qualify as biobased and whose biobased carbon content can be accurately validated. Modifying the existing D6866 (and ISO) standards to accommodate products made with recycled carbon dioxide

devoid of carbon-14 content could negatively impact the credibility and market acceptance of biobased products and open the door to non-verifiable products. Separate verifiable standards and validation criteria for environmental benefit should be developed for these products. Approaches using carbon tagging or an audit approach would be useful to develop. Future standards for products captured from recycled CO₂ containing only petroleum-based carbon are critical in order to develop this new class of chemicals and polymers.

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Want to help ASTM D20.96 ?

ASTM D20.96 Environmentally Degradable Plastics and Biobased Products subcommittee is moving forward with developing a recycled/capture carbon content standard and is actively seeking individuals interested in helping. If you have interest in this, please email Kelvin Okamoto (kelvin@greenbottomline.com).