SUSTAINABLE AND ENVIRONMENTALLY BENIGN POLYMERS: CHALLENGES AND OPPORTUNITIES FOR RESEARCH AND INDUSTRY

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1950-2010

NCL

Celebrating Sixty Years of Science

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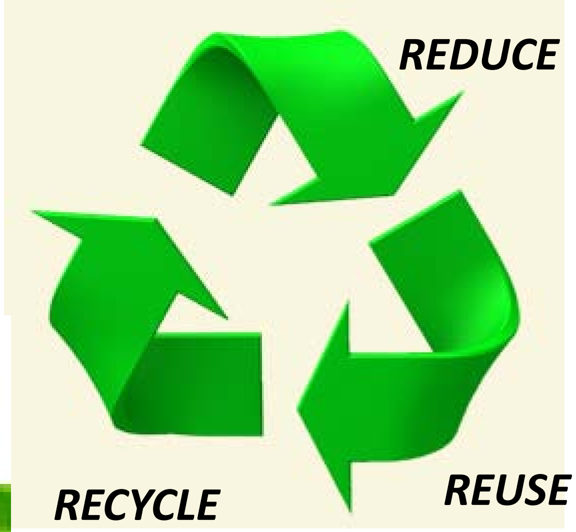
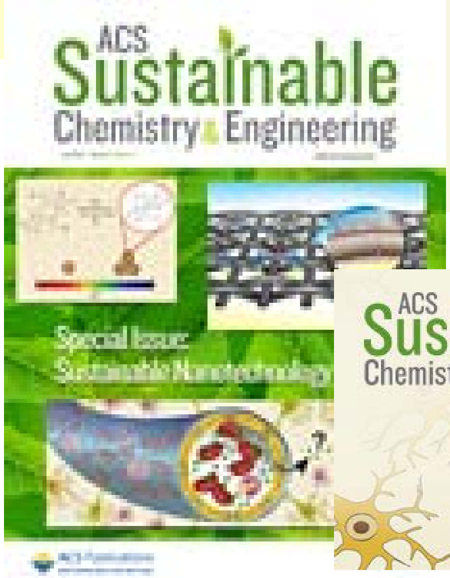
ORGANIC POLYMERS

- **Exclusive dependence on fossil fuel based resources**
- **Generation of wastes that need disposal**





Sustainability is the key concern of science, technology, industry and society today

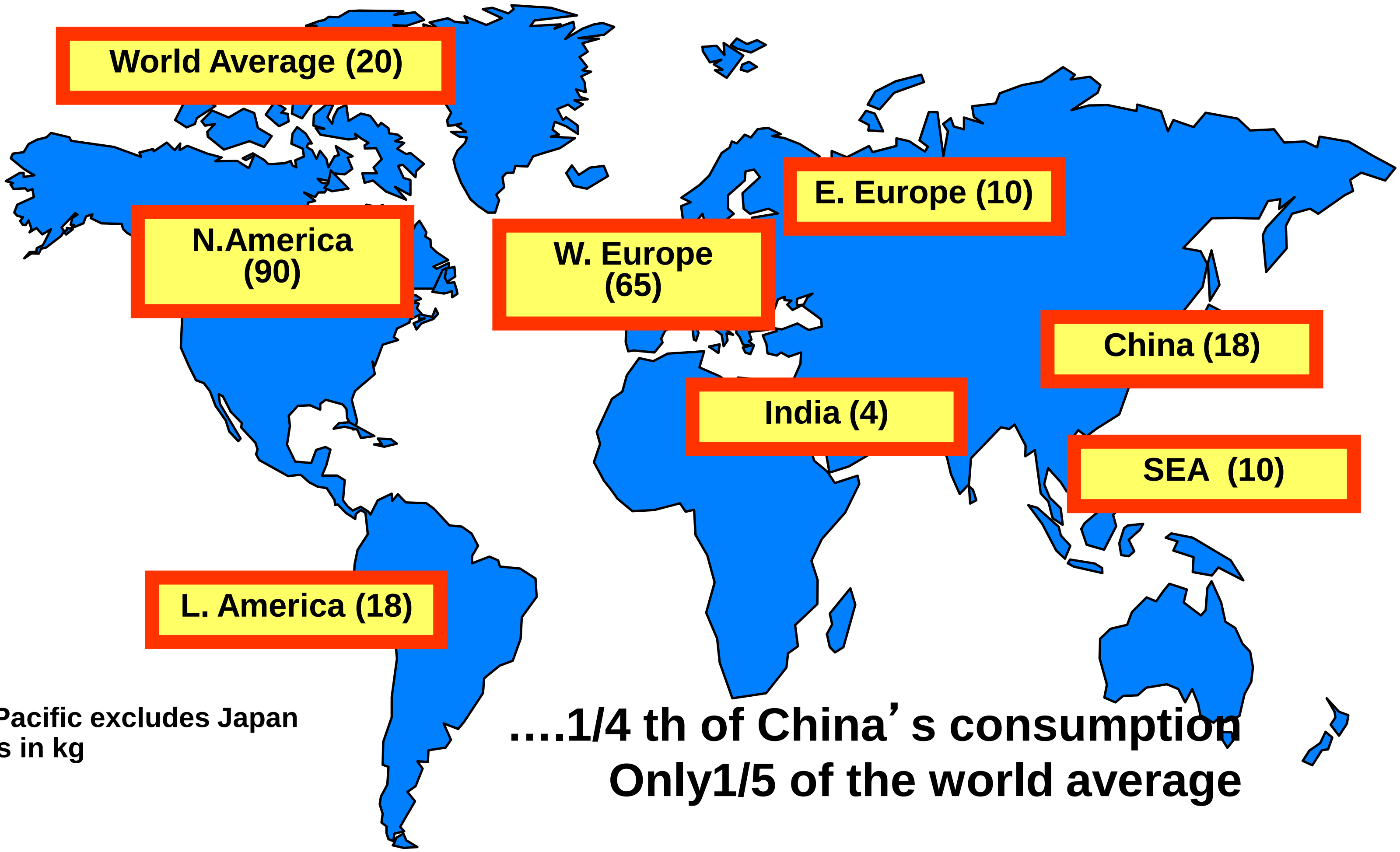
Can the materials needs of humankind be based on the concept of sustainability of both resources and environment?

POLYMER MATERIALS

- Global production : 200 million tons
- Employment : 60 million jobs
- Global consumption : 30 kg per capita
- Business value : US $ 1200 billion per annum
- Consume less than 10% of fossil hyf=drocarbons
- India's production : 15 million tons by 2015

Polymers are a post war industry, fuelled by the availability of inexpensive hydrocarbon resources; industry grew from zero to present capacities in about fifty years

PER CAPITA PLASTICS CONSUMPTION



Note :
- **Asia/ Pacific excludes Japan**
- **figures in kg**

….1/4 th of China's consumption
Only1/5 of the world average

MANUFACTURE OF POLYMERS ARE GREAT EXAMPLES OF GREEN CHEMISTRY

- Most polymers are manufactured in gas phase or melt phase where only the reactants are present (Polyolefins, PET, Nylons, PC etc)
- Most frequently used medium : water for emulsion and suspension polymers (Polystyrene, PVC)
- Current catalytic processes have turn over frequencies approaching those of enzymatic catalysts with less than 1 % of the monomer vented as unreacted monomer and low residual metal impurities (less than 3 ppm)
- Very little solid or liquid wastes
- Highl energy efficiency
- Exploit fully the economy of scale

Polymers are truly miracles of chemistry and engineering

OUR INSATIABLE DESIRE TO CONSUME

- W. Europe consumes an average of 16 tons of materials per person per year, of which 6 tons ends up as waste, including 3 tons of landfill
- We consume 30 kg of packaging material per person per year, all of which ends up as waste
- We discard about one trillion single use plastic bags each year; generate 2 billion tons per annum of municipal waste; 13 billion plastic bottles thrown away annually; 5 million tons of plastics find their way into our oceans
- Global recycling rate is only about 10 % of the materials consumed
- Delhi generates 10,000 tons per day of solid municipal waste; By 2020 Delhi will need 28 sq km of land for landfill, equivalent to the area of New Delhi !
- Using resources at the current rate we will need " the equivalent of more than two planets to sustain us " by 2050 !

Unsustainable consumption of finite resources requires resource innovations

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PETE

Poly(ethylene terephthalate)

Every second we throw away about 1500 bottles

Over 30 billion liters of bottled water is consumed annual*ly*

What is the solution ?

THE PRINCIPLES OF RESOURCE SELECTION

- **Abundance of "Cheap" resources will lead to its wasteful use (r-selection)**
- **Scarcity of resources will lead to more sustainable use (k-selection)**
- **Post industrial communities represent r-selection; but it is necessary for our survival to move to k-selection**
- **The easiest way to drive this process is to make resources artificially scarce, before they disappear**
- **This, however, flies in the face of all that we 'know' about how economics works : 'Cheap' resources are better; in practice, the rational choices that individuals and companies make in their own self interest end up depleting the overall resource available**

The Tragedy of Commons

NATURE'S APPROACH TO SUSTAINABLE MATERIALS

Nature designs material with great care and attention to details

- **Economy in the use of raw materials**
- **Minimum use of energy**
- **Easy to recycle under ambient conditions**

Nature achieves this sophistication through highly organized fabrication methods and hierarchies of structural features

MATERIAL SYNTHESIS : NATURE'S PRINCIPLES

- **Optimal use of energy and raw materials**
- **Minimal energy consumption – most synthesis occurs at <45^{o}C**
- **Molecular control leading to flawless materials: Self healing and self-correcting principles**
- **Use of compatible chemistries**
  - **Ceramics : $CaCO_3$, SiO_2**
  - **Non-ceramics : Proteins, polysaccharides**
  - **Water : Plasticizer**
  - **Partitioning and separations : Lipid (Bilayer membranes)**
  - **Hydrophobic interaction : Orientation**
  - **Liquid crystallinity : Processing of materials**

Will the twenty first century be the age of bio-inspired organic materials

ADVANTAGES OF MATERIALS MADE BY NATURE

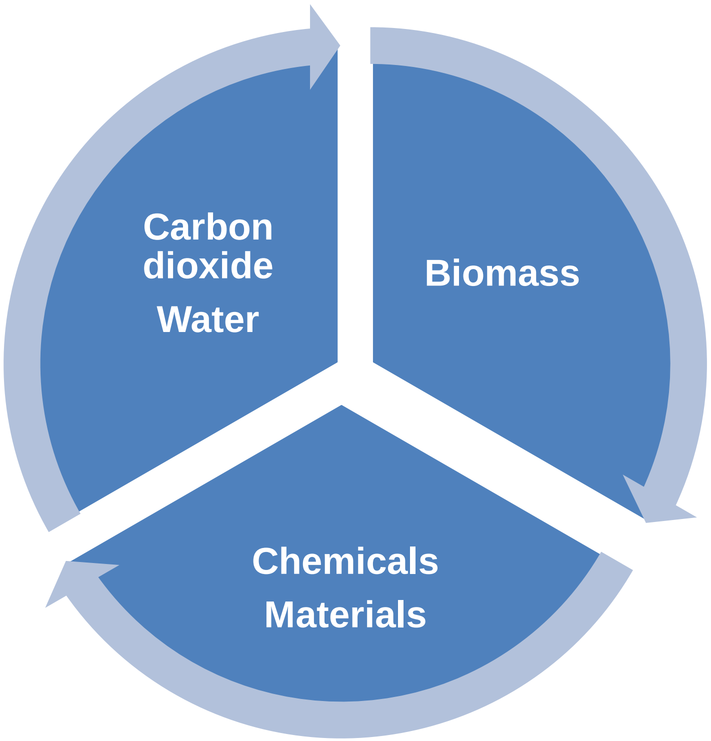
- **Efficient synthesis, if you are prepared to wait long enough**
  - **Fastest rate of bone growth : 1 μm/day**
  - **Growth of egg shells : 5 g/day**
- **Recycling**
  - **Animals/Plant continuously recycle/ repair their constituent materials**
  - **Choice : make materials that are strong/ tough with finite probability of catastrophic failure (man)**

    or

    make materials that are relatively weaker, but have self healing or repair capabilities (nature)

Self-healing structures and smart materials are emerging from an understanding of nature's processes

FROM HYDROCARBONS TO CARBOHYDRATES : FROM NON RENEWABLES TO RENEWABLES



Can a part of the chemicals / materials manufacturing progressively shift to renewable carbohydrate resources (biomass) ?

Is such a virtuous cycle just a dream ?

POLYMERS FROM RENEWABLE RESOURCES

Biodegradable polymers

- Polyesters
- Starch

•Environmental sustainability
•CO_2 mitigation – closing the carbon cycle
•Food Vs material

Bio-derived monomers and polymers

- PTT / PBS
- Nylon-11/ 4,6 / 6,10
- Bio –PE
  Bio-PET

Reduce dependence on fossil fuel

FOOD versus FUEL

Using land to grow crops for fuels lead to destruction of forests, wetlands and grasslands that store enormous amount of carbon

April 7, 2008

Corn diverted to fuel ethanol in USA

↓

Soyabean growers switch to corn in USA

↓

Farmers in Brazil plant soyabean in land previously used as cattle pasture lands

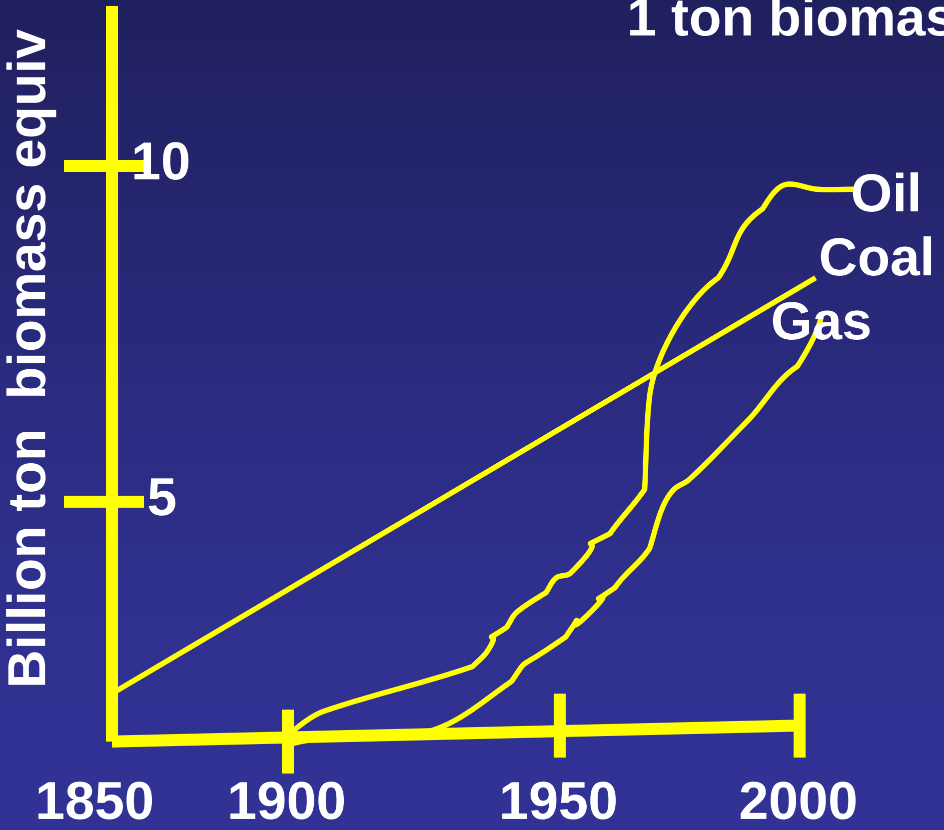
↓

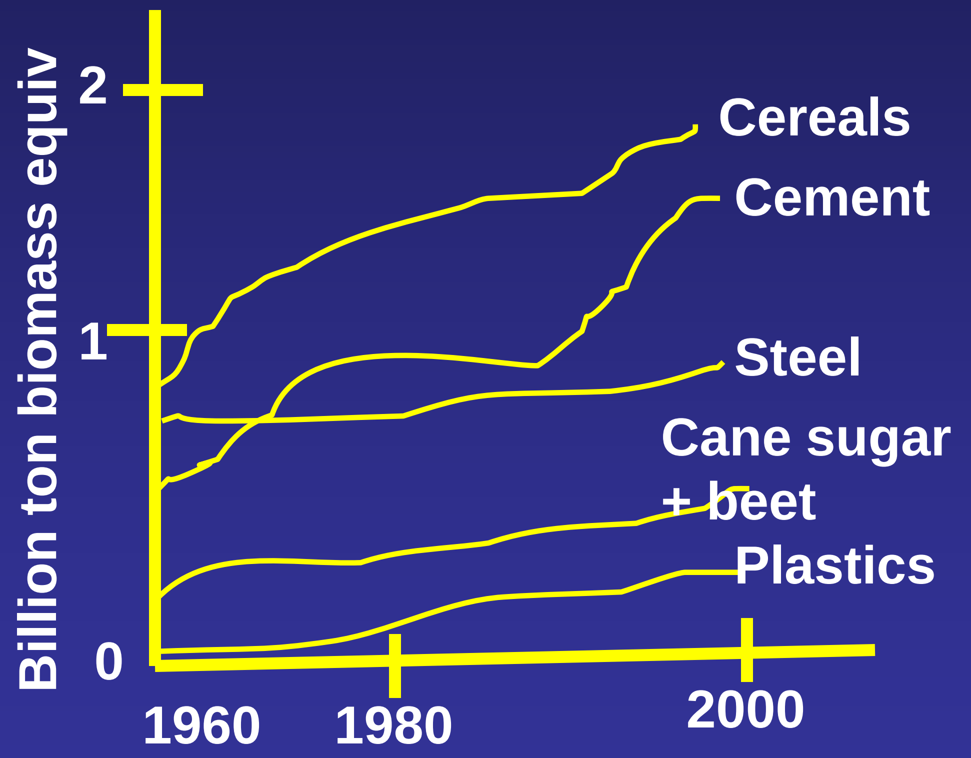
Leads to clearing of forest lands in Amazon rain forest

Law of unintended consequences !

BIOMASS PRODUCTION FOR FOOD, ENERGY AND MATERIALS

1 ton oil equiv = 42 GJ
1 ton biomass equiv = 18 GJ



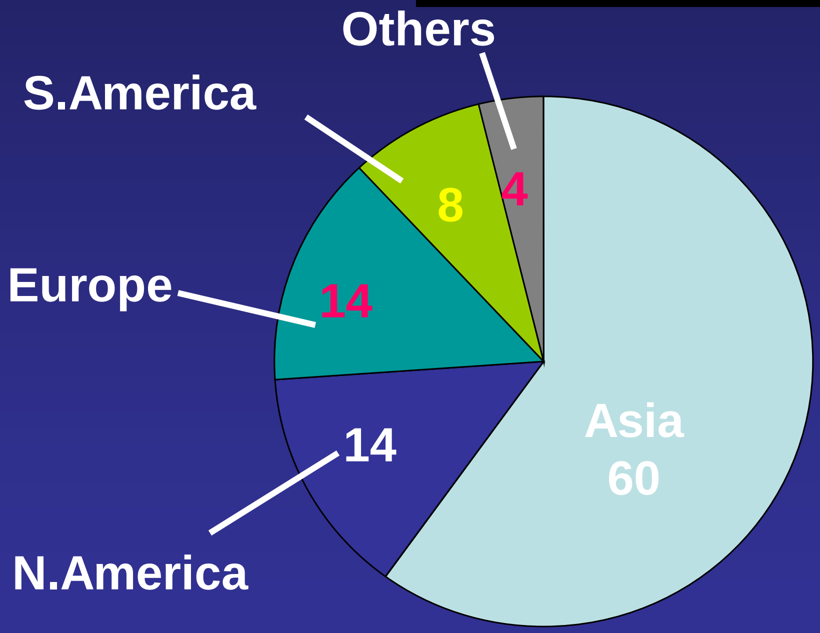


Clearly using food crops for fuels is not sustainable

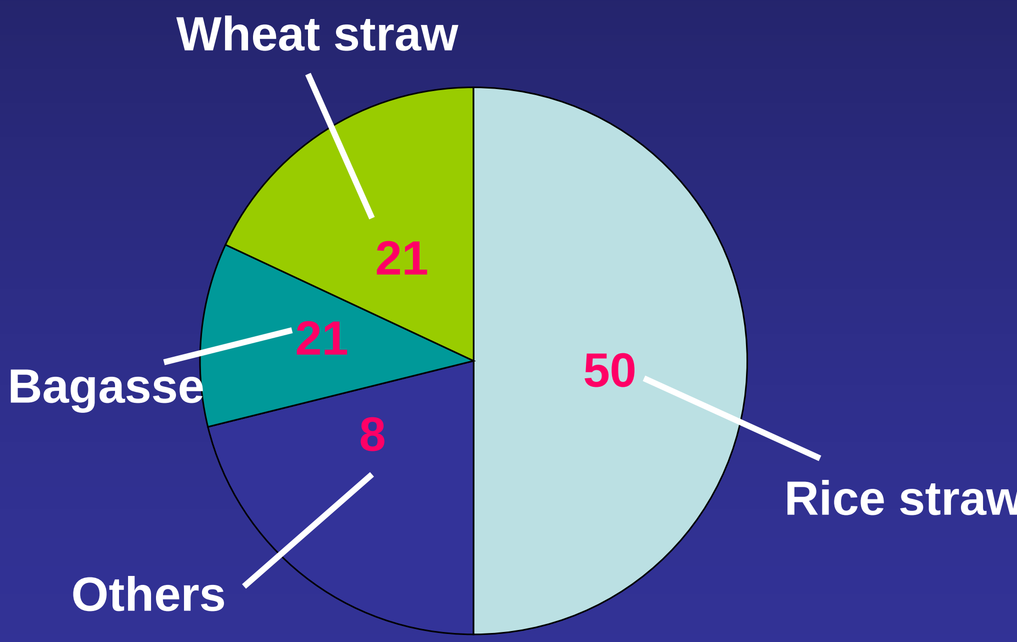
WORLD - WIDE AVAILABILITY OF AGRICULTURAL RESIDUES

Crop residues : > 2 billion tons; half of organic carbon on earth is in the form of cellulose, the most abundant polymer

An unique Indian advantage ?



By Geography



By type

FEEDING THE BILLIONS : FOOD FOR INDIA

	Million tons		Productivity t/hectare	
	2003-04	2020-21	Present	Future
Wheat	72	84	2.6	3.2
Rice	88.5	122	2.1	3.0
Pulses	15	24	0.6	1.2
Sugar	27[a]		20-40[b]	

a 2006-07, Sugarcane : 270 million tons
b per acre

Typical Sugar plant : 16000 tons of sugarcane crushed per day
40 KL of ethanol / day 65 MW power

INDIA'S COMPETITIVE ADVANTAGE IN BIO DERIVED RESOURCES

- Agricultural Wastes
- Urban Municipal Waste
- Sugar cane Bagasse (Second largest producer, cellulose, lignin)
- Castor Oil (world's largest producer)
- Guar gum, a rigid rod polymer of over 1 million molecular weight ; a mannose chain with a galactose side chain (world's largest producer)
- Coconut residues (World's third largest producer), 15 billion nuts per year; hardly 10 % of the coconut is edible
- Downstream of paper and pulp industry (second largest paper consumer)
- Cashew nut shell liquid (world's largest producer)

GREATEST OPPORTUNITY : MANY OF THE FEEDSTOCKS CAN BE READILY CONVERTED TO HIGH VALUE FUNCTIONAL MATERIALS

POLY(LACTIC ACID)S : AN ALIPHATIC POLYESTERS FROM A SIMPLE AB MONOMER

- Monomer Lactic acid (R or S) is produced by fermentation of sugars
- PLLA is hydrophobic, impermeable to water, hydrocarbon resistant
- Biodegradable and compostable
- Clarity and physical properties similar to PET
- Requires ~ 49 % less fossil fuel to produce PLLA compared to PET
- 0.75 kg of CO_2 emitted per kg of PLLA produced versus 3.4 kg of CO_2 per kg of PET

IF PLLA IS SO ATTRACTIVE FROM A SUSTAINABILITY POINT OF VIEW, WHY IS IT STILL NOT A PART OF OUR EVERY DAY LIFE ?

BIO-BASED / BIODEGRADABLE POLYMERS : SOME FACTS

- **250 companies,363 locations; highly fragmented**
- **Niche products serving specializing markets**
- **1.5 % of total polymer consumed; expected to grow to 3 % by 2020**
- **US $ 1 billion in market value**
- **Most plant capacities <6000 tpa. Exceptions, 140,000 tpa PLLA by Cargill-Teijin, 45,000 tpa 1,3-propane diol, DuPont – Tate & Lyle**

SOME OF THE BETTER KNOWN BIO-BASED POLYMERS

Bio-based polymers	Type of Polymer	Structure / Production Method
Starch polymers	Polysaccharides	Modified natural polymers
Polylactic acid (PLA)	Polyester	Lacti acid by fermentation, followed by polymerization
Polyesters from biobased intermediates a) Polytrimethylene terephthalate (PTT) b) Polybutylene terephthalate (PBT) c) Polybutylene succinate (PBS)	Polyester	a) 1,3-propanediol by fermentation plus terephthalic acid b) 1,4-butanedil by fermentation plus terephthalic acid c) Succinic acid by fermentation plus terephthalic acid
Polyhydroxyalkanoates (PHAs)	Polyester	Direct production of polymer by fermentation or in a crop
Cellulose polymers	Polysaccharides	a) Modified natural polymer b) Bacterial cellulose by fermentation

BIO-PLASTICS : COMMERCIAL REALITY

Polymer	Trade Name	Producer
Synthetic polymers		
•Poly 3-hydroxybutyrate	Biogreen	Mitsubishi Gas Chemicals
•Polybutylenesuccinate	Bionolle 1000	Showa Highpolymer
•Polybutylenesuccinate/ adipate	Bionelle 3000	Shows Highpolymer
	EnPol 4000	Ire Chemicals
•Polybutylenesuccinate/ carbonate	Iupec	Mitsubishi Gas Chemicals
•Polybutylenesuccinate/ terephthalate	Biomax	DuPont
•Polybutylenedipate/ terephthalate	Ecoflex	BASF
•Polytetramethyleneadipate/ terephthalate	EastarBio	Eastman Chemicals
•Polybutyleneadipate/ terephthalate	EnPol 8000	Ire Chemical

BIO-PLASTICS : COMMERCIAL REALITY

Polymer	Trade Name	Producer
•Polycaprolactone	CelGreen PH	Daicel Chemical
	TONE	Dow Chemical
•Polyethylenesuccinate/ adipate	Lunare SE	Nippon Shokubai
•Polylactic acid	NatureWorks	Cargill Dow
	LACEA	Mitsui Chemicals
•Polyvinyl alcohol	Poval	Kuraray
	Gosenol	Nippon Synthetic Chemical
	Dolon VA	Aicello Chemical

BIO-PLASTICS : COMMERCIAL REALITY

Polymer	Trade Name	Producer
Modification of Natural Polymers		
•Modified starch	Cornpol	Japan CornStarch
•Starch-based synthetic polymer	Placorn	Nihon Shokuhin Kako
	Mater-Bi	Chemitech
•Cellulose acetate	CelGreen PCA	Daicel Chemical
	Unknown	Teijin
•Chitosan/ Cellulose/ Starch	Dolon CC	Aicello Kagaku

Source : Biodegradable Plastics Society

SOME OF THE KEY PRODUCERS AND BRANDS OF BIO BASED POLYMERS

Resin Producer	Trade Name	Polymer Family
BASF	EcoFlex	Copolyester polybutylensuccinate/ terephthalate
DuPont	BIOMAX	Polyesters (polytrimethylene terephthalate)
Innovia Films		Cellophane
Metabolix/ADM (JV)	BIOPOL	Polyhydroxyalkoanates (PHA)[1]
Mitsubishi Chemical		Polybutylene succinate (PBS)
National Starch	ECO-Foam	Starch[2]
NatureWorks (Cargill)	NatureWorks®	Polylactic acid
Novamont	MATER-BI, Eastar Bio Ultra	Starch polymer, copolyester
Soy Works Corporation	SoyPlus™	Soy protein
Dow	Renuva™	Bio Polyols
Arkema	Rilsan™	Polyamide 11

1. *Other manufacturers are Nodex, P&G, Kaneka*
2. *Other starch based polymers include Rodenburg biopolymers, BIOP, biotec*

"DROP- IN" BIOPOLYMERS : DOES IT MAKE SENSE ?

- Bio PE, Bio PP, Bio PET, Bio PVC !
- All monomers derived from sugar ethanol
- Apart from competition from food large scale fermentation processes are not carbon neutral; every Kg of ethanol by fermentation results in 1 Kg of carbon dioxide
- Poor atom efficiency; starch to ethylene has an overall carbon atom efficiency of 65%; A cracker converts ethane to ethylene in > 90 % carbon atom efficiency
- Selling price of PE is $ 34 per million Btu; ethanol from corn sells at $35 per million Btu
- We will need 400 sq miles of land planted with sugar cane to prset up one world scale plant of PE of 350,000 tpa

Are we managing sustainability or mere perceptions

COMPARISON BY GREEN DESIGN METRICS

	Atom Economy, %	Carcinogens, kg benzene eqv/L	Non-Carcinogens, kg toluene eqv/L	Respiratory Effects, kgPM2.5 eqv/L	Ecotoxicity, kg benzene eqv/L	Cumulative Energy Demand, MJ Eqv/L	% Renewable Material	Distance of feedstocks
Polymer								
PET	80	1.1×10^{-2}	62.9	4.9×10^{-3}	5.72	123.8	0	Intern
Bio-PET	62	1.3×10^{-2}	72.7	5.7×10^{-3}	6.98	146.2	15	Intern

Environ. Sci. Technol., 44, 8264 (2010)

- **Switching to renewable resources results in increases in impact categories:**
  - **eutrophication**
  - **human health impacts**
  - **eco-toxicity**

- **The impacts result from increased use of fertilizer and pesticide, increased land use requirement for agricultural production, as well as, from fermentation and other chemical processing steps**

CHALLENGES FOR BIO DERIVED POLYMERS

- Volatility in oil prices; supply, demand and geo-political issues; emergence of shale; all impact economic viability of bio based polymers
- Bio derived polymers are expensive, 10 to 100 % of petrochemical derived polymers; Braskem's Bio-PE carries a price premium of 30 to 60% without any additional new functionality
- Inadequate labeling guidance for consumers; how do consumers know whether a given polymer should be landfilled, composted or recycled?

CHALLENGES FOR BIO DERIVED POLYMERS

- Implications of contamination of compostable and bio degradable polymers with those which are generally recycled or landfilled
- Inadequate availability of industrial composting infrastructure
- Technology gaps in using waste agricultural residues as feedstocks for making polymers; all biopolymers today are derived from edible sugars
- Range of accessible properties; Polyesters are the only class of polymers that are biodegradable; no performance differentiator for bio polymers, except their biodegradability

CHALLENGES FOR BIO DERIVED POLYMERS

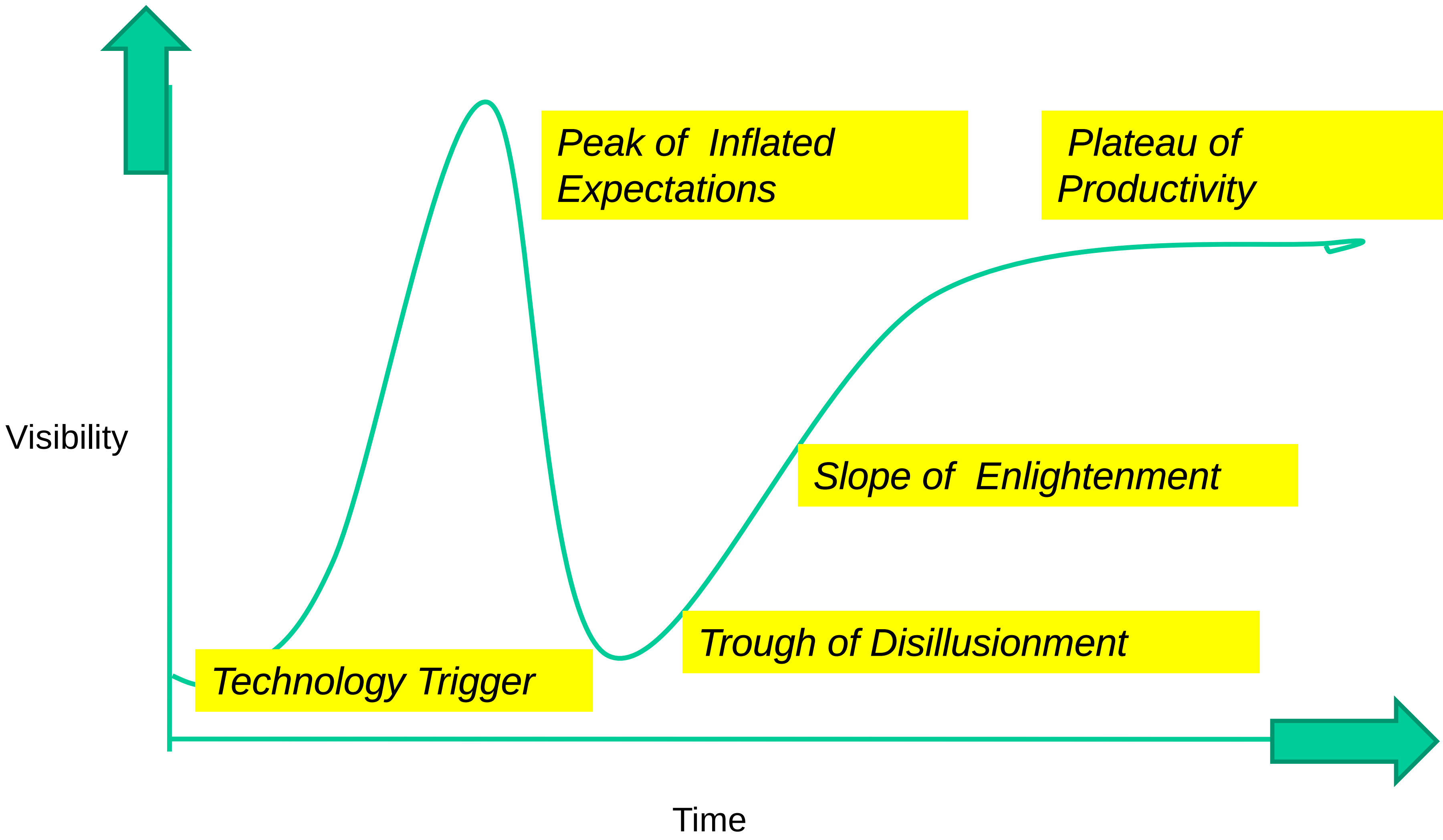
- Transportation and storage of feedstocks; supply chain issues and integration
- Feedstocks quality variability; regional and geographic and climatic
- Engineering challenges : handling of high bulk density solids, corrosion and material of construction; drying and water recycling
- Process challenges : robust catalysts with long life time; catalyst fouling issues
- Separation science and technology

New paradigms in manufacturing : distributed manufacturing; part processing of feedstocks close to where it is produced; skid mounted mobile process plants

Decouple of economics with scale : large single location biomass derived manufacturing inconceivable; risks too high

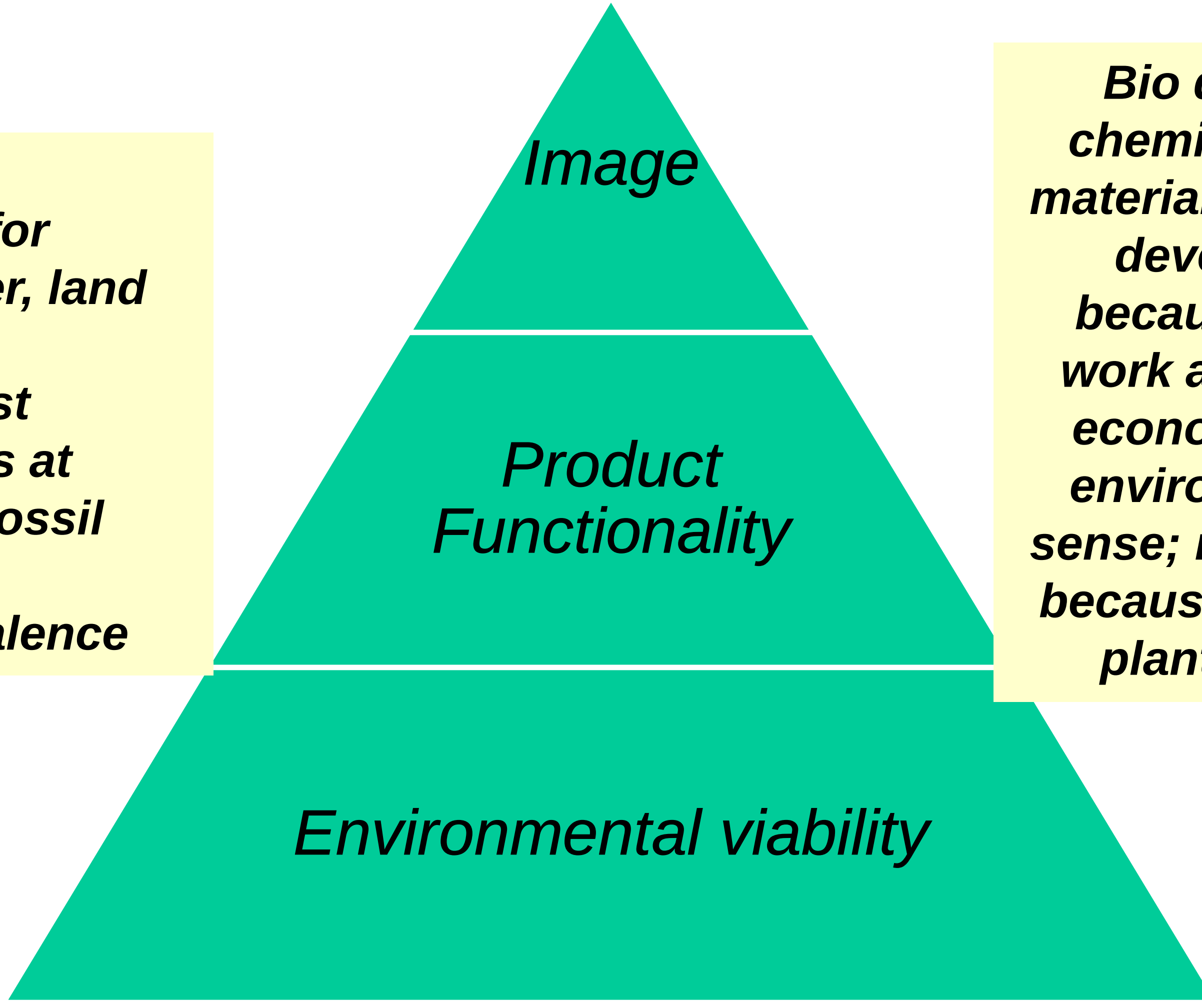
Evolution of Technologies : The Hype Cycle

(http://en.wikipedia.org/wiki/Hype_cycle)



THE BIOVALUE PYRAMID

- ***CO_2 Neutral***
- ***Competition for resources (water, land and food)***
- ***Operating cost competitiveness at $100/ barrel of fossil fuel***
- ***Capex Equivalence***



Bio derived chemicals and materials must be developed because they work and make economic and environmental sense; not merely because they are plant based

www.rolandberger.com/chemicals 2030

SUMMARY

- Creation of sustainable and environmentally friendly polymers for diverse applications and capable of substituting what we currently use appears to be a formidable challenge.
- There are no easy answers
- We need to focus on, both consumption as well as end of use disposal of short life cycle materials
- Who will drive this change? consumers, industry, Governments ?
- Can industry drive the change ? For this to happen industry have to become more honest and transparent

Can men who row the boat , rock it ?

THANK YOU