MICHIGAN STATE UNIVERSITY

BIOBASED (CARBON) CONTENT OF COMPLEX ASSEMBLIES

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BIO PREFERRED PROGRAM

The BioPreferred^{SM} program aims to increase the purchase and use of renewable, environmentally friendly biobased products while providing "green" jobs and new markets for farmers, manufacturers, and vendors.

The BioPreferred program offers three major benefits:

- **Climate Change Impact Reduction**
  - **reducing CO_2 emissions**
- **Energy/Environmental Security**
  - **Reduced dependence on petro feedstock; use bio/renewables**
- **Economic Development**
  - **Rural, farm and forestry based industries**

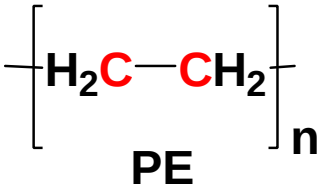
Value Proposition for Biobased (Biomass/Renewable) Products

Switching the origins of a product's CARBON from "petro/fossil" to "bio" reduces the carbon footprint

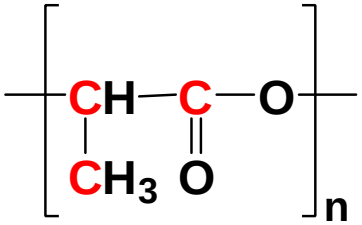
- **Using (renewable) biomass feedstock as opposed to petro/fossil feedstock – energy/environmental security**
- **Reducing heat trapping CO_2 emissions -- Minimizing global warming/climate change problems**
- **Economic development – empowering rural farm, forestry and allied manufacturing industry**

Carbon footprint (global warming impact category, GWP):

- **MATERIAL/PRODUCT CARBON FOOTPRINT – Impact of replacing completely or in part the petro/fossil carbon with bio carbon – the origins of the carbon**



PE



PLA

$C_aH_bO_cX_d$

a,b,c,d are set positive integers; and X = N, S,

- **PROCESS CARBON FOOTPRINT – Impact of converting feedstock to product**
  - **Carbon emissions from all stages of unit operations to convert the selected C-feedstock (petro or bio/renewable) to product**
  - **Material (Carbon) balance – life cycle inventory analysis (LCI)**
  - **Impact on the environment of the carbon emissions – global warming potential (GWP)**

- **Environmental Footprint (LCA methodology)**
  - **Carbon footprint + other impact footprint categories like human health, ozone depletion, eutrophication, acidification, photochemical smog, etc**

Terminology:

BIOBASED (BIOMASS OR RENEWABLE BASED)

Biobased (Biomass or Renewable) based Materials **– Organic material/s containing in whole or part biogenic carbon (carbon from biological sources)**

- **Refers to using biomass or crop feedstock (New carbon) vs petroleum or fossil feedstock (Old carbon)**
- **Reducing carbon footprint**

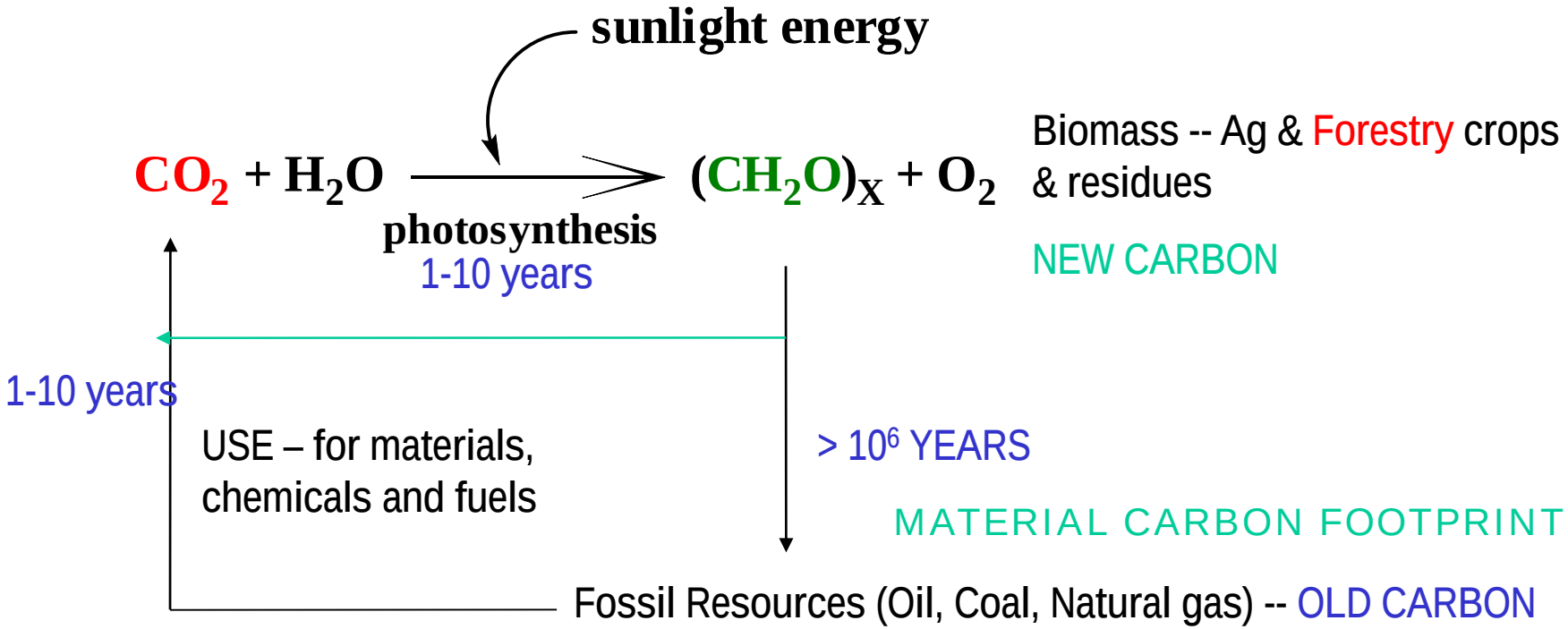
Organic Material/s **-- material(s) containing carbon based compound(s) in which the carbon is attached to other carbon atom(s), hydrogen, oxygen, or other elements in a chain, ring, or three dimensional structures (IUPAC nomenclature)**

Biobased (carbon) Content **-- The bio content is based on the amount of biogenic carbon present, and defined as the amount of bio *carbon* in the plastic as fraction weight (mass) or percent weight (mass) of the total organic carbon in the plastic. (ASTM D6866)**

% bio or biobased content = Bio (organic) carbon/total (organic carbon) * 100

ASTM D6866 – Standard Test Methods for Determining the Biobased Content of Solid, Liquid, and Gaseous Samples Using Radiocarbon Analysis

Terminology: Fundamentals, & Rationale



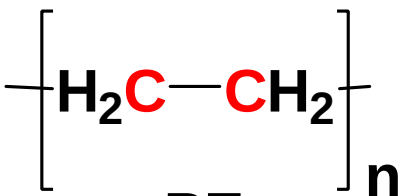
Rate and time scales of CO_2 utilization is in balance using bio/renewable feedstocks (1-10 years) as opposed to using fossil feedstocks

Material Carbon Footprint

What is the impact of the material/product's carbon footprint on the environment ? –

- **100 Kg of polyethylene will result in net ?? Kg of CO_2 released into the atmosphere**
  - **Based on "petro carbon" vs "bio carbon"**

- **100 Kg of polyester (PET)acid will results in net ?? Kg CO_2 release into the atmosphere**
  - **based on how many "petro carbons" vs "bio carbons"**



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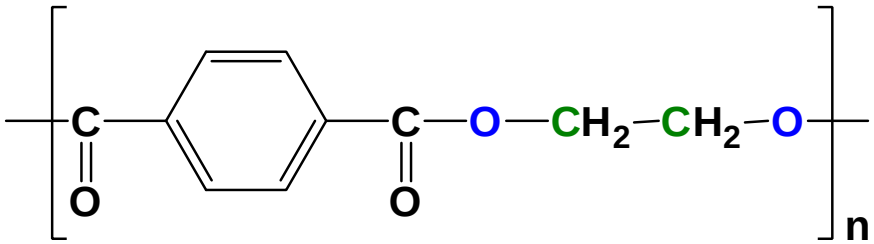
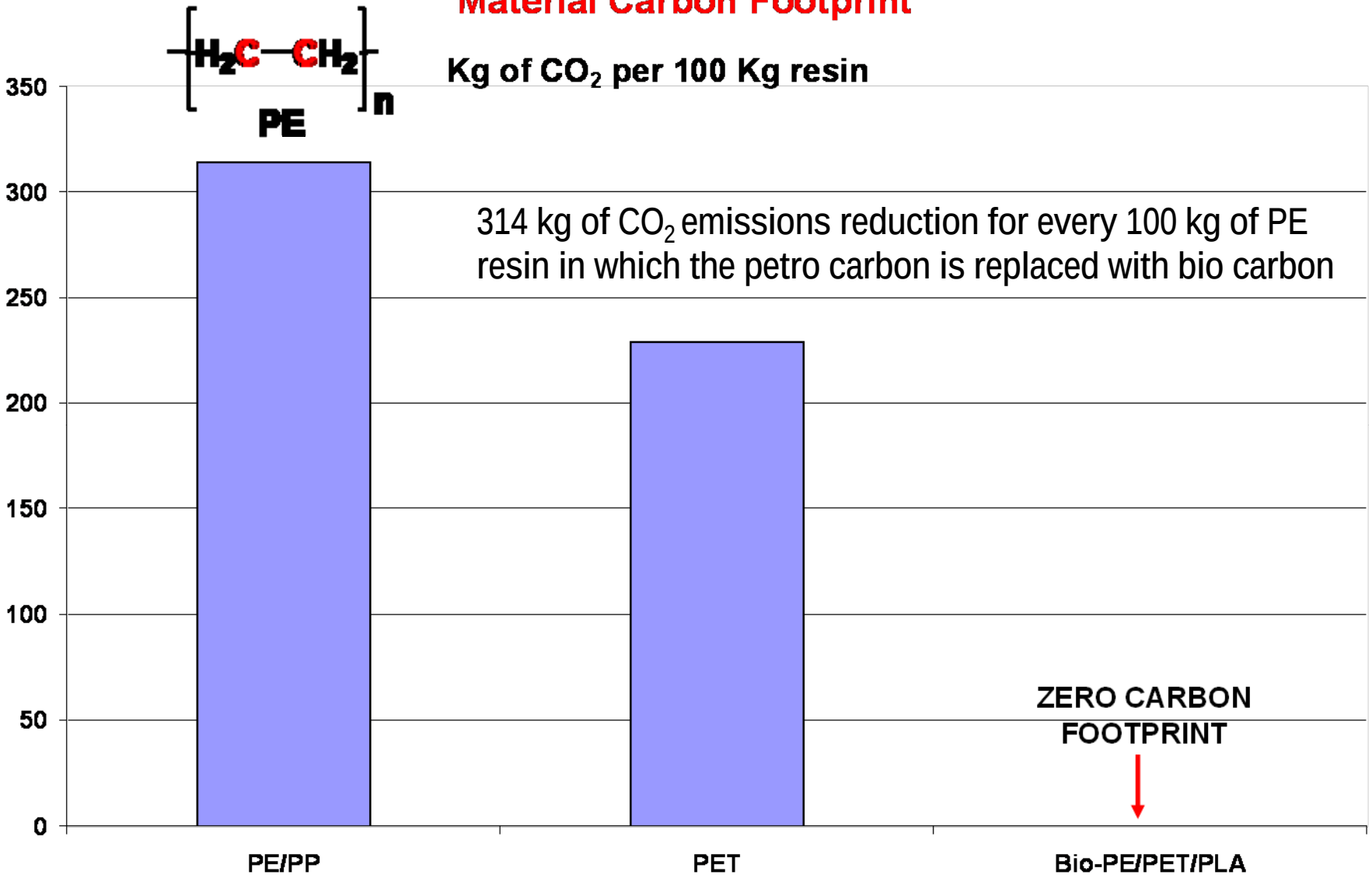


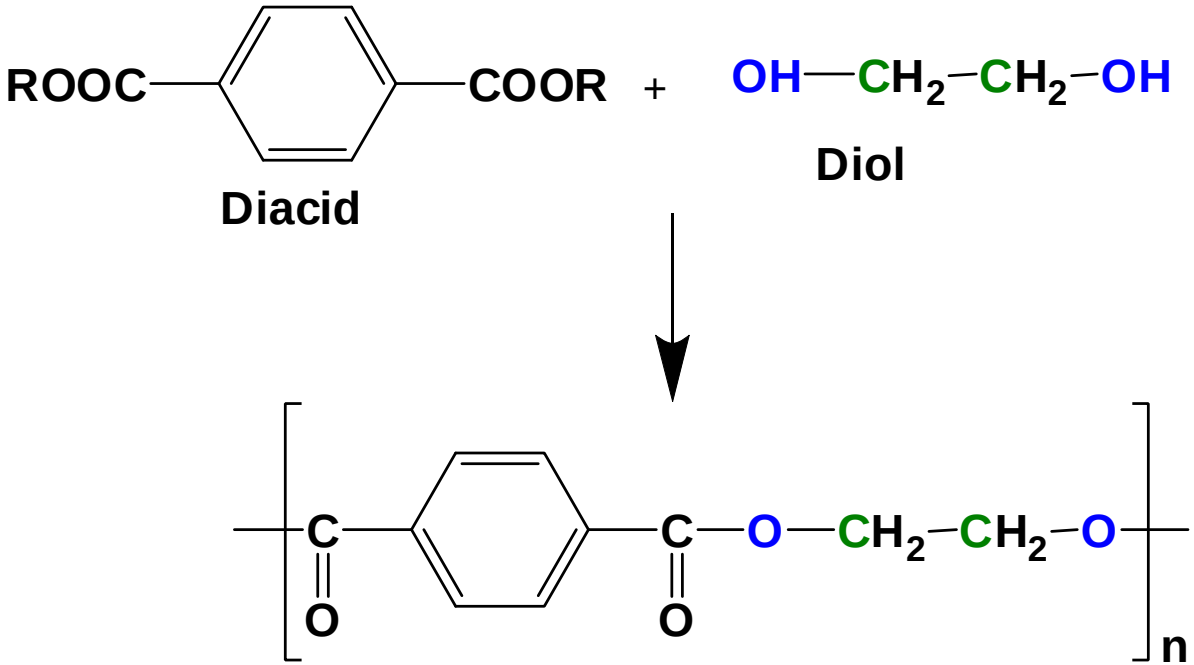
PET

Material Carbon Footprint



Ramani Narayan, Michigan State University

Material carbon footprint calculations – PET exemplar

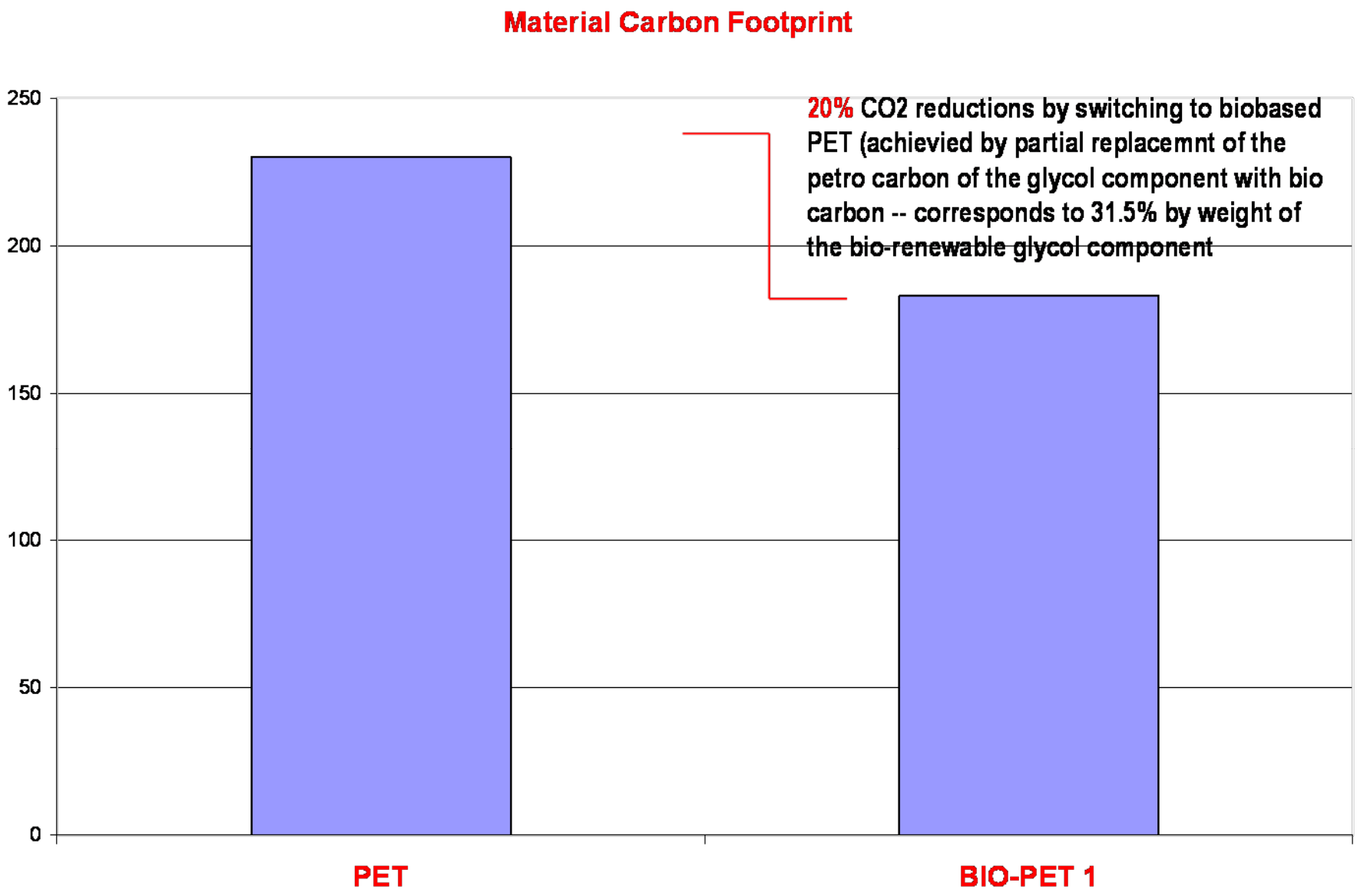


PET

Acid component = 8C; glycol component = 2C;
Acid component = 68.75%; glycol component = 31.25% on mass basis

Bio (carbon) content is 20% if two petro carbons substituted by bio carbons – by using the glycol (diol) component from bio(plant sources)

Material carbon footprint calculations – PET exemplar



Communicating and presenting CO_2 emissions reduction data – "material carbon" footprint

Considering that the world wide use of PET resin for bottles and fiber is 37.5 million metric tons, this first step of replacing the glycol petro carbon with bio carbon offers an annual CO2 reduction of 17.19 million metric tons.

To visualize this CO2 reduction in practical ready-to-understand terms the following equivalency applies (equivalency calculator):

- Eliminate CO2 emissions from consuming 40 million barrels of oil each year
- Eliminate CO2 emissions from driving 3 million passenger vehicles each year
- Eliminate CO2 emissions from consuming 1,951,191,82 gallons of gasoline each year
- Eliminate CO2 emissions from using electricity in 2,384,189 homes each year

GHG, equivalency calculator; www.epa.gov

Measurement of bio (carbon) content – the Principle

$^{14}CO_2$ – Solar radiation

$\updownarrow$

$^{12}CO_2$

$\longrightarrow$

Biomass/Bio-organics

$(^{12}CH_2O)_x \longleftrightarrow (^{14}CH_2O)_x$

NEW CARBON

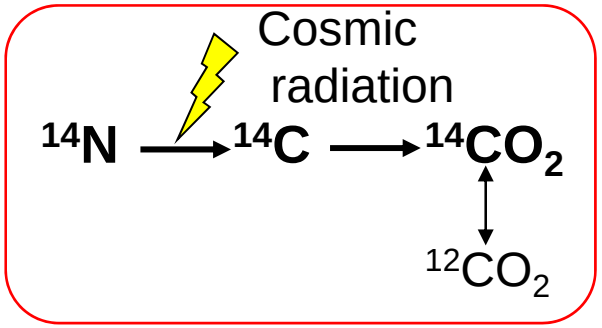
$\downarrow$ **> 10^6 years**

Fossil Resources
(petroleum, natural gas, coal)

$(^{12}CH_2)_n$ $(^{12}CHO)_x$

OLD CARBON

C-14 signature forms the basis of Standard test method to quantify biobased content (ASTM D6866)



Narayan, *ACS (an American Chemical Society publication) Symposium Ser.939, Chapter 18, pg 282, 2006*

Measurement of biobased (carbon) content – ASTM D6866

C-product combusted to CO_2

$^{14}C/^{12}C$ ratio is compared directly with a oxalic acid radiocarbon standard reference material (SRM 4990c) that is 100% new (bio) carbon.

14.27 dpm/g is the absolute value of the primary oxalic acid standard (SRM 4990b) actually 13.27 dpm/g (0.93 of of the reference standard) to correct for the post 1950 ^{14}C injection into the atmosphere

Contains concentration of 1.2×10^{-12} % of C-14 isotope equivalent to 100% bio carbon content

IMPORTANT NOTE:

To calculate percent bio carbon present in product

multiply the experimental biobased content (from ASTM D6866) with the percent total organic carbon (TOC) (as determined by standard elemental analysis)

COMPLEX MATERIALS

- **Beverage bottle composed of three components, the bottle, the cap, and sleeve**
- **Computer composed of multiple components – organic and inorganic materials**
- **Automobile composed of multiple components – organic and inorganic materials – more complex**
- **Many more products in between these complexities**

COMPLEX MATERIALS

- **Bio Carbon** – Carbon containing concentration of 1.2×10^{-12} % of C-14 isotope (14.27 dpm/g)
- **Organic carbon** – Carbon present in the form of organic compounds
- **Constituent** : individual chemical materials and substances that comprise the components which go into making a product. The constituents can be readily analyzed for its biobased and organic carbon content using ASTM test methods
- **Component** : part of a product (or a packaging) that can be separated by hand by using simple physical means
- **Integrated Component :** part of product that can be (easily) differentiated but not (easily) separated by hand or by using simple physical means

Biobased (Carbon) content of complex materials

Biobased carbon content of complex product ($BCC_{product}$) comprising i constituents whose biobased and organic carbon content can be experimentally determined equals:

$$W_i * BCC_i * OCC_i / W_i * OCCi$$

W_i = mass of the ith component

BCC_i = biobased carbon content of ith component

OCCi = organic carbon content of the ith component

Minimum organic carbon content of constituent i (OCC_i) = 30%

Minimum biobased carbon content of constituent I (BCC_i) = 20%

Japan -- carbon footprint labelling

Narayan

Europe – biobased carbon labelling

20-40%	40-60%	60-80%	> 80%

Bio carbon content

- **On a basis of the determined percentage of renewable raw materials (% Bio-based), your product can be certified as one-star-bio-based, two-star-bio-based, three-star-bio-based or four-star-bio-based.**
- **In contrast to LCA (Life Cycle Assessment), the investigation method behind the OK biobased certification is very simple and the exact value can be precisely and scientifically measured and calculated. This renders checks and re-checks very transparent and also allows “apples to be compared with apples” with the greatest ease.**
- **For raw materials, intermediate, and finished products**

www.okbiobased.be

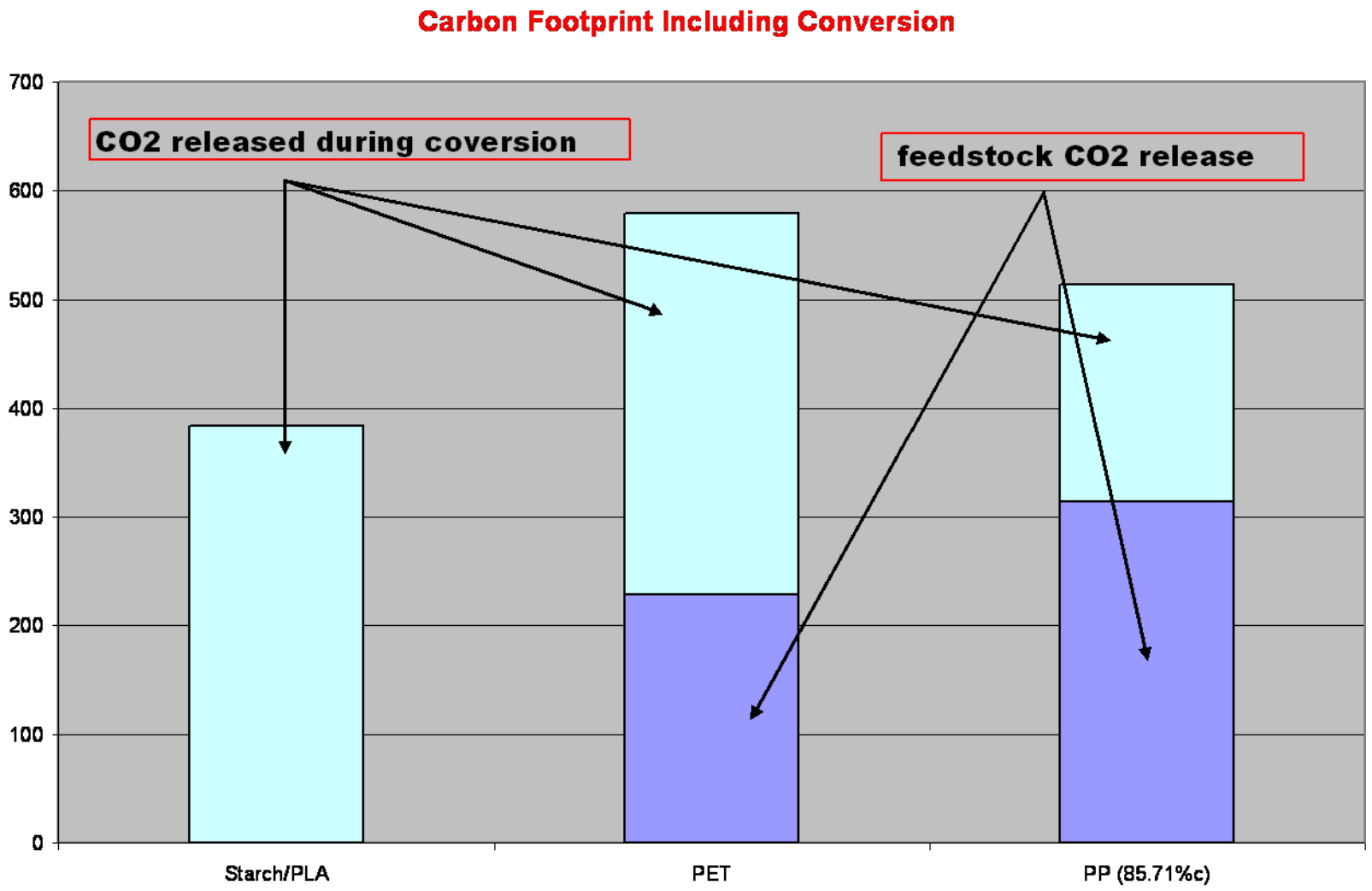
Process Carbon Footprint

- Carbon footprint from the conversion of feedstock to product – cradle to factory gate scenario and total environmental footprint to be calculated using LCA methodology ASTM D7075 or ISO 1440
- End of life scenarios – disposal system can give skewed/misused LCA's
- Transport (of product from factory/production point to customer) and disposal can be considered to have the same footprint for petro and bio feedstock derived products
  - B2B value chain analysis OR carbon to factory gate analysis

LCA and bio carbon content summary

- **Life Cycle Assessment is a useful and important tool to compute and report on the environmental footprint of product, process, or service offering**
- **Remember – LCA methodology provides the process carbon and environmental footprint not material carbon replacement footprint**
- **Beware of skewed/misused LCAs because of data quality or imposed boundary conditions, specifically end-of-life options**
- **B2B (cradle –to-factory gate)carbon and environmental footprinting is an important and viable methodology to compute and report on the value proposition for bioplastic/products**
- **The material carbon footprint reductions value proposition of "BIO" -- providing for a reduced carbon footprint is given by biocarbon content analysis**

Process Carbon Footprint – the LCA trap



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