

BIOBASED & BIODEGRADABLE PLASTICS 101

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**CHEMICAL
ENGINEERING**

&

MATERIALS SCIENCE

www.msu.edu/user/narayan

www.ktmindustries.com

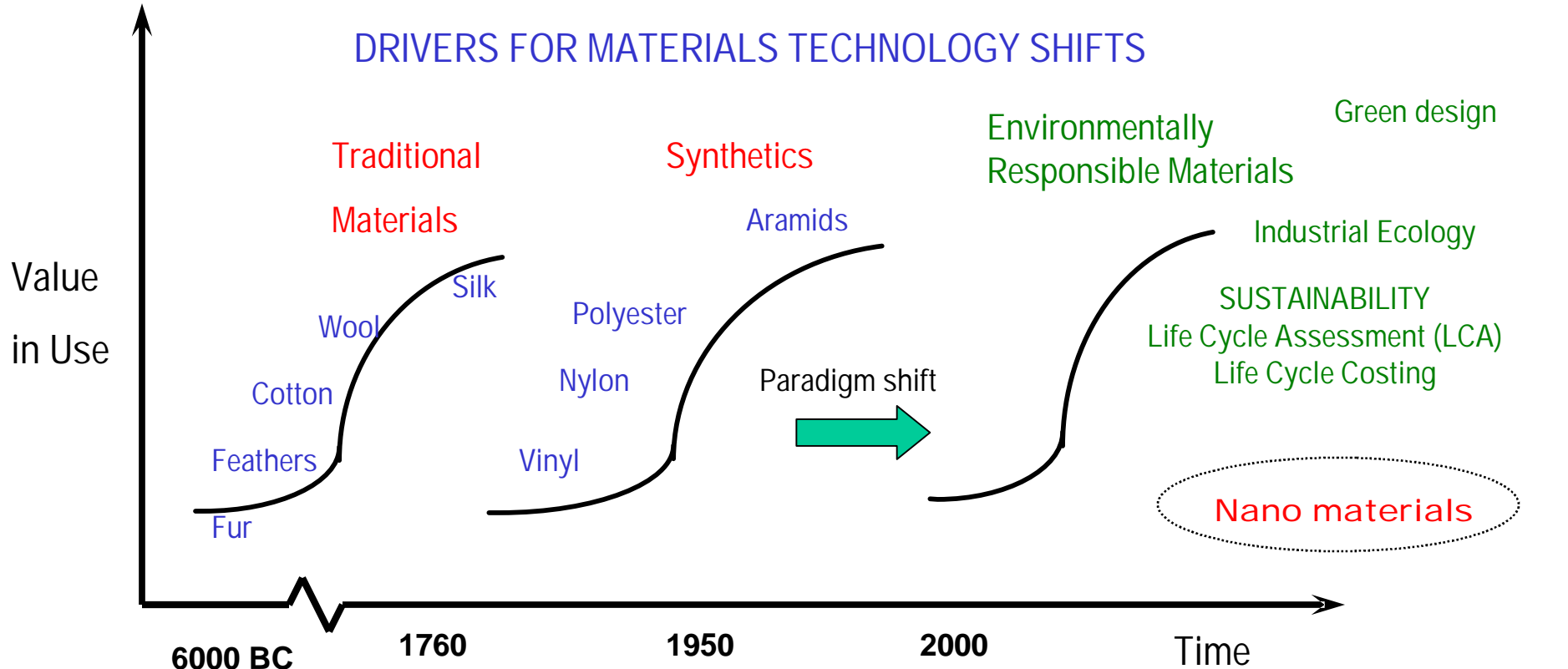
www.ecosynthetix.com

www.biopolymerinnovations.com

www.bioplasticpolymers.com

MATERIALS FRONTIER

DRIVERS FOR MATERIALS TECHNOLOGY SHIFTS



- Natural Ingredients
- Labor Intensive
- Attractive Aesthetics

- Cheap petroleum
- Ease of manufacture
- Low labor input
- Excellent functionality

- Biodegradable
 - bio based (renewable resource)
 - Recyclabl -- recycling friendly
 - Non-polluting
 - Energy efficient
 - Tailored Functionality
- BIOBASED MATERIALS**



BIOBASED PRODUCTS – WHY? WHAT VALUE IN THE SUSTAINABILITY – LIFE CYCLE EQUATION

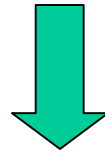
What is the **major** basic element that is the building block of biobased products, petroleum based products, biotech products, fuels, even life itself ?

CARBON
“ORGANIC”

ISSUE – MANAGING CARBON !!!!!

BIOBASED PRODUCTS - WHY?
WHAT VALUE IN THE SUSTAINABILITY -
LIFE CYCLE EQUATION

SUSTAINABILITY & SUSTAINABLE DEVELOPMENT
OF
CARBON BASED PRODUCTS
"ORGANIC"

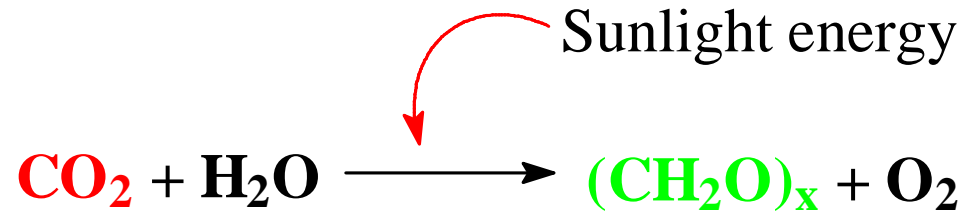


ECOSYSTEM CARBON CYCLES
"biological carbon cycle"

ISSUE - MANAGING CARBON !!!!!

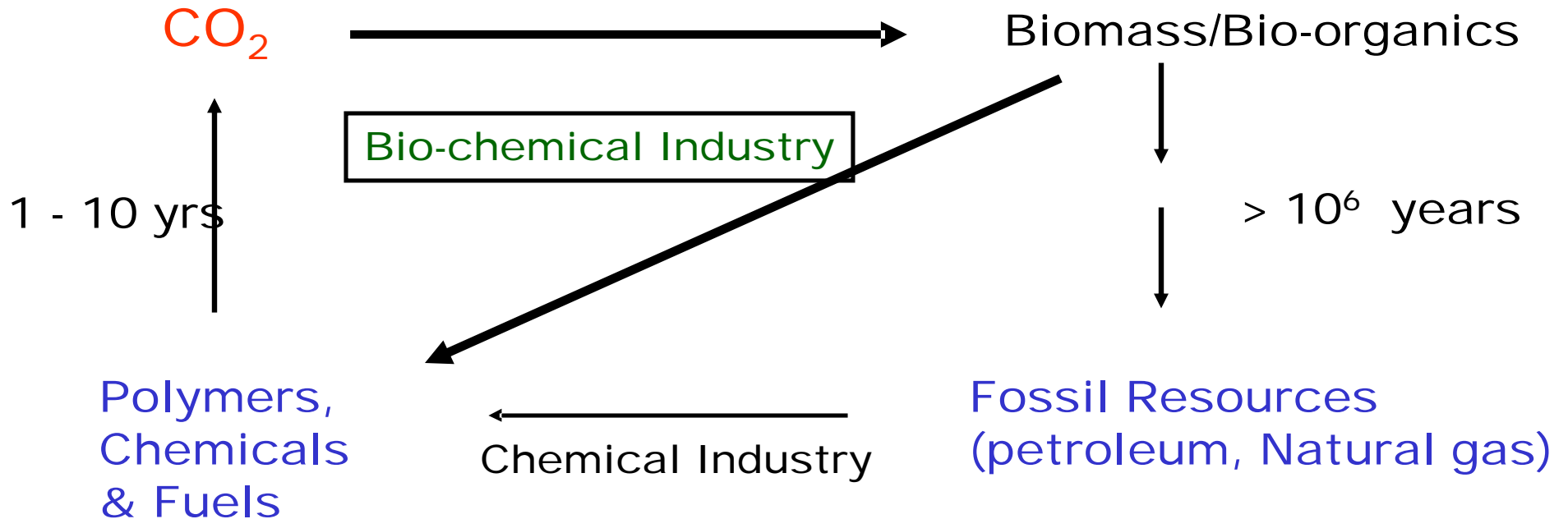
GLOBAL CARBON CYCLING THE ECO DRIVER

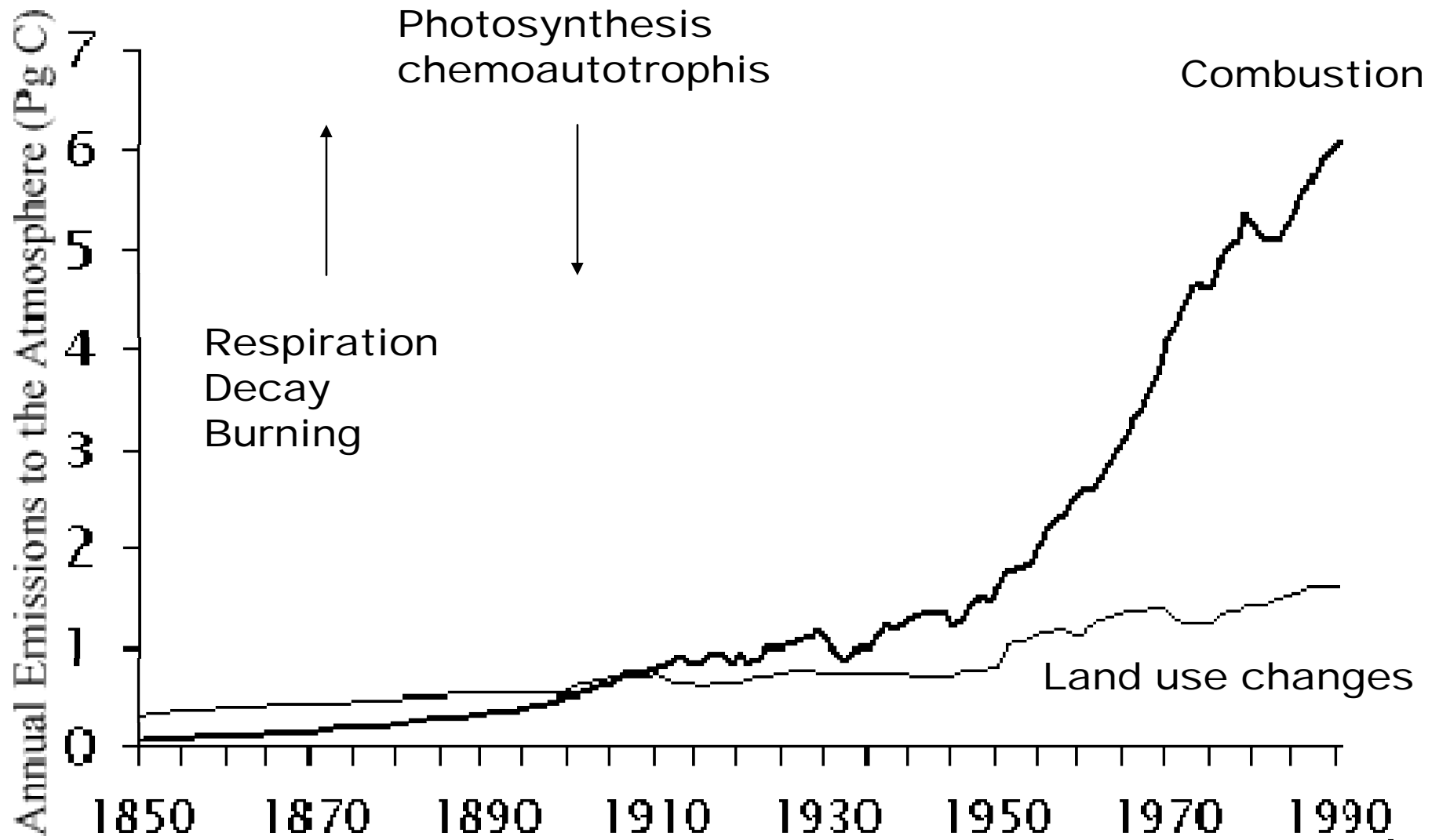
CO_2  Biomass/Bio-organics



photoautotrophs -- algae, plants, and some bacteria fix inorganic carbon to **organic matter** (carbohydrates) using sunlight as the energy

GLOBAL CARBON CYCLING THE ECO DRIVER





RENEWABLE BIOMASS RESOURCES AGRICULTURAL FEEDSTOCKS



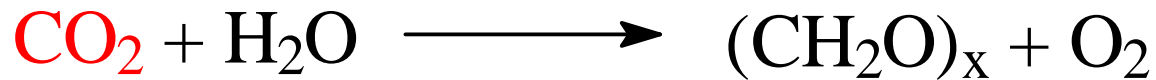
BIOBASED MATERIALS

- For sustainable development of carbon based polymer materials
- Control and even reduce CO₂ emissions and help meet global CO₂ emissions standards – Kyoto protocol
- Improved environmental (LCA) profile
- improved strategic security and balance of payments
- healthier rural economies
- technology export
- a sustainable resource supply

TERMINOLOGY

- **Biobased material(s)**

Organic material(s) in which the carbon comes from contemporary (non-fossil) biological sources



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 structure

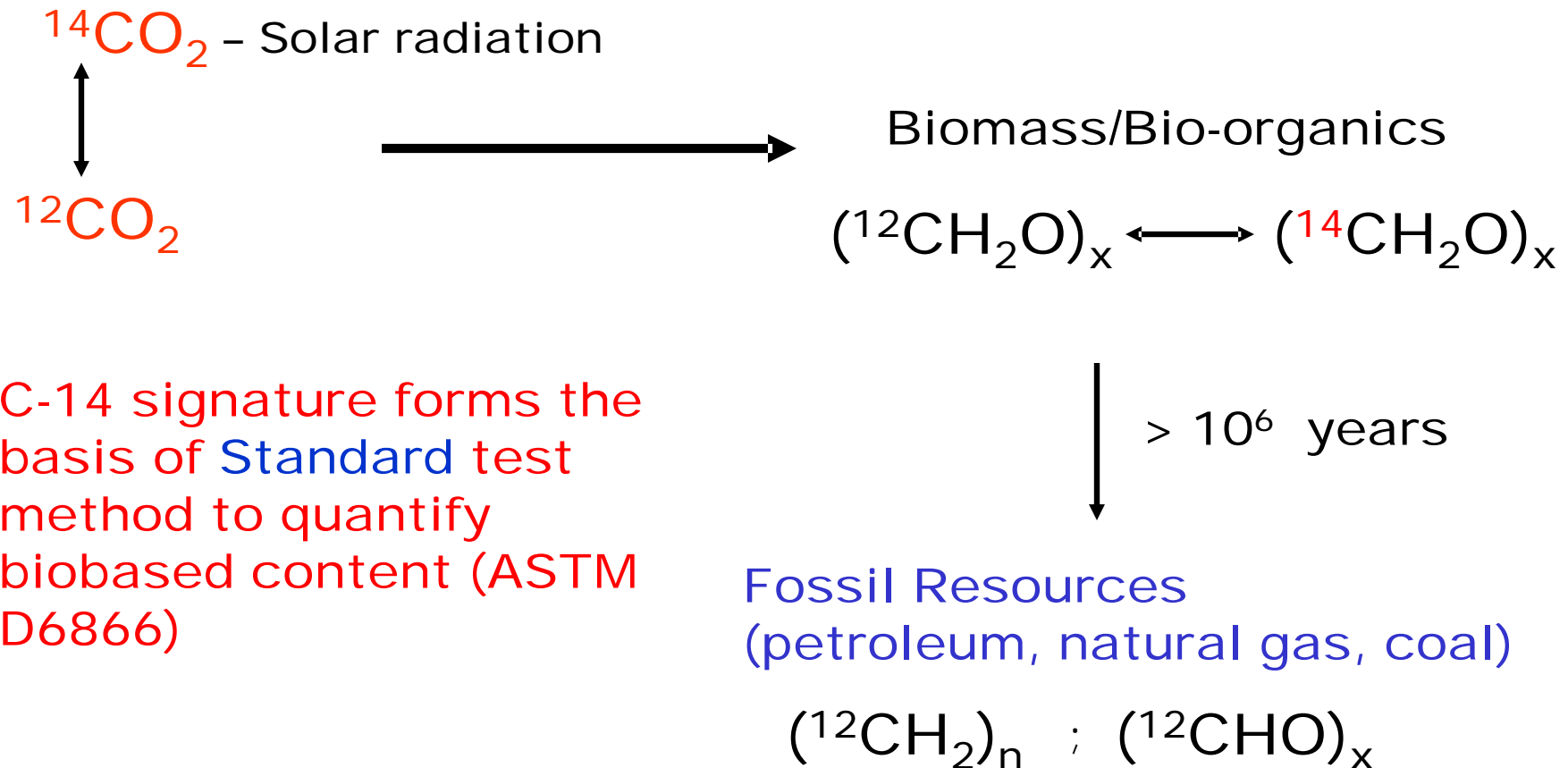
Thus, to be classified **biobased**, the material must be organic and contain recently fixed (new) carbon present in biological sources

TERMINOLOGY (Contd)

- Biobased materials may contain 100% bio/new carbon or be mixed (physically, chemically, or biologically) with fossil/old carbon
- biobased content, or gross biobased content -
Amount of *biobased carbon* in the material or product as fraction weight (mass) or percent weight (mass) of the total *organic carbon* in the material or product.

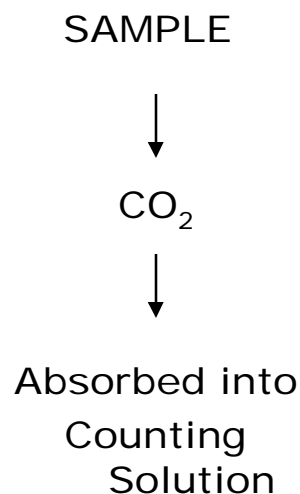
Standards -- Identify & Quantify Biobased Content

- How does one distinguish between new (contemporary) and old(fossil) carbon – identify biobased carbon?
- How does one quantify biobased carbon content?



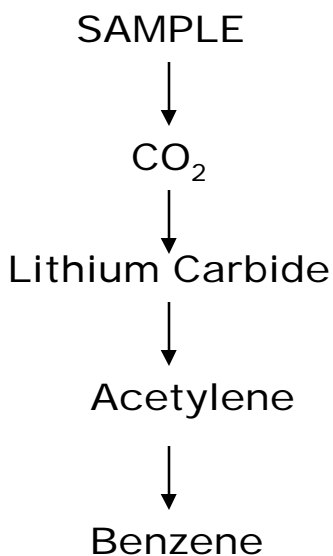
Radiocarbon Methods : ASTM D6866-04a

Method A CO₂ Absorption



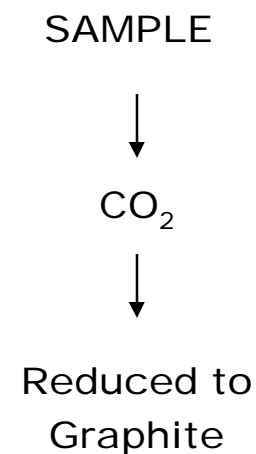
Precision <= 5-10%
absolute
Standard LSC detection
Rapid through-put

Method C Benzene Synthesis



Precision <= 2% absolute)
Standard LSC detection
Rapid through-put

Method B AMS (Accelerator Mass Spectroscopy)



Precision <= 2% absolute)
Very small sample
requirements

BIOBASED CONTENT -- EXAMPLES

Product 'O' is a fiber reinforced composite with the composition
30% biofiber (cellulose fiber) + 70% PLA (biobased material)

Product 'P' is a fiber reinforced composite with the composition
30% glass fiber + 70% PLA (biobased material)

Product 'N' is a fiber reinforced composite with the composition
30% biofiber (cellulose) + 70% polypropylene (petroleum based
organic)

1. Product 'O' biobased content = 100%
2. Product 'P' biobased content = 100%; organic content only 70%
3. Therefore must define biobased content and organic content!
4. Product 'N' biobased content = 18.17% -- not 30%!!!!
5. Because biobased content is on a carbon basis -
 $13.32/73.31 * 100$



U.S. Farm Security and Rural Investment Act of
2002 (P. L. 107-171), Title IX Energy, Section 9002
FARM BILL



FEDERAL BIOBASED PRODUCTS
PREFERRED PROCUREMENT PROGRAM
FB4P (www.biobased.oce.usda.gov)

- Provides that Federal agencies must purchase biobased products designated by this program
- Authority for the program included in the Farm Security and Rural Investment Act (FSRIA) of 2002



U.S. Farm Security and Rural Investment Act of 2002
(P. L. 107-171), Title IX Energy, Section 9002
FARM BILL



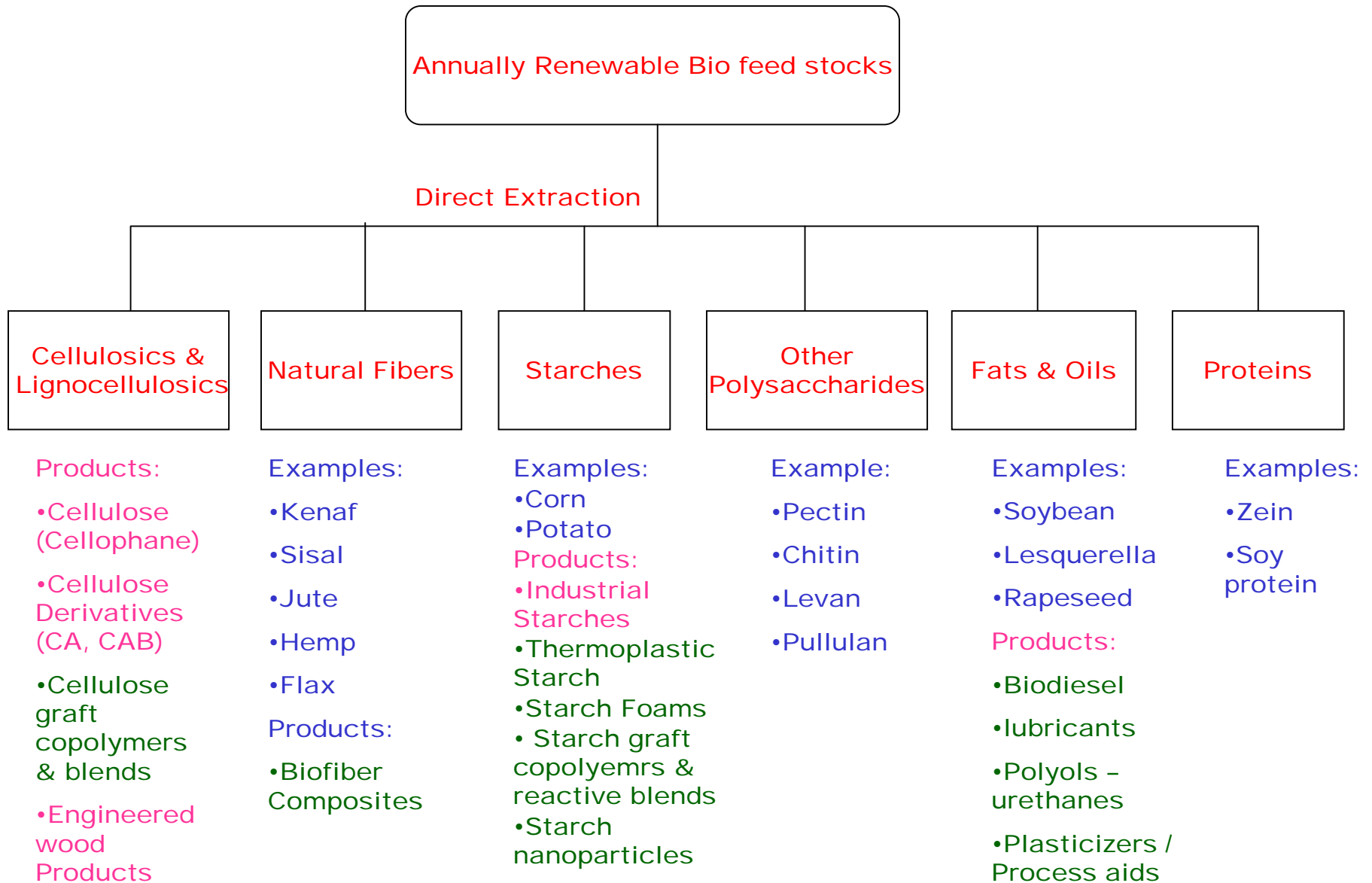
n Federal Procurement of Biobased Products

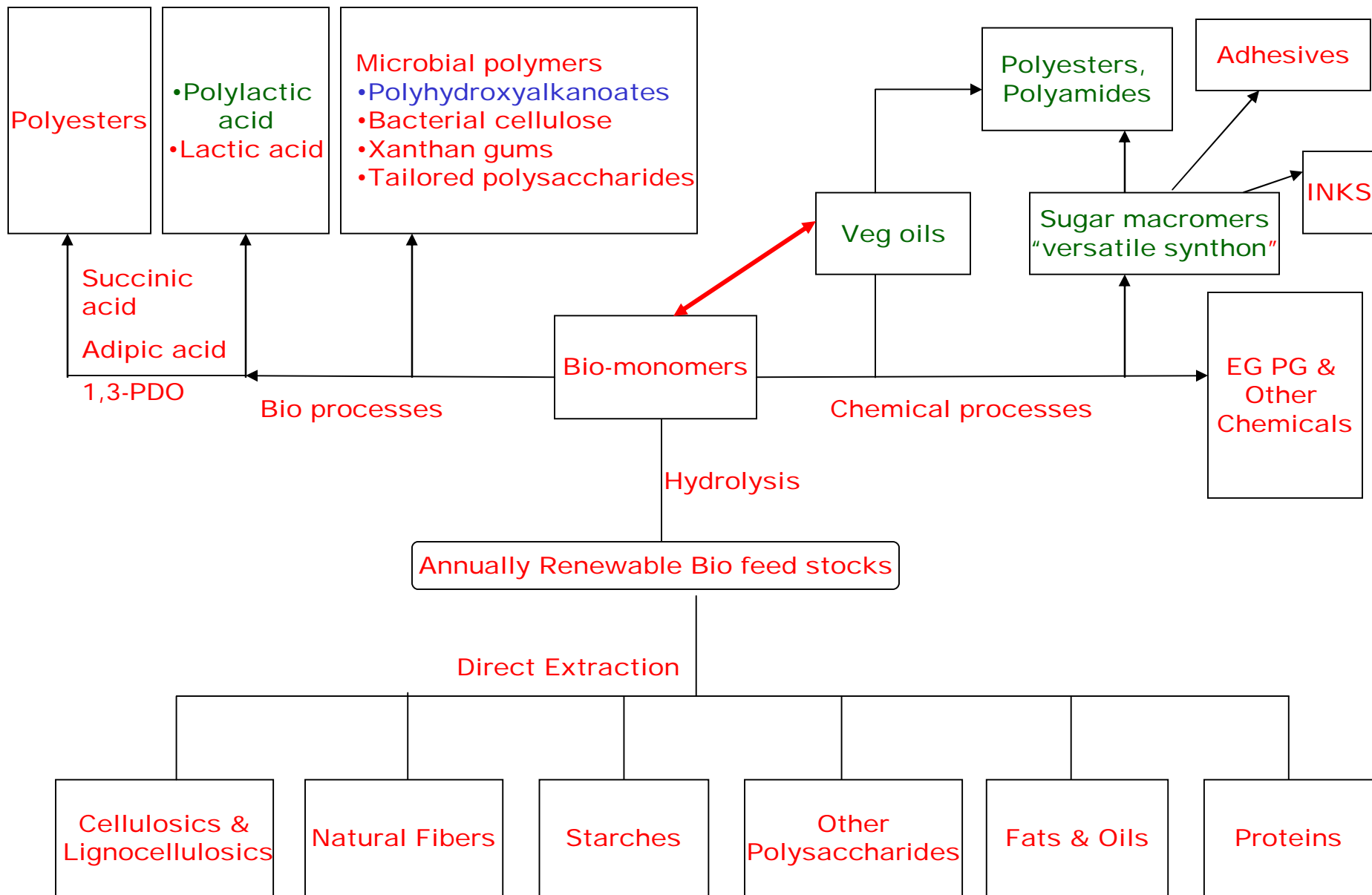
- develop guidelines for designating biobased products
 - PUBLISHED – FEDERAL REGISTER
- publish a list & issue criteria for a designated biobased products list (DBL) for federal purchase;
 - six *items* for preferred procurement by Federal agencies: mobile equipment hydraulic fluids; urethane roof coatings; water tank coatings; diesel fuel additives; penetrating lubricants; and bedding, bed linens, and towels

n Will include:

- † Definition, content verification, ASTM D6866
- † environmental profile using LCA – ASTM Standard
 - † ASTM D7075 "Standard practice for evaluating and reporting environmental performance of biobased products". -- LCA TOOLS/BEES analysis
 - † To incorporate life cycle costing
- † performance requirements; and
- † assurance that products are available.

BIOBASED FEEDSTOCKS





MATERIALS DESIGN PRINCIPLES FOR THE ENVIRONMENT

BIODEGRADABLE & BIOBASED

Single use, short-life, disposable, controlled-life time products

Packaging, disposable plastics, agricultural films, marine disposable

BIODEGRADABLE & DURABLE

Soy polyurethanes for automotive and farm vehicles

Biofiber composites for industrial and automotive

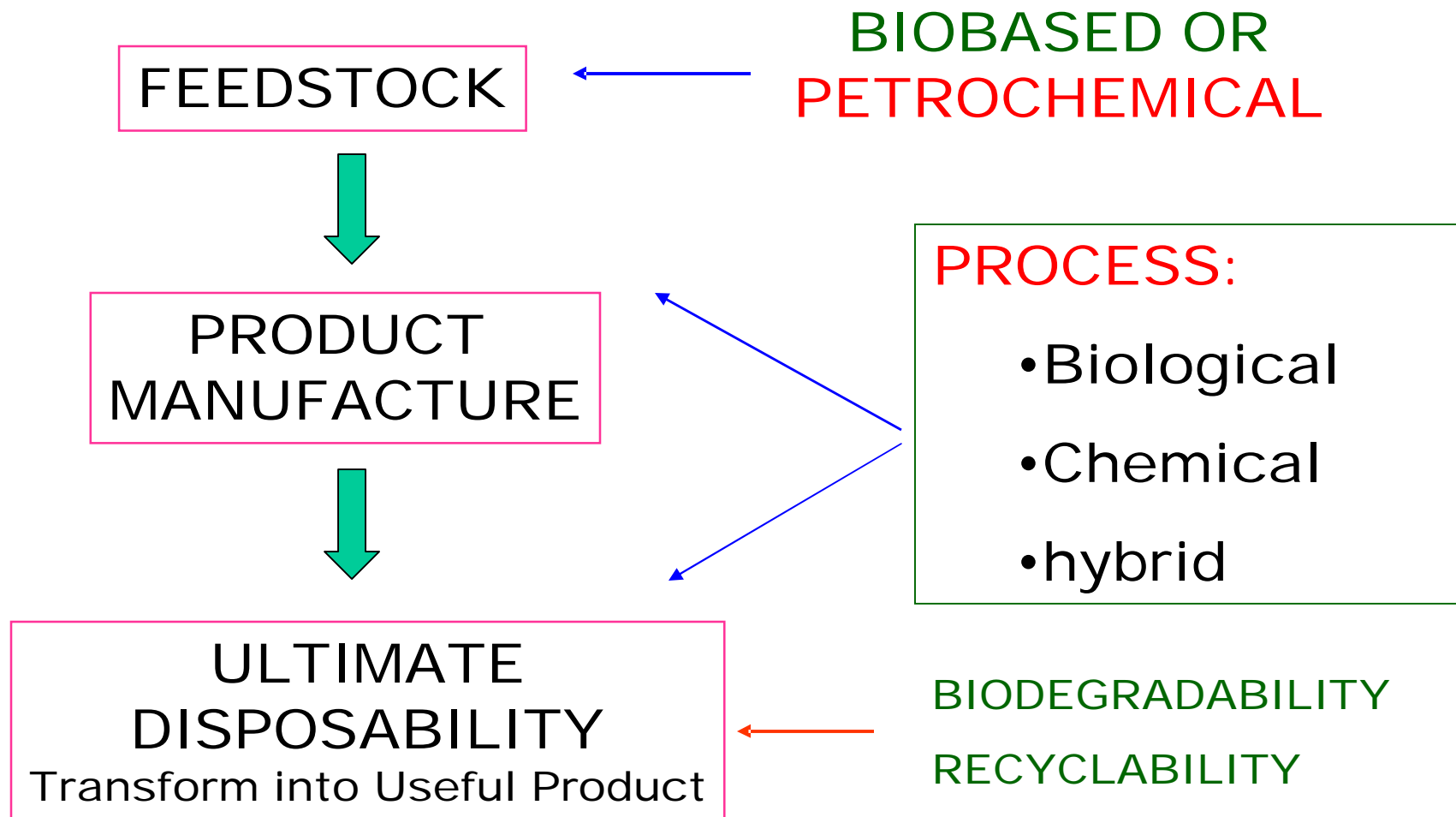
Perform LIFE CYCLE ASSESSMENT (LCA) to document positive environmental attributes

† ASTM D7075 "Standard practice for evaluating and reporting environmental performance of biobased products". -- LCA TOOLS

† To incorporate life cycle costing

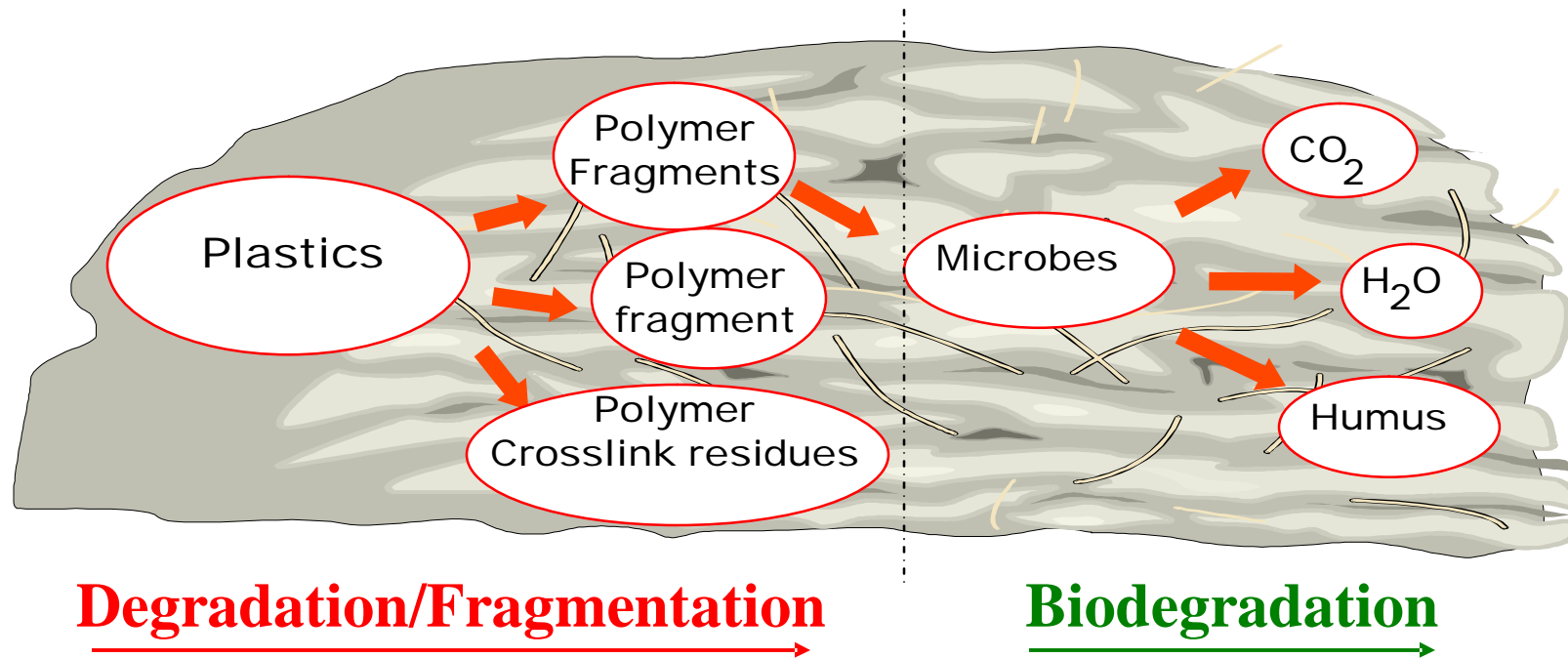


MATERIALS DESIGN PRINCIPLES FOR THE ENVIRONMENT



"LIFE CYCLE ASSESSMENT - LCA"
ASTM D7075

What does Biodegradable Mean?



Degradation/Fragmentation

Biodegradation

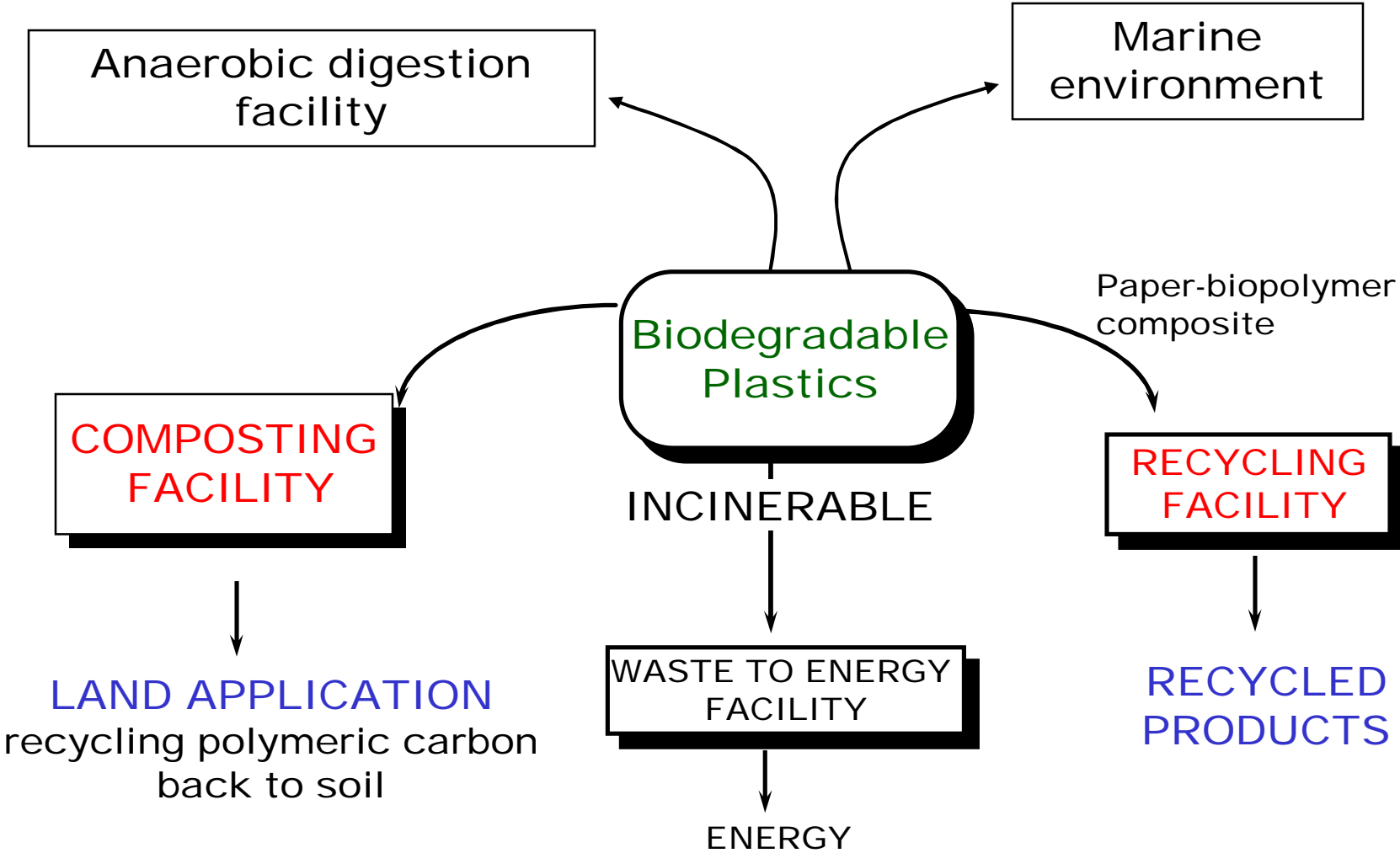
Biodegradability – complete assimilation of the degraded products as a food source by the soil microorganisms would ensure returning the carbon into the ecosystem safely and effectively

APPLICABLE TO SINGLE-USE, SHORT LIFE DISPOSABLE
PACKAGING & CONSUMER GOODS

TIME!!! & ENVIRONMENT!!

Ramani Narayan, Michigan State University, www.msu.edu/~narayan

Integration of biodegradable plastics with disposal infrastructures



COMPOSTING & THE ENVIRONMENT

- COMPOSTING IS AN ECOLOGICALLY AND ENVIRONMENTALLY SOUND APPROACH TO TRANSFERRING BIODEGRADABLE WASTE (INCLUDES THE BIODEGRADABLE PLASTICS) TO USEFUL PRODUCT
- COMPOSTING IS BIOLOGICAL RECYCLING OF CARBON
- COMPOST USE REDUCES CHEMICAL INPUTS, SUPPRESSES CROP DISEASES, REPLENISHES ORGANIC CARBON, INCREASES WATER & NUTRIENT RETENTION, IMPROVES SOIL PRODUCTIVITY

“SUSTAINABLE AGRICULTURE”

SCIENCE & ENGINEERING OF COMPOSTING,
HOITNIK & KEENER, EDS. 1993

Narayan -- Biodegradation of polymeric
materials during composting, p. 339

**DEGRADABLE
VS
BIODEGRADABLE**

Major Environmental Problems

Designing products to be degradable or partially biodegradable causes irreparable harm to the environment

Degraded products may be invisible to the naked eye. However, out of sight does not make the problem go away

- Degradable, biobased, single-use, disposable packaging and consumer plastics, and plastic-paper combination products (non-durable goods) have serious environmental consequences.
- Must ensure complete biodegradability in a short defined time frame (determined by the disposal infrastructure like composting)
 - TIME --- ONE GROWING SEASON; MAYBE TWO
 - DISPOSAL ENVIRONMENT – Composting, anaerobic digestion plants, marine/oceans, soil



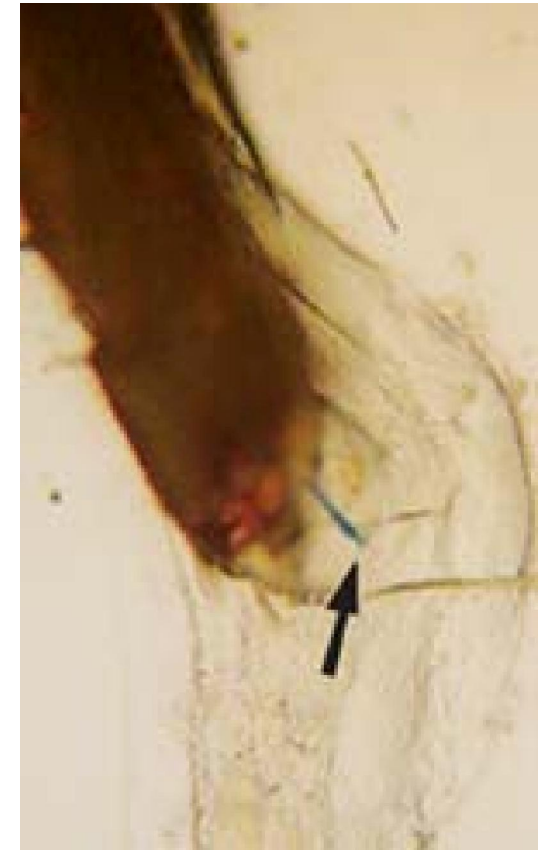
WHITE POLLUTION - CHINA



Major Problems/Issues with Degradable Materials/Products (contd.)

- Plastic debris around the globe can erode (degrade) away and end up as microscopic granular or fiber-like fragments, and that these fragments have been steadily accumulating in the oceans
- fragments come from several sources, the researchers suggest. These include mechanical erosion of nondegradable plastic bottles and packaging, **nondegradable parts of biodegradable plastics**, and plastic pieces used as abrasives in cleaning agents.

– **Science 304, 838, 2004**



FLOTSAM Lab experiments show that marine animals consume microscopic bits of plastic, as seen here in the digestive tract of an amphipod. © *Science* 2004



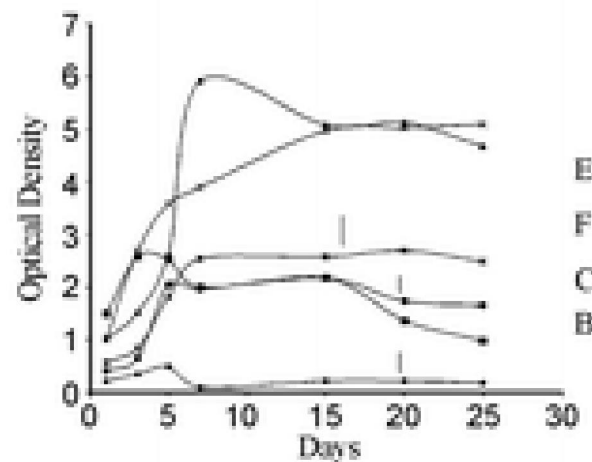
Problems with Degradables – Toxic Chemicals Transport

- 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 -- endocrine disruptors
 - 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.
 - Mato et al Environ. Sci. Technol. 2001, 35, 318-324



BIODEGRADABILITY CLAIMS

- Chem. Commun., 2002, (23), 2884 - 2885
 - A hypothesis was developed, and successfully tested, to greatly increase the rates of biodegradation of polyolefins, by anchoring minute quantities of glucose, sucrose or lactose, onto functionalized polystyrene (polystyrene-co-maleic anhydride copolymer) and measuring their rates of biodegradation, which were found to be significantly improved
- PRESS
 - Sugar turns plastics biodegradable. Bacteria make a meal of sweetened polythene and polystyrene.



weight loss of only 2-12%,

Increase in rates of biodegradation for sugar linked polystyrene

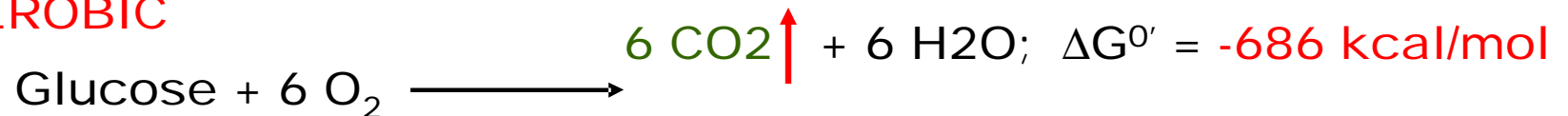
METRICS FOR BIODEGRADABILITY??

METRICS FOR BIODEGRADABILITY??

Why CO_2 as a quantitative measure of biodegradation/bioassimilation?

Microorganisms extract **chemical energy** for use in their life processes by the **aerobic oxidation** of glucose and other **utilizable substrates** -BIODEGRADABLE PLASTICS??

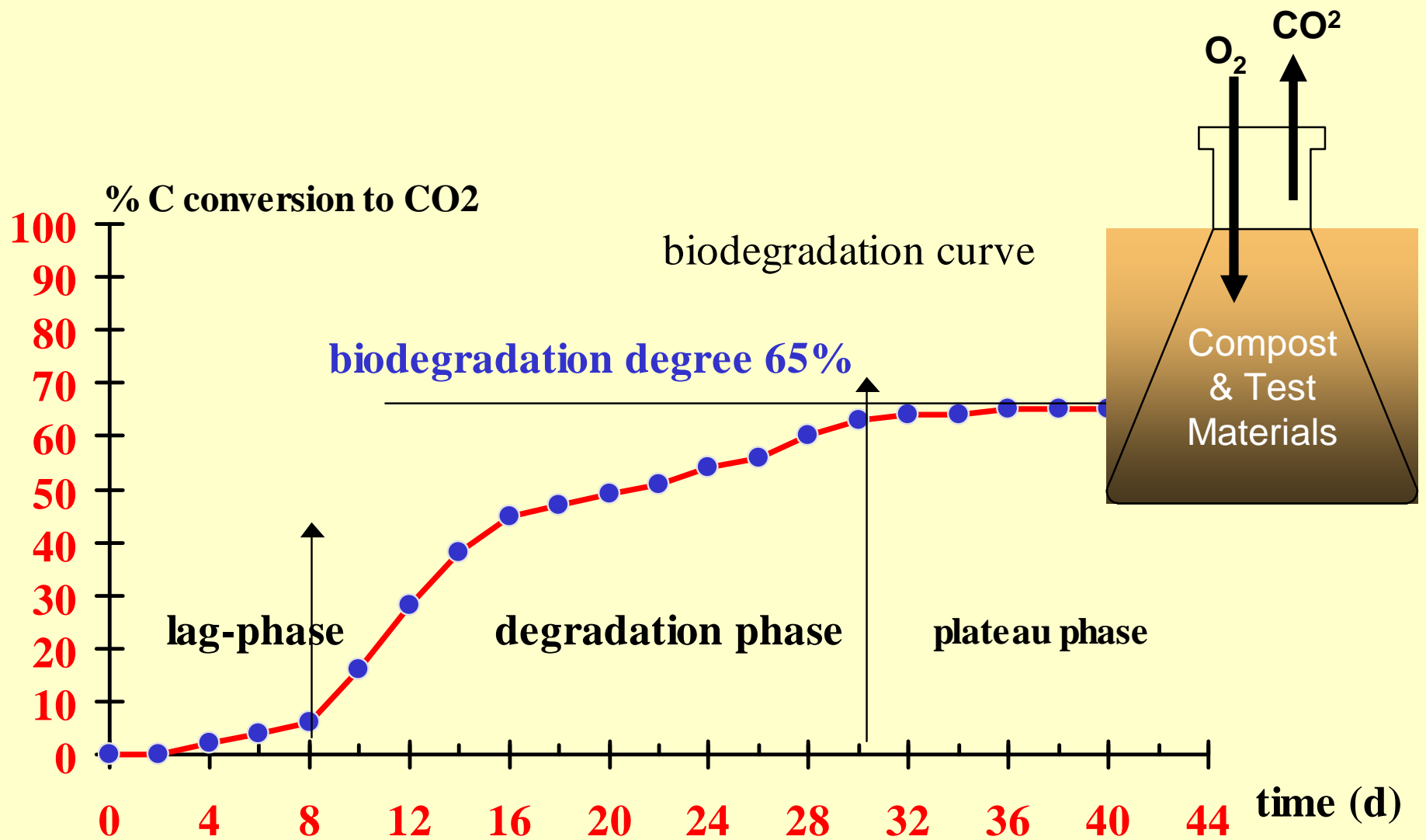
AEROBIC



ANAEROBIC



R



Specification Standard for Biodegradable/Compostable Plastics

- ASTM D6400 identified 3 criteria

- Mineralization (D5338):

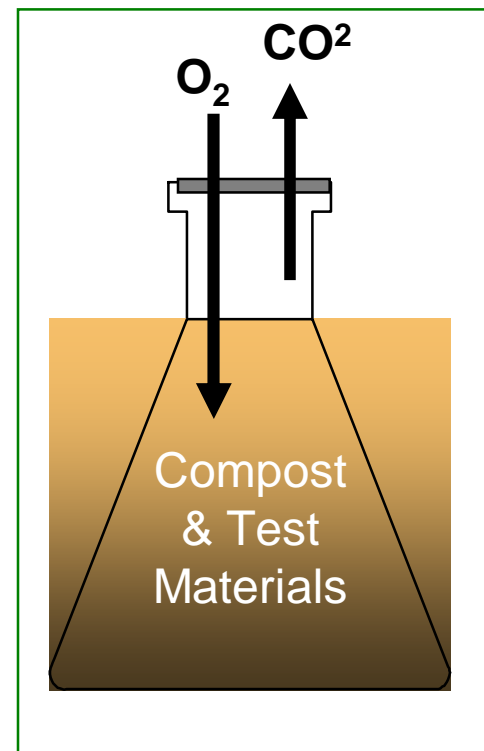
- Conversion to carbon dioxide, water & biomass via microbial assimilation
 - 60% of carbon conversion to CO₂ for homopolymer & 90% carbon conversion to CO₂ for block, segmented copolymers, and blends, including addition of low MW additives
 - Same rate as natural materials Leaves, paper, grass & food scraps
 - Time -- 180 days or less; if radiolabeled polymer is used 365 days or less

- Disintegration

- <10% of test material on 2mm sieve

- Safety

- No impacts on plants, using OECD Guide 208
 - Regulated (heavy) metals less than 50% of EPA (USA, Canada) prescribed threshold

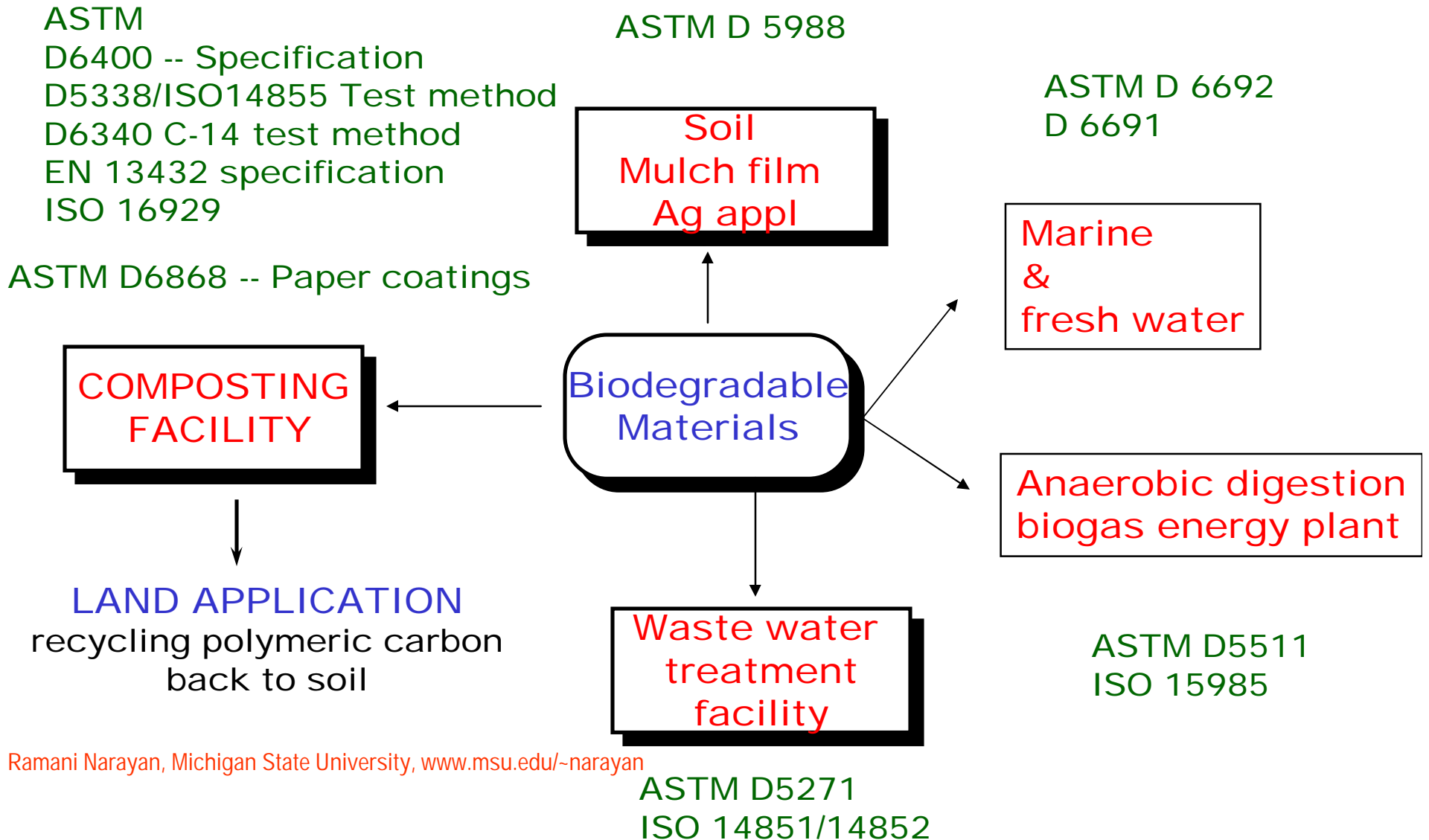


Basis for standards in Europe, Japan, China, Korea, Taiwan



Cradle to Cradle Concept for Material Design

(Integration of Biodegradable Materials with Disposal Infrastructures)



Global Standards for Biodegradability

