MICHIGAN STATE UNIVERSITY

Emerging Issues: Bio-based Chemicals, Materials & Products

Ramani Narayan
University Distinguished Professor
narayan@msu.edu

- Ramani Narayan, *Biobased & Biodegradable Polymer Materials: Rationale, Drivers, and Technology Exemplars;* ACS (an American Chemical Society publication) Symposium Ser. 939, Chapter 18, pg 282, 2006;
- Ramani Narayan, *Rationale, Drivers, Standards, and Technology for Biobased Materials;* Ch 1 in Renewable Resources and Renewable Energy, Ed Mauro Graziani & Paolo Fornasiero; CRC Press, 2011
- Ramani Narayan, *Carbon footprint of bioplastics using biocarbon content analysis and life cycle assessment,* MRS (Materials Research Society) Bulletin, Vol 36 Issue 09, pg. 716 – 721, 2011

GREEN CHEMISTRY PRINCIPLES

Green chemistry Principle 4

- **Use renewable (biobased) feedstocks:** Use raw materials and feedstocks that are renewable rather than depleting. Renewable feedstocks are often made from agricultural products or are the wastes of other processes; depleting feedstocks are made from fossil fuels (petroleum, natural gas, or coal) or are mined
  - Why is it "green" – what is the value proposition

Green Chemistry Principle 12

- **Design chemicals and products to degrade after use:** Design chemical products to break down to innocuous substances after use so that they do not accumulate in the environment.
- **Design chemicals and products to biodegrade after use:**
  - **End-of-life – what happens to product after use when it is disposed?**
  - **Disposal environment & time**
  - **Beware of misleading claims**

STANDARDS -- REFERENCE

NSF International and Green Chemistry Institute

"Standard for **Greener Chemicals and Processes Information**"

Gate-to-gate information on chemical products and their manufacturing processes

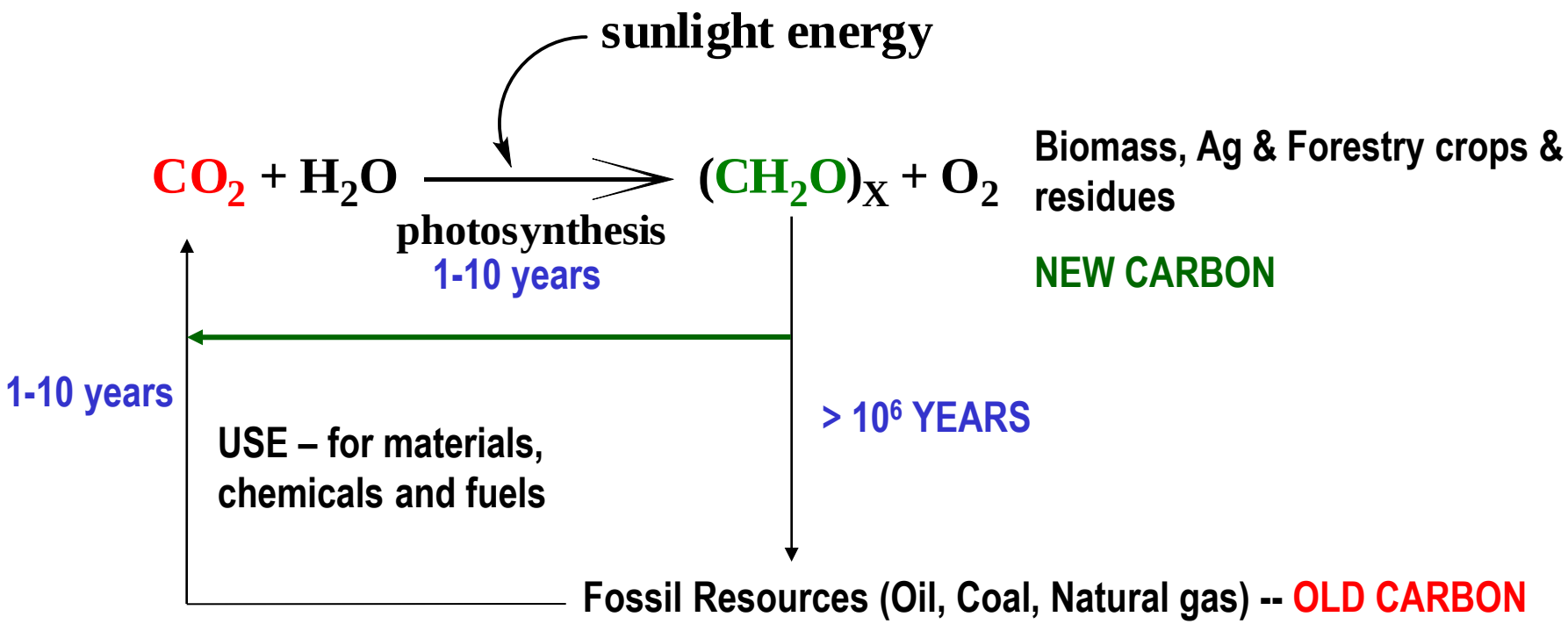
NSF/GCI/ANSI 355 – 2011NSF

FOR BIOBASED CONTENT & BIODEGRADABILITY-COMPOSTABILITY STANDARDS

ASTM D 6866 -- Standard Test Methods for Determining **the Biobased Conten**t of Solid, Liquid, and Gaseous Samples Using Radiocarbon Analysis; parallel EN & ISO standards under development

ASTM D6400, D6868, EN 13432, ISO17055 – Specification Standards for biodegradability under composting conditions – aggressive biological environment

Understanding the Value Proposition based on the origins of the carbon in the product -- bio carbon vs petro/fossil carbon

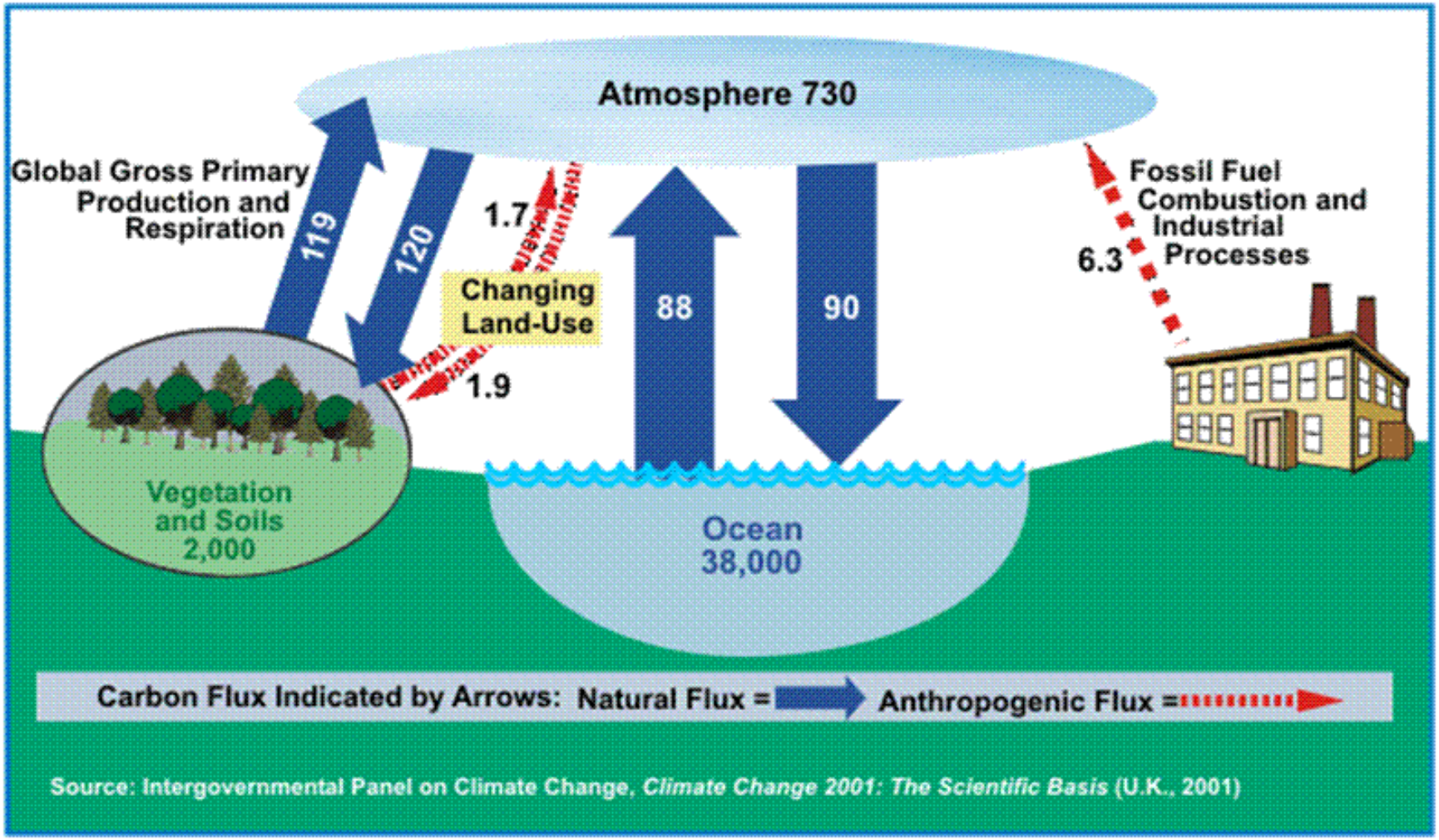


Rate and time scales of CO_2 utilization is in balance using bio/renewable feedstocks (1-10 years) as opposed to using fossil feedstocks

Short (in balance) sustainable carbon cycle using bio renewable carbon feedstock

MATERIAL CARBON FOOTPRINT

Carbon emissions – the problem



VALUE PROPOSITION BASICS –MATERIAL CARBON FOOTPRINT – Origins of the carbon

PROCESS CARBON FOOTPRINT

MATERIAL CARBON FOOTPRINT

Oil, Coal, Natural gas → Naptha → ethylene/propylene → Polyethylene (PE) polypropylene (PP)

Bio/renewable feedstock

Crops & residues (e.g. Corn, soybean sugarcane)

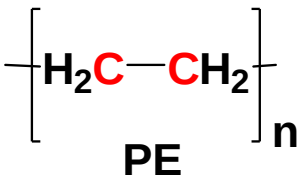
Tree plantations Lignocellulosics

Algal biomass

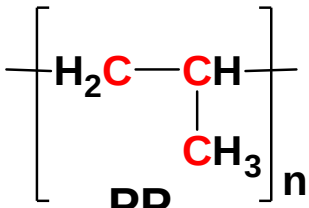
→ BIO monomers sugars, Oils

EtOH

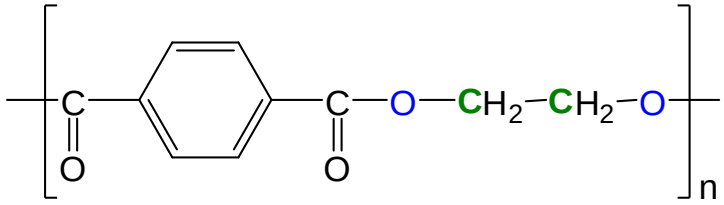
PLA, PHA's



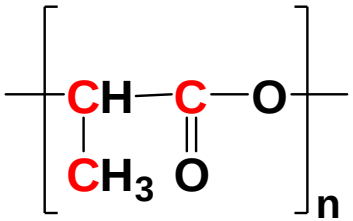
PE



PP

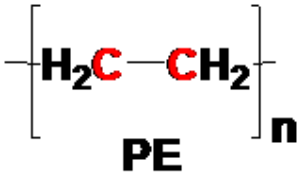


BIOPET



PLA

Material Carbon Footprint



PE

Kg of CO_2 per 100 Kg resin

314 kg of CO_2 emissions reduction for every 100 kg of PE resin in which the petro carbon is replaced with bio carbon

Experimentally determine using ASTM D6866 based on the principle of C-14 analysis

Sucrose —Fermentation→ Ethanol —Dehydration H+→ Ethylene —Polymerization→ PE

Energy Yield: 97% 99% ~100%

High performance process:

- ✓ Heterogenous catalyst
- ✓ High energy yield
- ✓ High purity ethylene (polymer grade)
- ✓ Low investment per ton (1450 US$/t)
- ✓ Low amount of effluents
- ✓ CO_2 emission -2,5 t/t produced PE

Braskem
new ways to look at the world

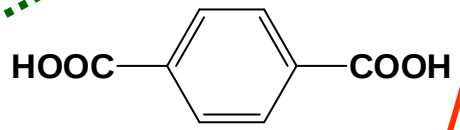
BIO-PET – Value Proposition

MATERIAL CARBON FOOTPRINT

PROCESS CARBON FOOTPRINT

Oil, Coal, Natural gas → Naptha → Ethylene → Ethylene oxide → Ethylene Glycol

EtOH



Bio/renewable feedstock

Crops & residues (e.g. Corn, soybean sugarcane)

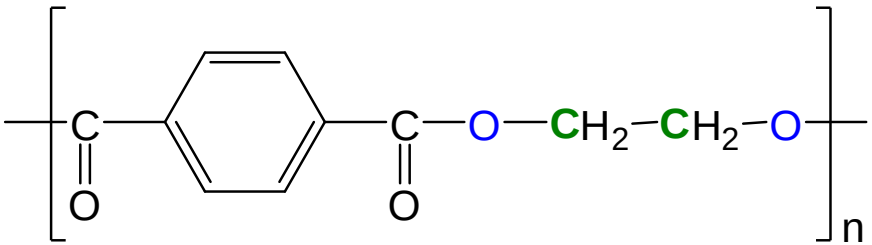
Tree plantations
Lignocellulosics

Algal biomass

BIO monomers

Sugars, Oils

For bottles:
37.5 MM tons PET used
17.2 MM tons CO_2 savings
40 million barrels of oil/yr savings



BIOPET

PlantBottle®: Better By Design

The only plastic bottle made with plants that is 100% recyclable and able to meet the high quality standards of The Coca-Cola Company

High Quality

Same Performance

+

Renewable

Less Carbon

+

Recyclable

Less Waste

=

plantbottle™
up to 30% plant-based
100% recyclable bottle
redesigned plastic,
recyclable as ever.

END-OF-LIFE OPTIONS FOR BIOBASED PLASTICS/PRODUCTS)

- **What happens to plastics/product after use when it enters the waste stream**
  - **Design for biodegradability (in what disposal environment?)**
    - **Composting**
      - **COMPOSTABLE PLASTICS!**
    - **anaerobic digestion BIOGAS for energy**
      - **Landfills– Cannot be a option; diversion from landfills to more environmentally responsible end-of-life options**
    - **Marine**
    - **soil**
  - **Recycling**
  - **Energy recovery (Collection, Buy back, mail back programs)**
- **Misleading and Deceptive biodegradability/compostability claims – Beware!**

Biodegradability/microbial utilization fundamentals

Microorganisms extract chemical energy for use in their life processes by the aerobic oxidation of glucose and other utilizable substrates – BIODEGRADBLE PLASTICS, food waste, paper, forest residues biological matter

AEROBIC (composting environment)

Glucose/C-bioplastic + 6 O_2 ⟶ 6 CO_2 ↑ + 6 H_2O; $\Delta G^{0'}$ = -686 kcal/mol

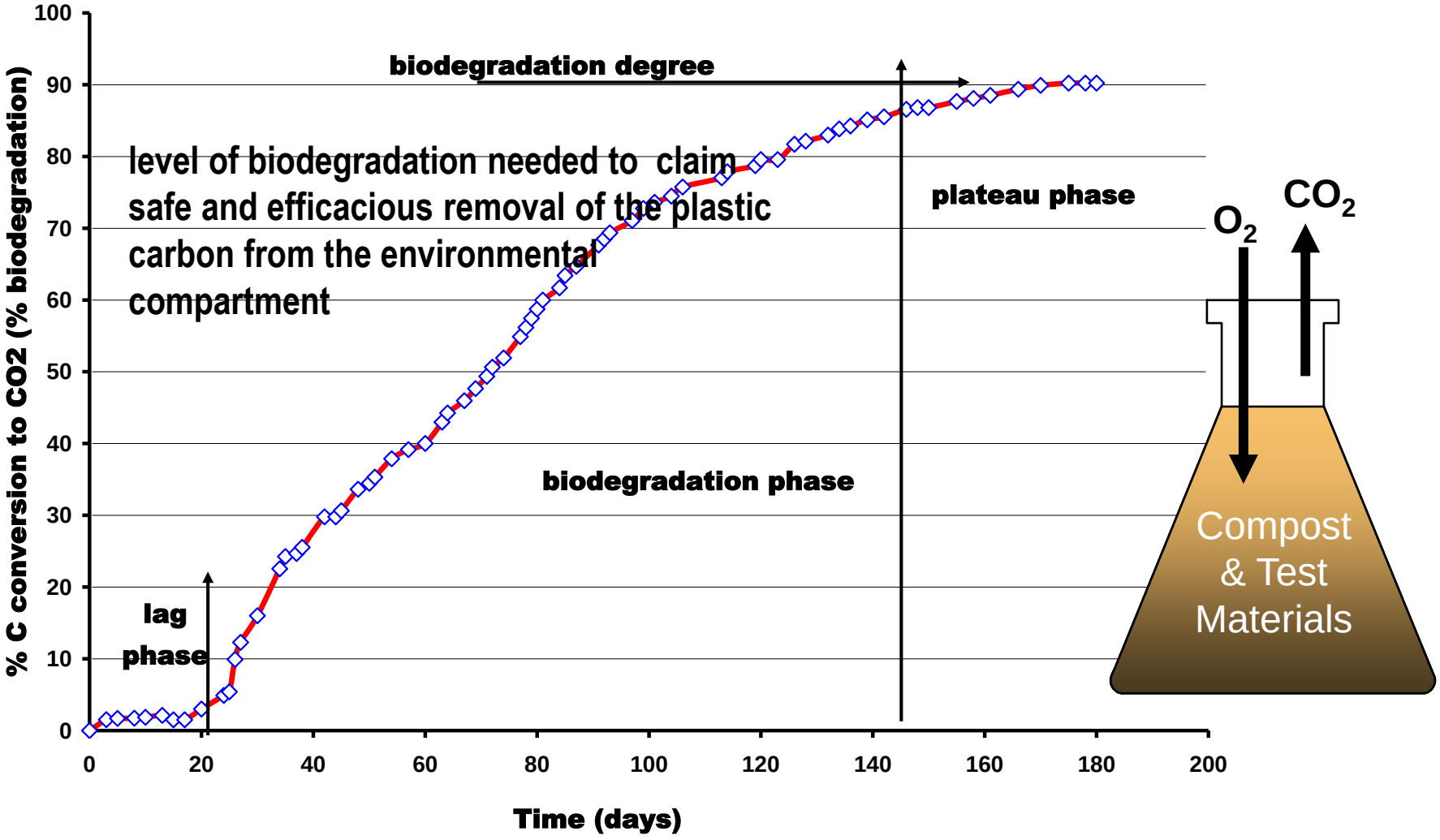
CO_2 is the quantitative measure of the ability of the microrganisms present in the disposal environment to utilize/assimilate the test C-bioplastic, which is the sole C-source available for the microorganisms – biodegradation or bioassimilation

ANAEROBIC

Glucose/C-bioplastic ⟶ 2 lactate; $\Delta G^{0'}$ = -47 kcal/mol

⟶ CO_2 + CH_4 ↑

Measuring biodegradability



ASTM D5338; ISO 14855; EN 13432

Problems with incomplete and partial biodegradation

- **Thompson, R.C. et al. 2004. Lost at sea: Where is all the plastic? Science 304, 838, 2004**
- **plastic pieces can attract and hold hydrophobic elements like PCB and DDT up to one million times background levels. As a result, floating plastic is like a poison pill**
  - **From Algalita Marine Research Foundation – www.algalita.org/pelagic_plastic.html**
- **PCBs, DDE, and nonylphenols (NP) were detected in high concentrations in degraded polypropylene (PP) resin pellets collected from four Japanese coasts.**
- **Plastic residues function as a transport medium for toxic chemicals in the marine environment.**
  - **Takada et al Environ. Sci. Technol. 2001, 35, 318-324**
  - **Blight, L.K. & A.E. Burger. 1997. Occurrence of plastic particles in seabirds from the Eastern North Pacific. Mar. Poll. Bull. 34:323-325**
  - **Phil. Trans. Royal. Soc. (Biology) July 27, 2009; 364**

What We Know About: Plastic Marine Debris

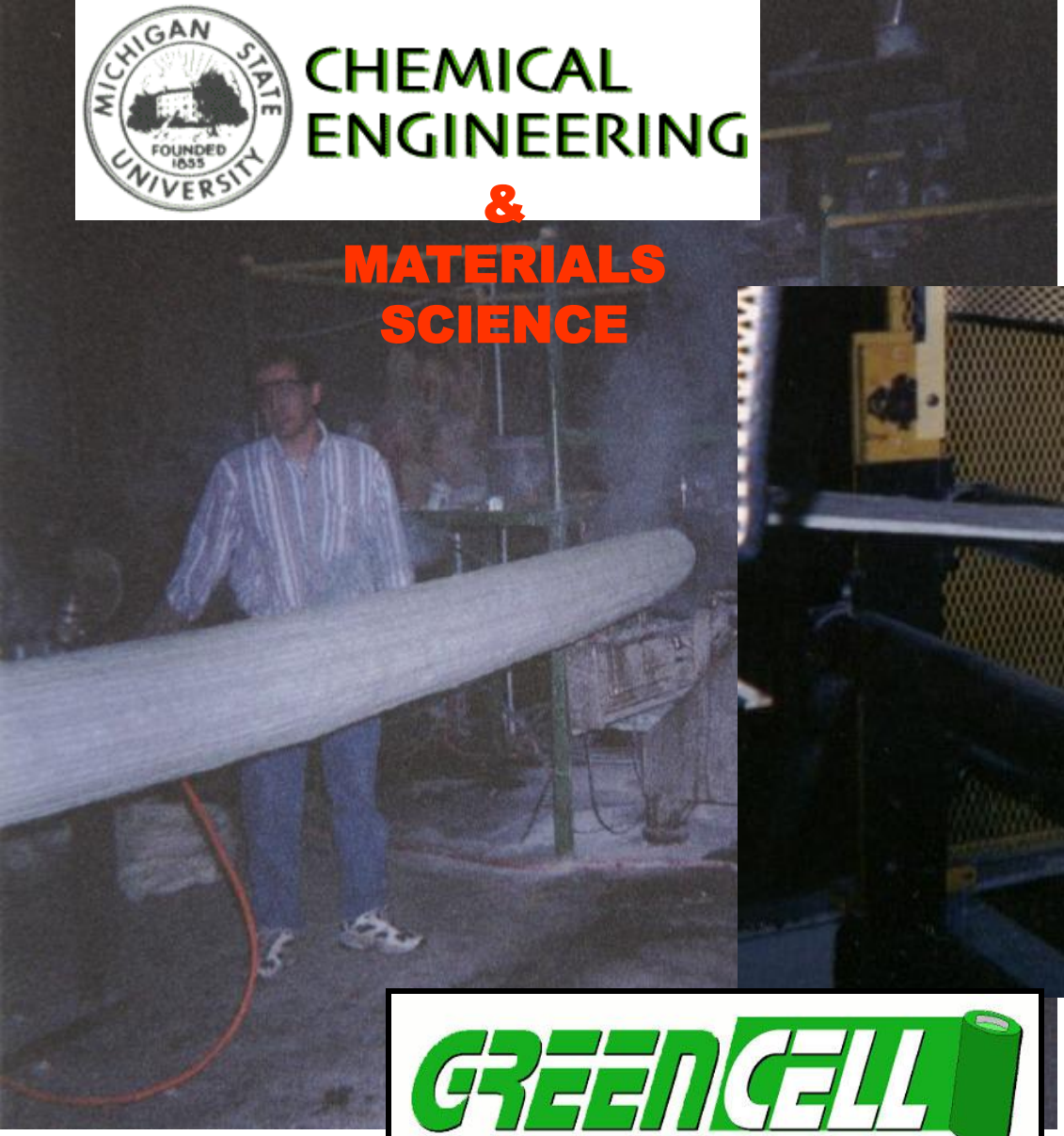
http://marinedebris.noaa.gov/info/plastic.html

CHEMICAL ENGINEERING

&

MATERIALS SCIENCE

STARCH FOAM SHEETS



GREENCELL

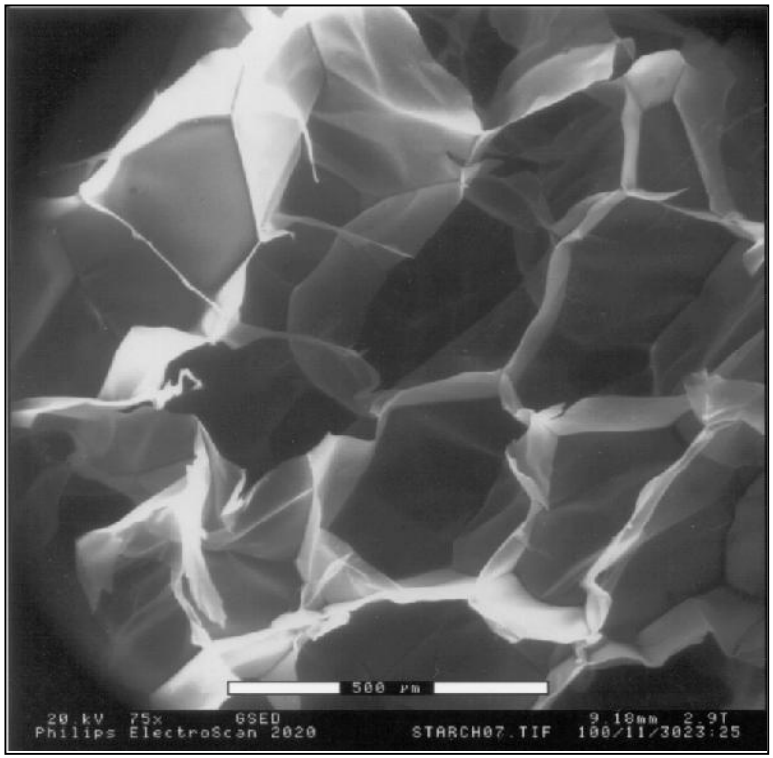
BIODEGRADABLE ENGINEERED FOAM

KTM

www.ktmindustries.com

Ramani Narayan, Michigan State University

Biodegradable Foam



Closed-Cell Structure

Cell Size 200 – 500 µm

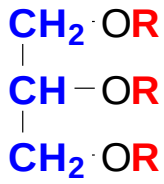
- Bio-based and completely biodegradable
- Multiple impact protection through improved cushioning properties
  - Cushion Protection – comparable to PE foam
- Excellent insulation – equivalent to PS foam, and better than PE foam
- Naturally anti-static

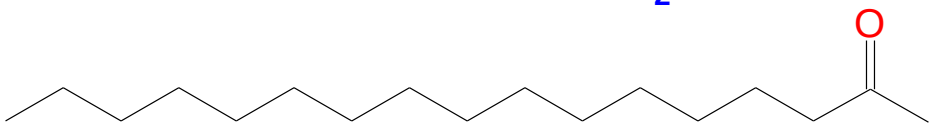
Narayan et al Amphiphilic Starch-Polyester Biodegradable Graft Copolymers, the Method of Preparation thereof and Its Use in Water Resistant Starch Foams" U.S. Patent Pending

Narayan et. Al., Twin-Screw Extrusion Production and Characterization of Starch Foam Products for Use in Cushioning and Insulation Applications, Polymer Eng. & Science, 46 (4), 438, 2005, 2006

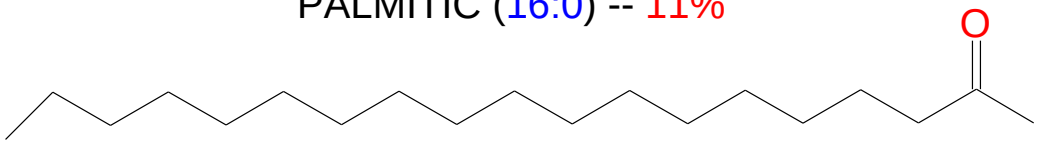
Vegetable Oil Platform

SOYBEAN OIL
(**Triglyceride**)

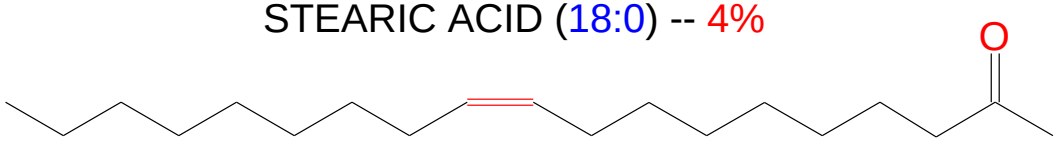




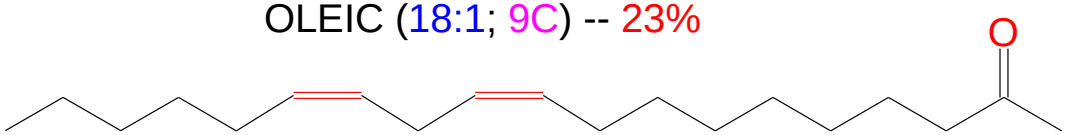
PALMITIC (16:0) -- 11%



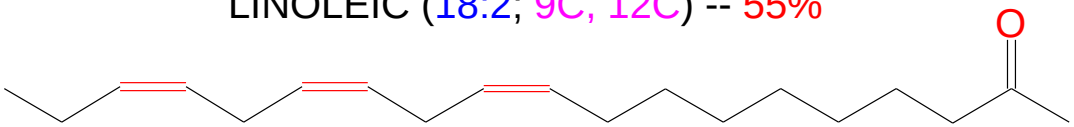
STEARIC ACID (18:0) -- 4%



OLEIC (18:1; 9C) -- 23%



LINOLEIC (18:2; 9C, 12C) -- 55%



LINOLENIC (18:3; 9C, 12C, 15C) -- 7%

COMPOSITION OF R GROUPS (FATTY ACIDS) IN SOYBEAN OIL

- **15 wt% saturated and 85 wt% unsaturated fatty acids**
- **4.6 double bonds on average per mole of triglyceride in "cis" configuration**

Entrepreneurial BIOENTERPRISE WITH

Zeeland Farm Services

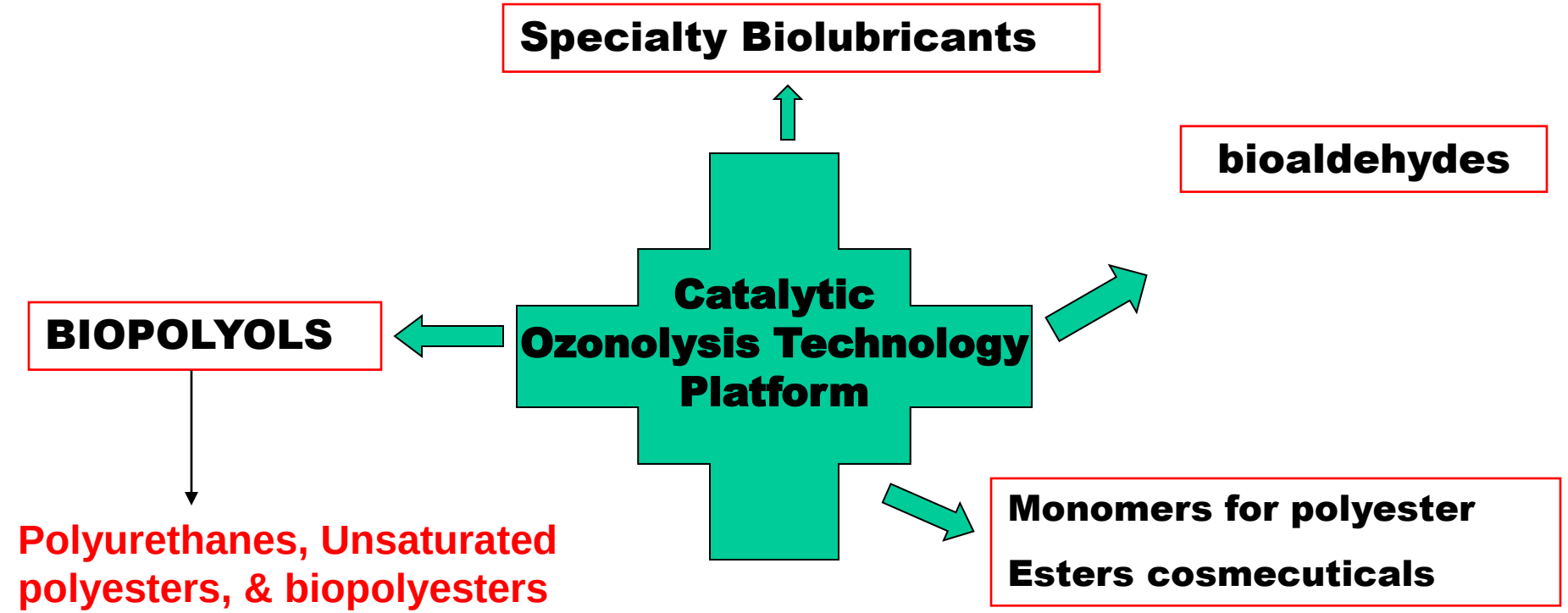
www.zfsinc.com

- a family owned (Meeuwsen brothers) Michigan business with over 50 years of service to the agricultural and transportation industries
- 200 employees with an annual gross sales revenue of over $150 MM
- process about 26,000 bushels of soybeans per day, operating 24 hours a day, 360 days a year, to produce two primary products: soybean meal and soybean oil.
  - 90% of the total soybeans processed in the State is done at ZFS – largest soybean processor in MI
  - 2500 MI farmers are serviced and ZFS buys 99% of their soybeans from MI farmers
  - successful Michigan business against multi national competitors such as Bunge Cargill and ADM

Naturelube 700
NSF H1
Food contact
Medium Temp
Industrial (Food ind)
Household

Naturelube 705
2-cycle engines
Household use
(Chain saws, Edgers
Blowers etc)

Naturelube 710
Marine 2 cycle
Meets NMMA spec



One Step Continuous Process

Value added bioproducts