AKADEMIA GÓRNICZO-HUTNICZA
IM. STANISŁAWA STASZICA W KRAKOWIE
AGH UNIVERSITY OF SCIENCE AND TECHNOLOGY

KRAKOWSKA INTERDYSCYPLINARNA SZKOŁA DOKTORSKA

Interdisciplinary Aspects of Materials Engineering
Materials from renewable resources

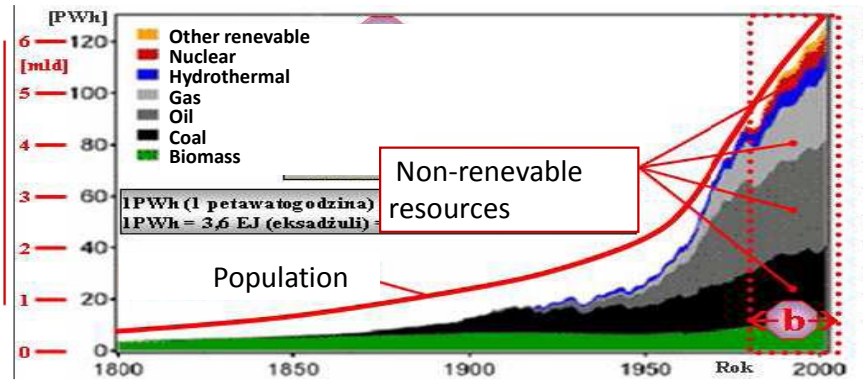
Elżbieta Pamuła
epamula@agh.edu.pl
Department of Biomaterials and Composites
Faculty of Materials Science and Ceramics

Interdisciplinary Aspects of Materials Engineering
Materials from renewable resources

- **Introduction - resources, raw materials and fossil fuels**
- Materials obtained from nonrenewable fossil raw materials
- Biobased materials and recycled materials
- Material life cycle, sustainable materials and carbon footprint
- Bioplastics

RAW MATERIALS AND ENERGY IN THE WORLD

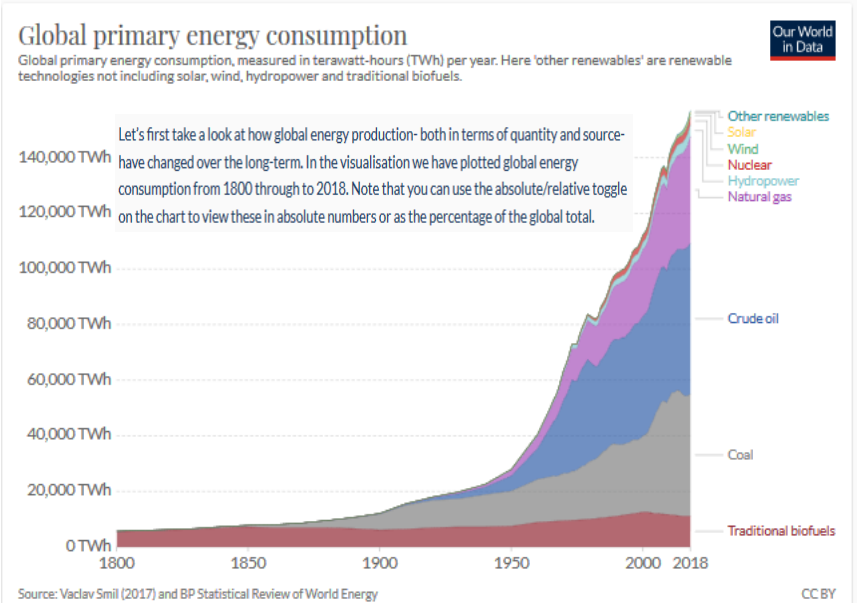
Global energy consumption of various sources of primary energy [PWh] and growth curve of the human population [Bln]



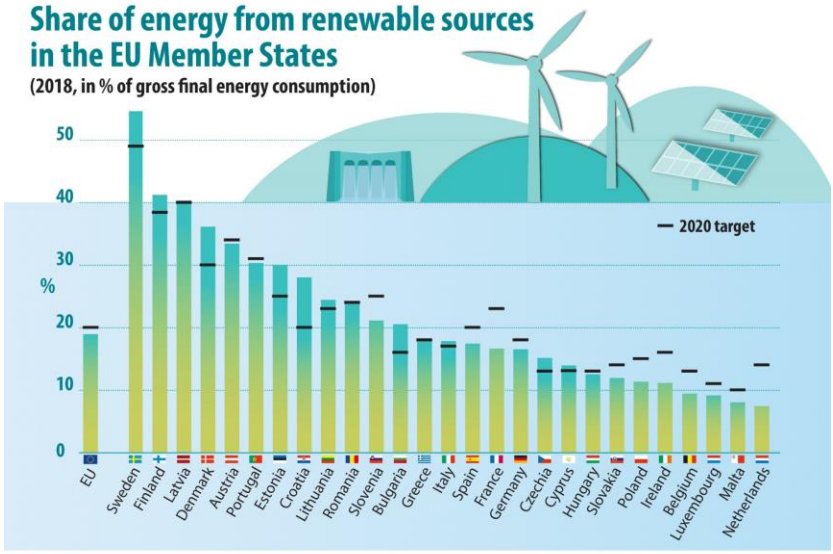
In the last 40 years our generation consumed more energy than all previous generations in the whole history of mankind.
Successively have been consumed coal, crude oil, natural gas, uranium, ….and the human population has increased up to 7 Bln.

Panel naukowy: *Strategia badań na rzecz rozwoju energetyki w Polsce*. Polska Akademia Nauk, Warszawa, 12.05.2009 r.

RAW MATERIALS AND ENERGY IN THE WORLD

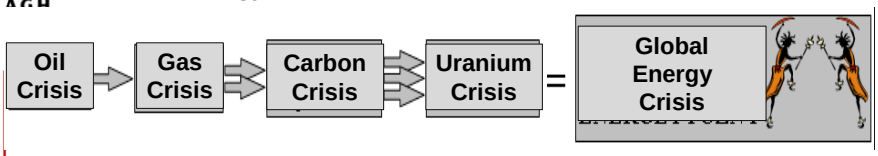


RAW MATERIALS AND ENERGY IN THE WORLD



RAW MATERIALS AND ENERGY IN THE WORLD

Global energy crisis → back to nature?



Public is not aware that **energy crisis is not local but global** and time is running out!

- Fossil resources (taking into account the current 2% average annual growth of energy consumption) will be exhausted by approx. **70 - 120 years**.
- Exploitation of methane hydrates may extend this period by approx. **60 years**.
- Nuclear technologies splitting atoms may extend this period by a further approx. **40 years**.

Panel naukowy: ***Strategia badań na rzecz rozwoju energetyki w Polsce***. Polska Akademia Nauk, Warszawa, 12.05.2009 r.

RAW MATERIALS AND ENERGY IN THE WORLD

- None of the used methods of primary energy production allows for the elimination of the threat of global energy crisis to our civilization.

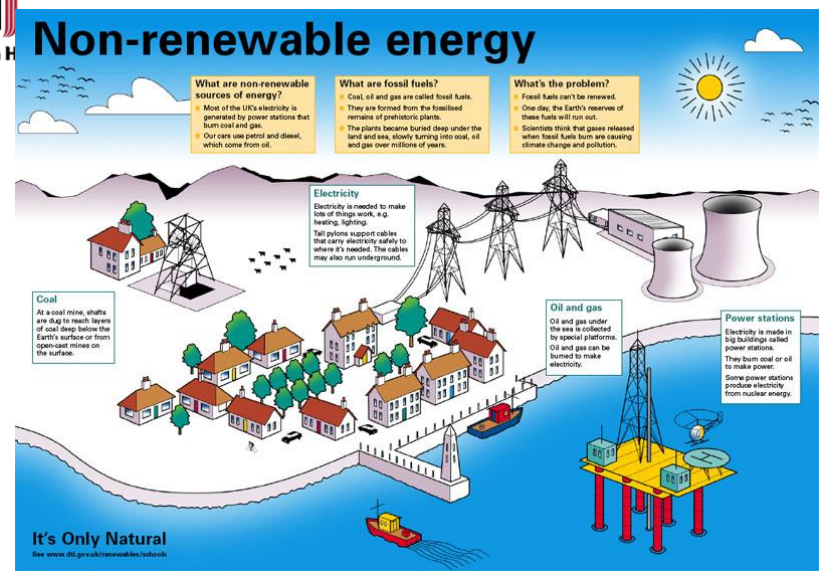
- There is a theoretical chance to avert this crisis by control nuclear, magnetic or laser fusion, as a cheap source of primary energy. We have in practice approx. 100 years (maybe even with 200 – 300 years). But what does it mean for our civilization?

- The seriousness of the situation does not reach to the international community, in particular the decision-making politicians.

- Only a global scale integrated anti-crisis actions may give a chance to take this greatest challenge of our civilization.

Panel naukowy: ***Strategia badań na rzecz rozwoju energetyki w Polsce*****. Polska Akademia Nauk, Warszawa, 12.05.2009 r.**

Non-renewable resources



Non-renewable raw materials will be exhausted.

Interdisciplinary Aspects of Materials Engineering

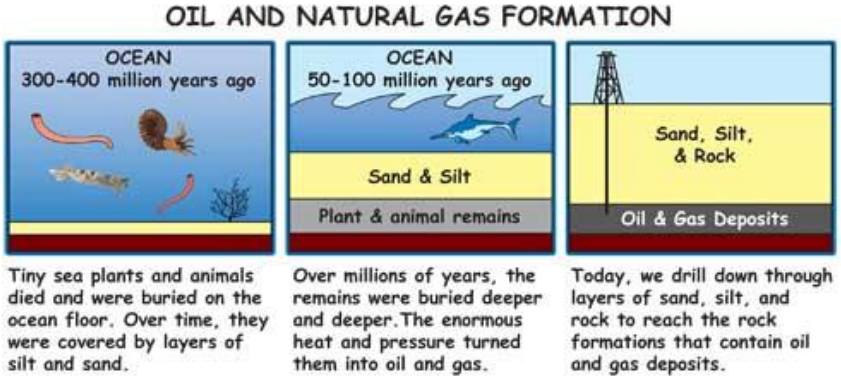
Materials from renewable resources

- Introduction - resources, raw materials and fossil fuels
- **Materials obtained from nonrenewable fossil raw materials**
- Biobased materials and recycled materials
- Material life cycle, sustainable materials and carbon footprint
- Bioplastics

Non-renewable resources

Natural materials are only available in limited quantity and do not undergo renewal in the time scale of human life.

– Examples: crude oil, natural gas, coal, minerals, underground water



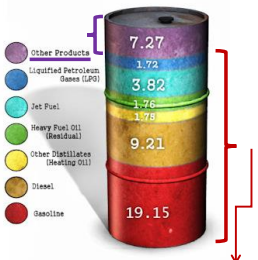
Non-renewable resources

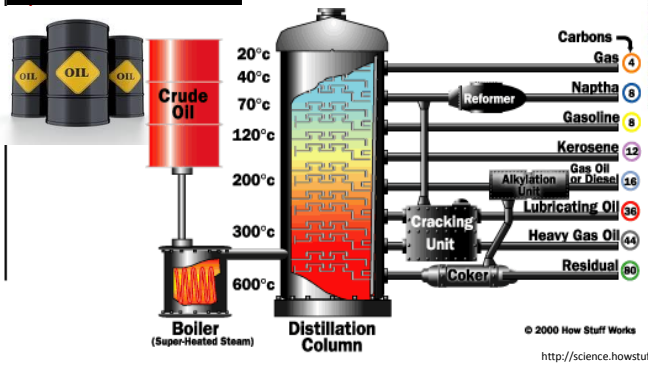
Raw materials and petrochemical products

Extraction

Processing

Application
(1 barrel of crude oil)





Energy
(combustion)

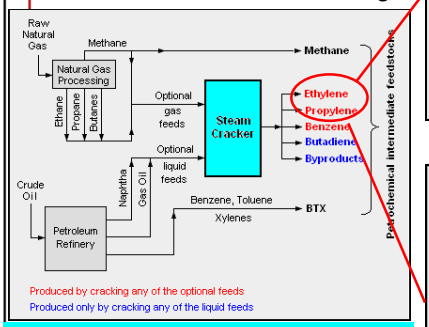
http://science.howstuffworks.com/environmental/energy/oil-refining5.htm

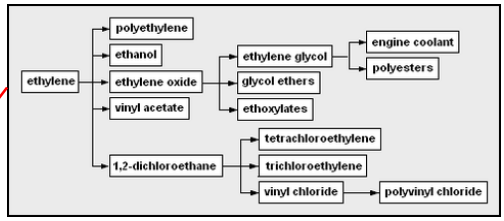
www.agh.edu.pl

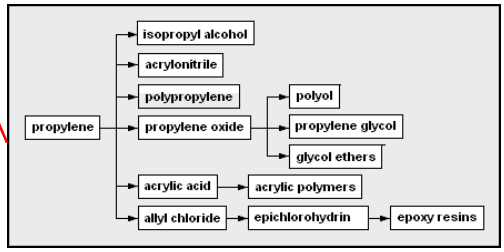
Non-renewable resources

Raw materials and petrochemical products

The classical production method of polymeric materials involves the use of substrates derived from crude oil and gas





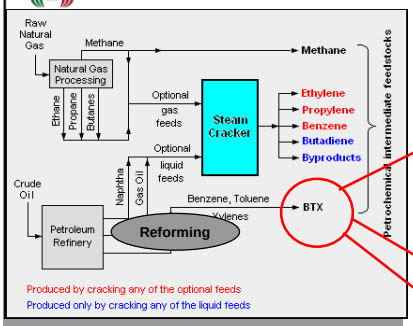


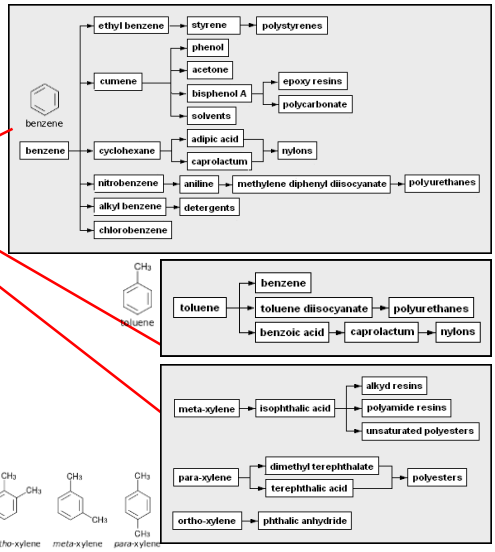
Cracking is the process whereby complex organic molecules such as long chain hydrocarbons from mazut and oil fractions are broken down into simpler molecules such as light hydrocarbons, by the breaking of carbon-carbon bonds in the precursors.

www.agh.edu.pl

Non-renewable resources

Raw materials and petrochemical products



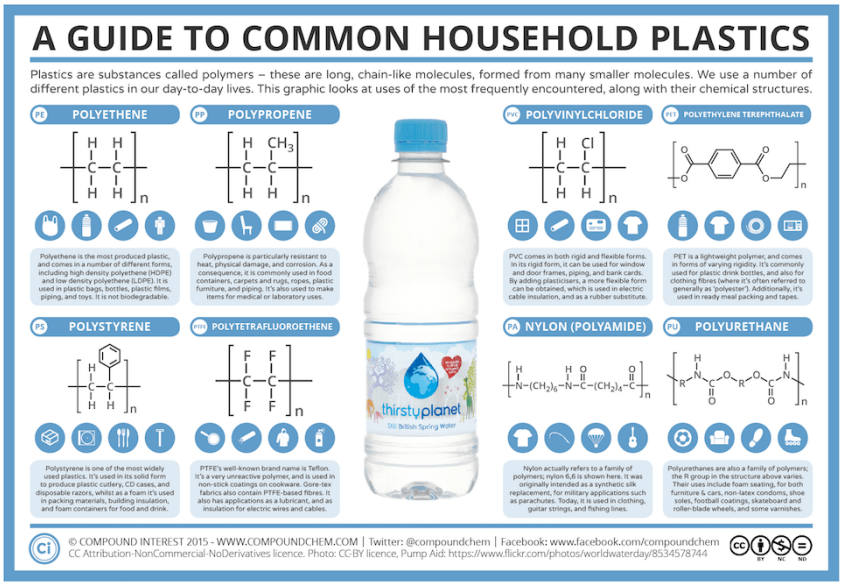


Reforming is a chemical process used to convert petroleum refinery naphthas distilled from crude oil (typically having low octane ratings) into high-octane liquid products.

Cracking and reforming are used to obtain a number of useful organic compounds which thanks to further reactions (e.g. polymerization) provide a wide range of polymeric materials.

Non-renewable resources

Raw materials and petrochemical products



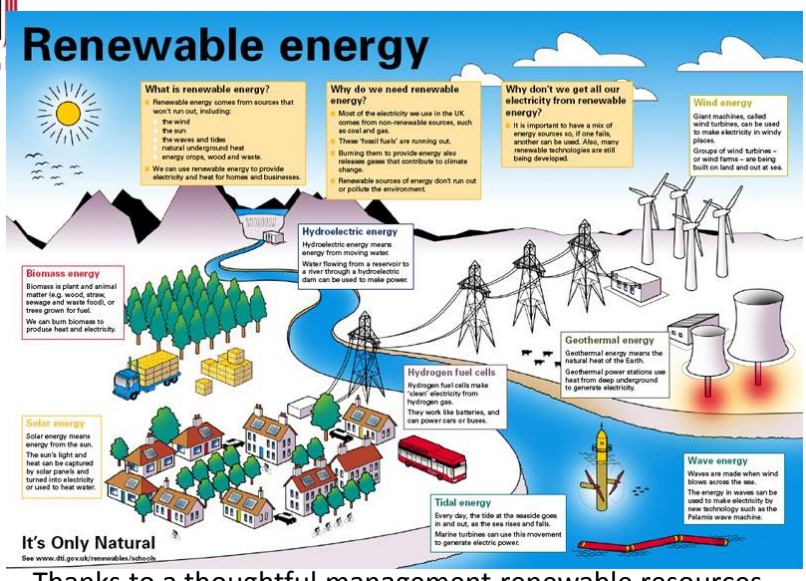
www.agh.edu.pl

Interdisciplinary Aspects of Materials Engineering

Materials from renewable resources

- Introduction - resources, raw materials and fossil fuels
- Materials obtained from nonrenewable fossil raw materials
- **Biobased materials and recycled materials**
- Material life cycle, sustainable materials and carbon footprint
- Bioplastics

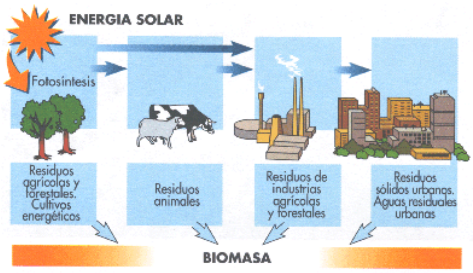
Renewable resources



Thanks to a thoughtful management renewable resources might not be exhausted.

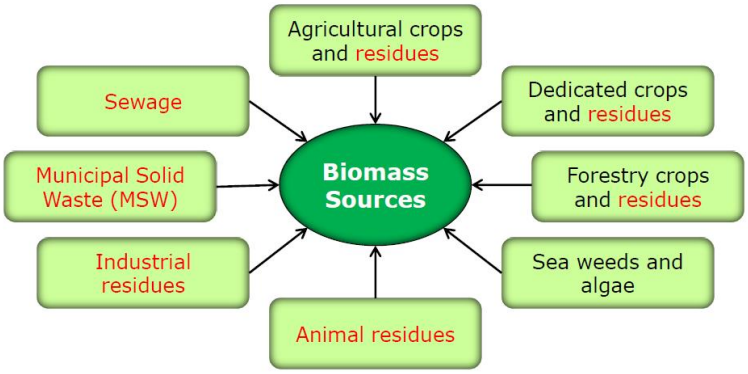
Renewable resources

- Natural resources can be renewed within the time scale of human life
- Water, soil, air
- Renewable energy (e.g. wind, solar, geothermal, biogas, biofuels)
- Living matter - biomass (e.g. plants, animals, bacteria, algae)



Renewable resources

Biomass



Sources of (waste) biomass for conversion to energy

Renewable resources

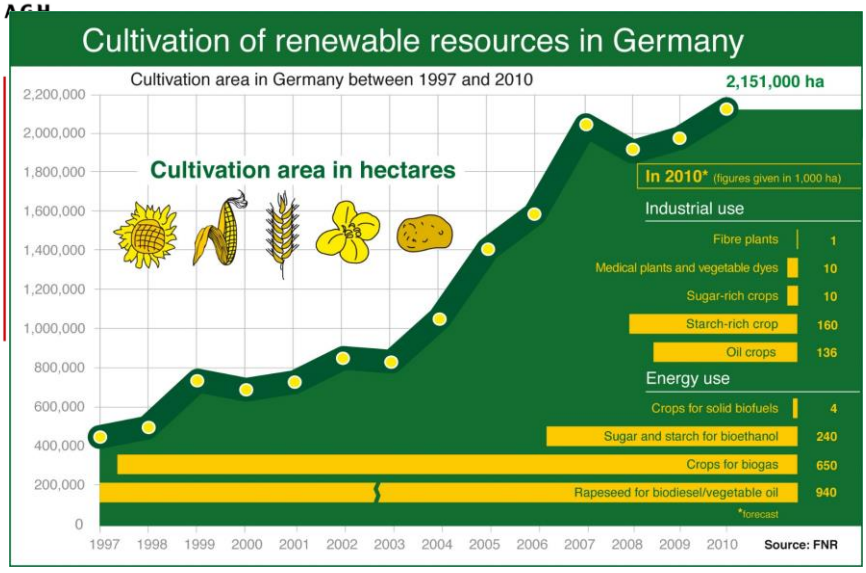
Biomass

- Biomass is:
  - Abundant
  - Renewable
  - Carbon neutral
  - The only sustainable source of hydrocarbons.

- Biomass can:
  - Fill the gap between energy demand and petroleum availability in near term.
  - Be a renewable source of hydrogen in the long term.

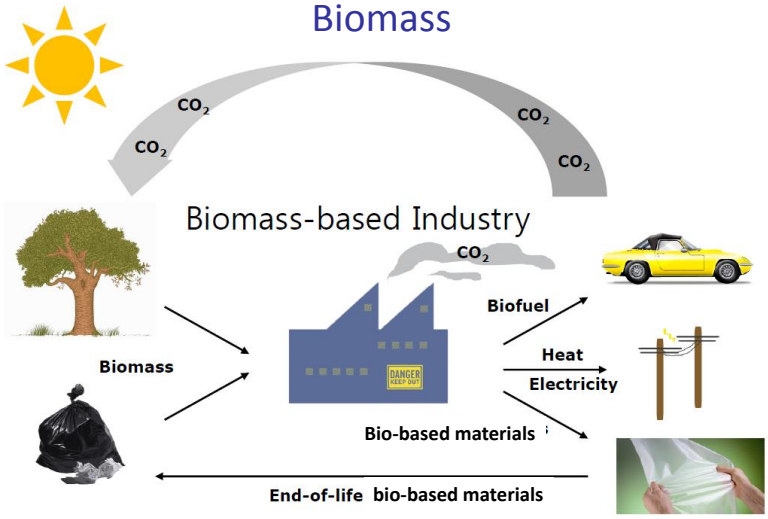
Renewable resources

Biomass



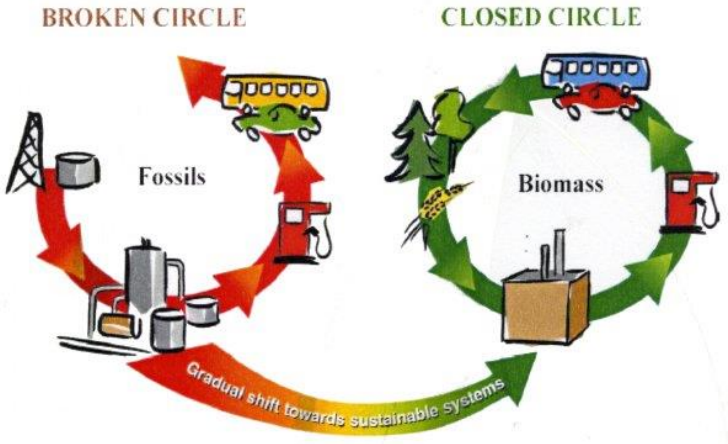
Renevable resources

Biomass



CO_2 released from combustion of biomass and biomass-derived products circulates in a closed circuit.

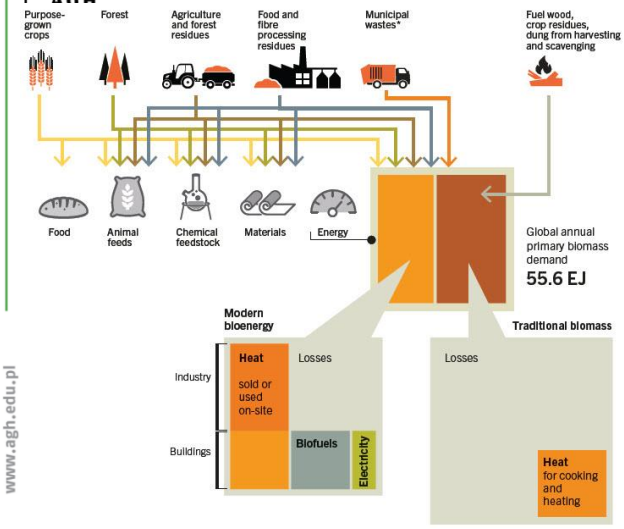
Non-renevable and renevable resources



CO_2 released during combustion of fossil fuels accumulates in the environment → Greenhouse effect

Renevable resources

Biomass



Biomass can be used for production of food for humans and animals, chemicals, energy, and polymeric materials.

Modern bioenergy: biomass processing is more energetically efficient (lower energy losses) as compared to traditional use of biomass – i.e. combusted without processing (very high energy losses).

http://cleanleap.com/02-market-and-industry-trends/biomass-energy

Renevable resources

Biomass → Energy

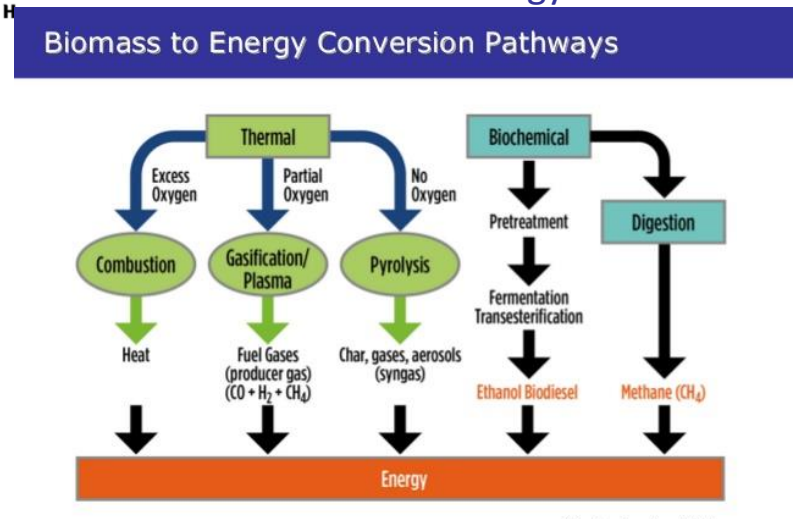
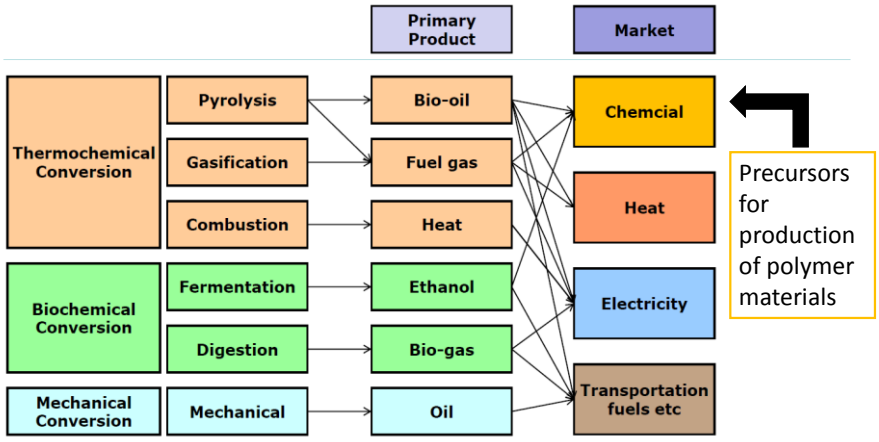


Illustration by NREL

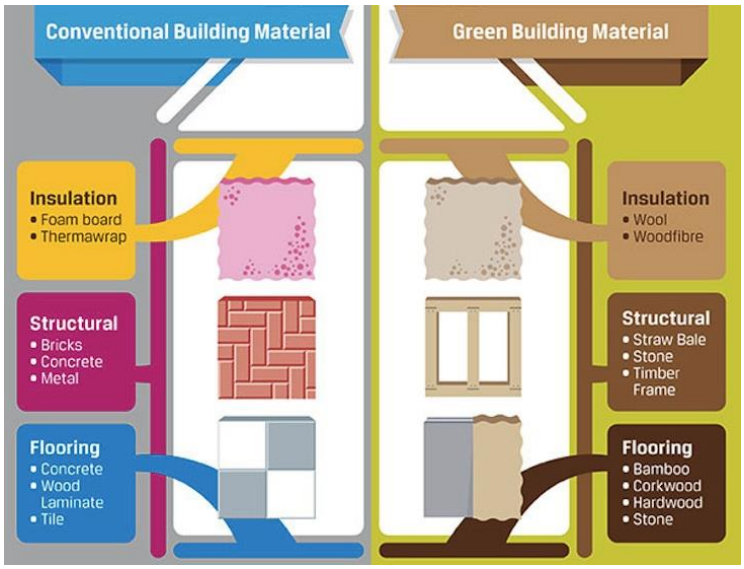
Renevable resources

Biomass → Energy and chemicals



http://what-when-how.com/energy-engineering/biomass-energy-engineering/

Biomass
Building materials



Renewable resources

Biomass

Wood: cellulose

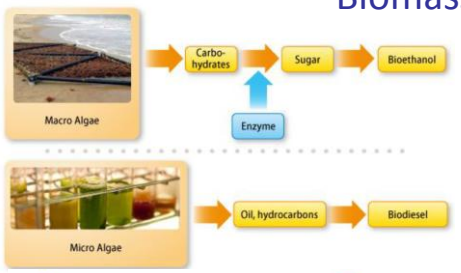
GreenHarvest Products Made With Rapidly Renewable Plant Fiber

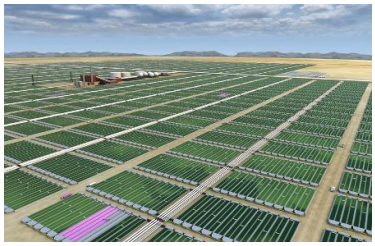
Production efficiency of toilet paper from different raw materials

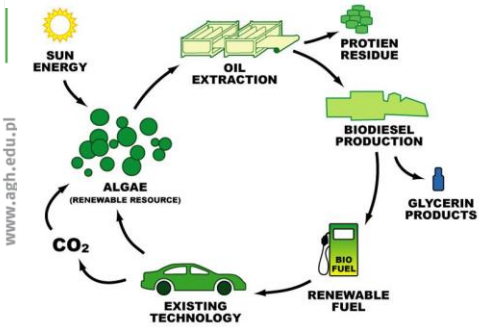
http://investor.kimberly-clark.com/releasedetail.cfm?ReleaseID=909120

Renewable resources

Biomass from algae







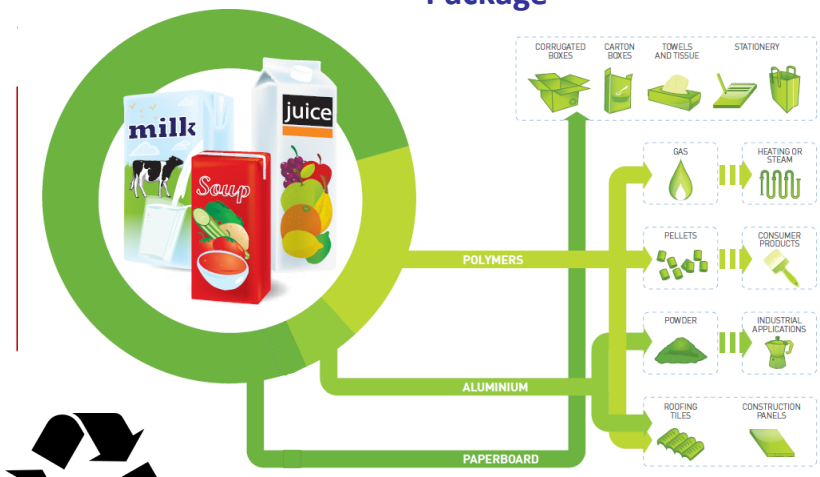
Algae the future of biomass production → huge yield

Feedstock	Yield (US gal/acre)
Soya	40-50
Rapeseed	110-145
Mustard	140
Palm	650
Algae	**10,000**

Source: Biodiesel 2020: A Global Market Survey, 2nd

Recycled materials

Package



Majority of products made of polymeric materials, glass, paper, metals can be reused and recycled
→ Waste products are valuable raw materials

Recycled materials

Automotive industry

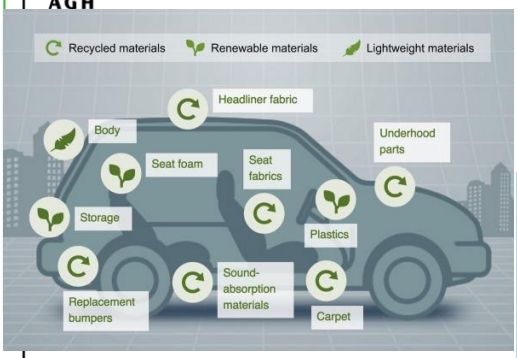
AGH

Ford Builds on Eco-Friendly Products and Process as More Consumers Live Sustainable Lifestyles

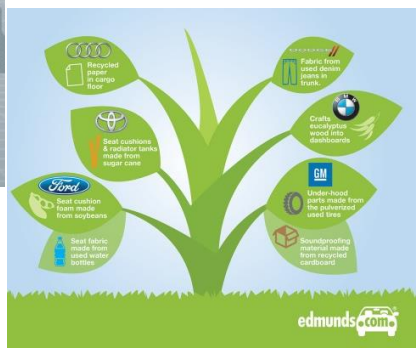
https://textontextiles.wordpress.com/2010/04/22/ford-is-making-greener-vehicles-through-increased-use-of-renewable-recyclable-materials/

Recycled materials

Automotive industry



Making Cars Greener



http://www.edmunds.com/car-technology/renewable-and-recycled-materials-help-make-cars-green.html

www.agh.edu.pl

Recycled materials

Automotive industry - tire production

Today	Sustainable Materials *Main Materials in the Concept Tire of "100% Sustainable Materials"*		
Natural Rubber from Para Rubber Tree	Expand the range of renewable resources	Conventional Natural Rubber + **Guayule**	Guayule grown in arid regions will diversify the source of natural rubber
Rayon (Reinforced Fiber)		Rayon + **New Cellulosic Fiber**	General grade pulp can produce the new fibers, resulting in more suppliability
Synthetic Rubber from Petroleum	Replace fossil resources with renewable materials	**Synthetic Rubber from Biomass**	Butadiene from bioethanol
Rubber Materials from Petroleum		**Rubber Materials from Biomass**	Curing agent and anti-aging chemical from biomass
Filler from Petroleum & Coal		**Filler from Biomass**	Reinforcing carbon black from vegetable fats and oils

http://www.bridgestone.com/corporate/news/2012092801.html

BRIDGESTONE
Your Journey, Our Passion

www.agh.edu.pl

Interdisciplinary Aspects of Materials Engineering
Materials from renewable

- Introduction - resources, raw materials and fossil fuels
- Materials obtained from nonrenewable fossil raw materials
- Biobased materials and recycled materials
- **Material life cycle, sustainable materials and carbon footprint**
- Bioplastics

Sustainable development

Sustainable development is development that meets the needs of the present without compromising the ability of future generations to meet their own needs.

Sustainable development has been described in terms of three domains: economic, environmental and social or *ecology, economy and equity*; this has been expanded to include a fourth pillar of *culture*.

Sustainable development ties together concern for the carrying capacity of natural systems with the **social, political, and economic challenges faced by humanity**.

Civilization has reached a level of prosperity possible to maintain, provided appropriate management is assured.

World Commission on Environment and Development

Sustainable materials and products

Sustainable products are those **products** that provide environmental, social and economic benefits while protecting public health and environment over their whole life cycle, from the extraction of raw materials until the final disposal.

Every material and product should be made so that it can be disassembled when its use is over, and so that all the materials of which it is made can then be returned to the Earth after composting, or endlessly recycled as raw materials.

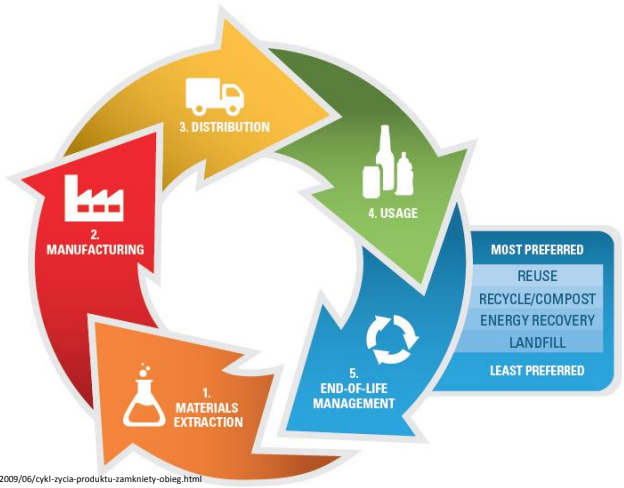
- Customer satisfaction: any products or services that do not meet customer needs will not survive in the market in a long term.
- Dual focus: ecological and social significance.
- Life-cycle orientation: constantly environmental-friendly during its entire life (there must be no permanent damage to the environment).
- Significant improvements: have to contribute to dealing with socio-ecological problems on a global level.
- Continuous improvement: should be continuously improved regarding social and environmental variation.
- Competing offers: may serve as a benchmark regarding social and ecological performance.

http://pl.wikipedia.org/

Sustainable materials and products

Life cycle

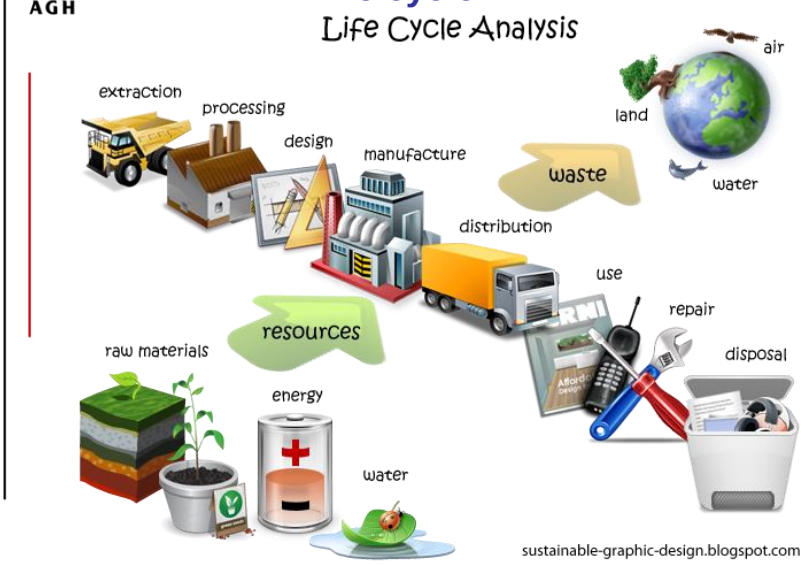
The entire lifecycle of a product from inception, through engineering design and manufacture, to service and disposal of manufactured products.



http://projekttechnologiczny.blogspot.com/2009/06/cykl-zycia-produktu-zamkniety-obieg.html

Sustainable materials and products

Life cycle

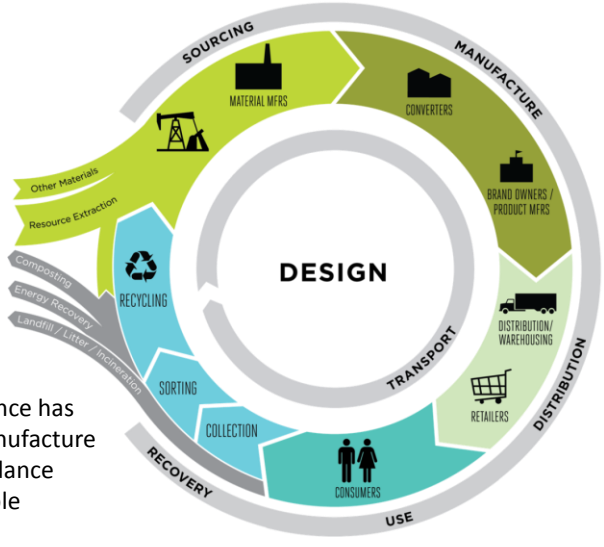


http://projekttechnologiczny.blogspot.com/2009/06/cykl-zycia-produktu-zamkniety-obieg.html

Sustainable materials and products

Life cycle of package materials

The development of knowledge in the field of environmental protection which have occurred in recent years has highlighted that the negative impact of packaging must be considered throughout their life cycle, not just in the phase of waste.

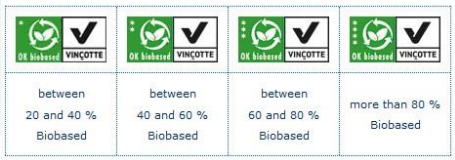


For this reason, great importance has been taken on the design, manufacture and use of packaging in accordance with the principle of sustainable development.

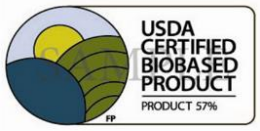
http://www.greenblue.org/

Certificates confirming that product contains materials from renewable sources

Germany



Belgium



USA

In Poland, the evaluation of packaging materials for their content of renewable raw materials was taken by COBRO and work is ongoing on the implementation of a certification system on the basis of the content of the isotope ^{14}C.

COBRO - Centralny Ośrodek Badawczo-Rozwojowy Opakowań

www.agh.edu.pl

How to distinguish if materials are from renewable or non-renewable resources?

AGH

Carbon footprint

A **carbon footprint** is historically defined as **the total set of greenhouse gas emissions** caused by an (individual, event, organization, product) expressed as carbon dioxide equivalent **CO_2e.**

A **carbon footprint** is a measure of the total amount of carbon dioxide (CO_2) and methane (CH_4) emissions of a defined population, system or activity, considering all relevant sources, sinks and storage within the spatial and temporal boundary of the population, system or activity of interest.

Carbon footprint is expressed in kg or tons of CO_2.

Different greenhouse gases to varying degrees contribute to global warming, and the emissions allows to **CO_2e** compare different gases on a common scale.
For example, a ton of methane is equivalent to 25 tonnes of CO_2e.

www.agh.edu.pl

How to distinguish if materials are from renewable or non-renewable resources?

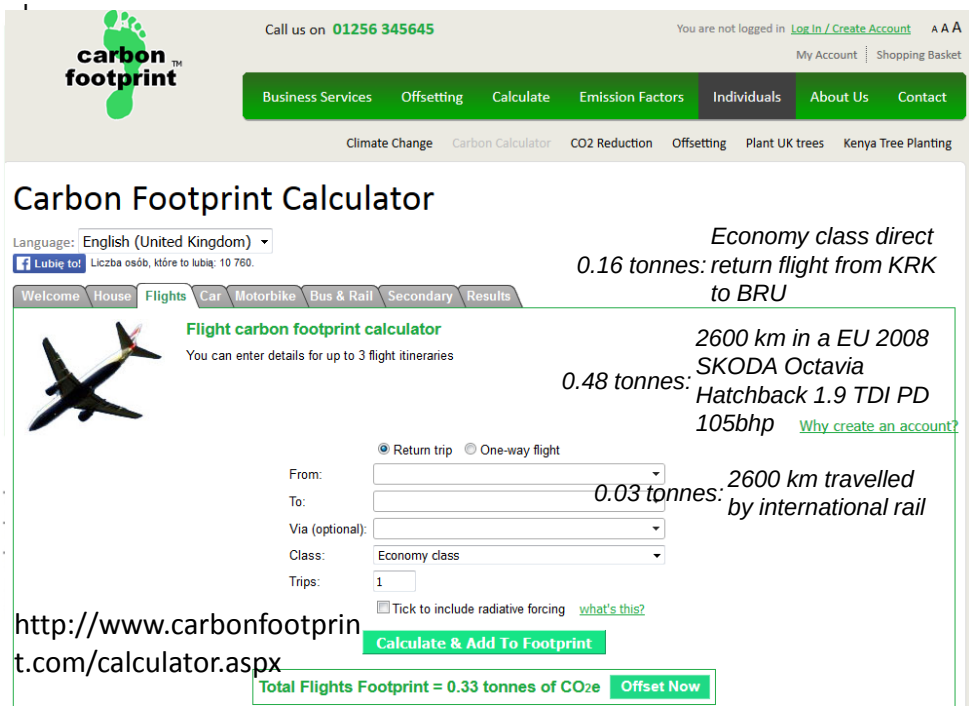
Carbon footprint

The carbon footprint of the product includes emissions from the extraction of raw materials from which it was produced, production, use and disposal or recycling after use.

Knowing what actions cause the greatest CO_2 emission, companies can adapt their technology by introducing energy-saving solutions and optimising production, transpotation, reuse, recycling, etc.

Conventional polymers produced from oil crude contain carbon formed millions of years ago. While the materials from pulp and crops (corn, sugar cane, potatoes, etc., as well as waste from the agro-food) contain a "new" carbon content derived from contemporary processes of photosynthesis.

http://www.carbonfootprint.com/calculator.aspx



0.16 tonnes: Economy class direct return flight from KRK to BRU

0.48 tonnes: 2600 km in a EU 2008 SKODA Octavia Hatchback 1.9 TDI PD 105bhp

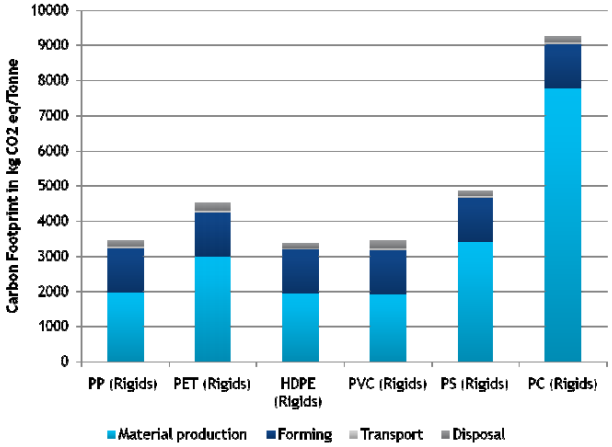
0.03 tonnes: 2600 km travelled by international rail

http://www.carbonfootprint.com/calculator.aspx

How to distinguish if materials are from renewable or non-renewable resources?

Carbon Footprint

An environmental comparison of polymers

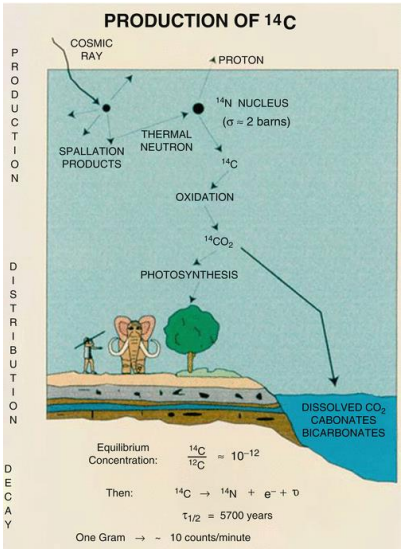


The carbon footprint of polymeric materials derived from petrochemical raw materials is different for different polymers

How to distinguish if materials are from renewable or non-renewable resources?

- In the upper atmosphere due to action of neutrons of cosmic ray ^{14}N constantly transforms in radioactive ^{14}C.
- This carbon ^{14}C spreads uniformly in the atmosphere and in the form of CO_2 enters an organic carbon cycle in a variety of metabolic processes (photosynthesis, respiration, nutrition, etc.).
- As long as the organism lives it exchanges organic matter with the environment and the level of radioactive carbon ^{14}C in its body is similar to that in the atmosphere.
- The situation changes, when the body dies - exchange of isotope ^{14}C stops and its concentration starts to decrease (half-life time for ^{14}C is 5730 years).

Radiocarbon dating

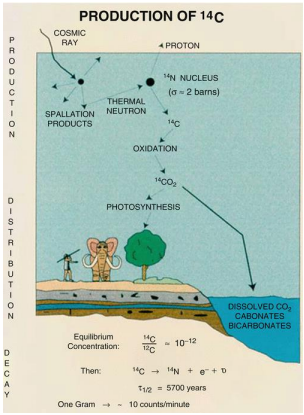


How to distinguish if materials are from renewable or non-renewable resources?

• To distinguish if polymeric materials are derived from renewable resources (biomass) it is possible to analyse the content of ^{14}C and to compare to that present in living organisms.

This method was developed by Willard Libby and his team in 1949.
In 1960. Libby received for this work the Nobel Prize in Chemistry.

Radiocarbon dating

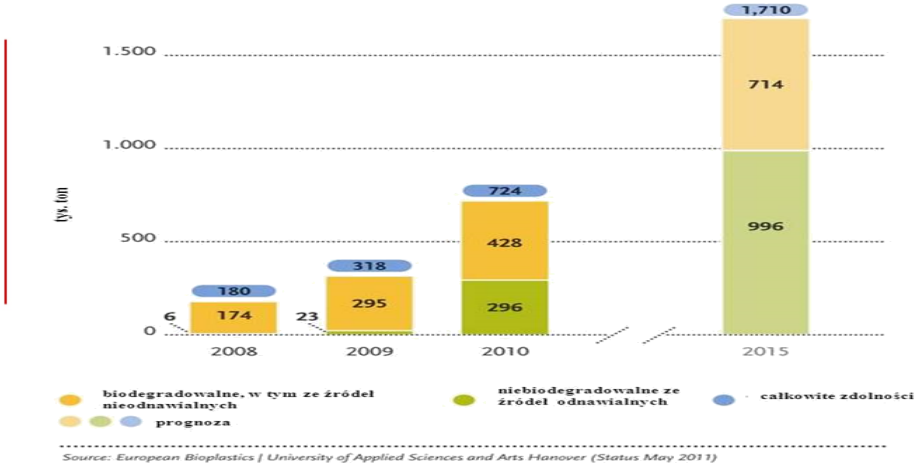


Willard Frank Libby (December 17, 1908 – September 8, 1980) was an American physical chemist noted for his role in the 1949 development of radiocarbon dating, a process which revolutionized archaeology and palaeontology.

Sustainable materials and products

Production of biobased polymers

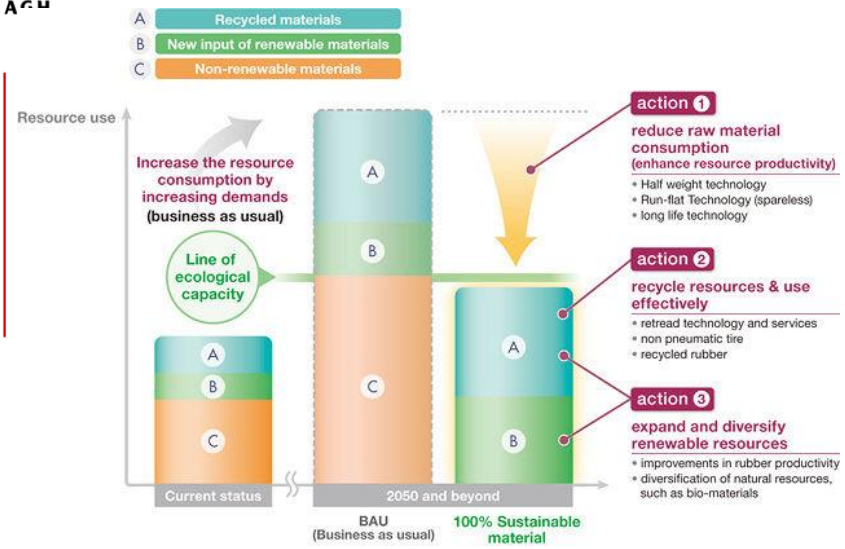
1,7 mln tonnes/year



Production of classical polymers from non-renevable resources (crude oil, gas) 265 mln tonnes/year

Sustainable materials and products

Aims and perspectives



http://www.bridgestone.com/responsibilities/environment/mission/resources.html

www.agh.edu.pl

Sustainable materials and products

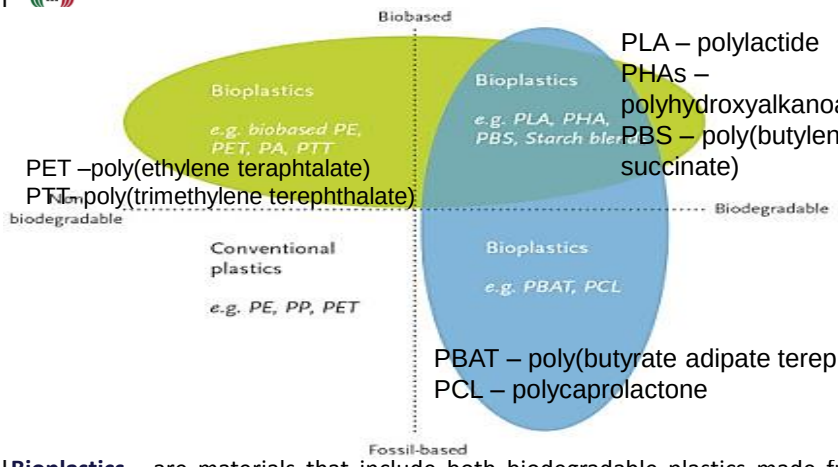
The future

www.agh.edu.pl

Interdisciplinary Aspects of Materials Engineering
Materials from renewable

- Introduction - resources, raw materials and fossil fuels
- Materials obtained from nonrenewable fossil raw materials
- Biobased materials and recycled materials
- Material life cycle, sustainable materials and carbon footprint
- **Bioplastics**

Classification of polymeric materials depending on the origin and degradability



PLA – polylactide
PHAs – polyhydroxyalkanoates
PBS – poly(butylene succinate)

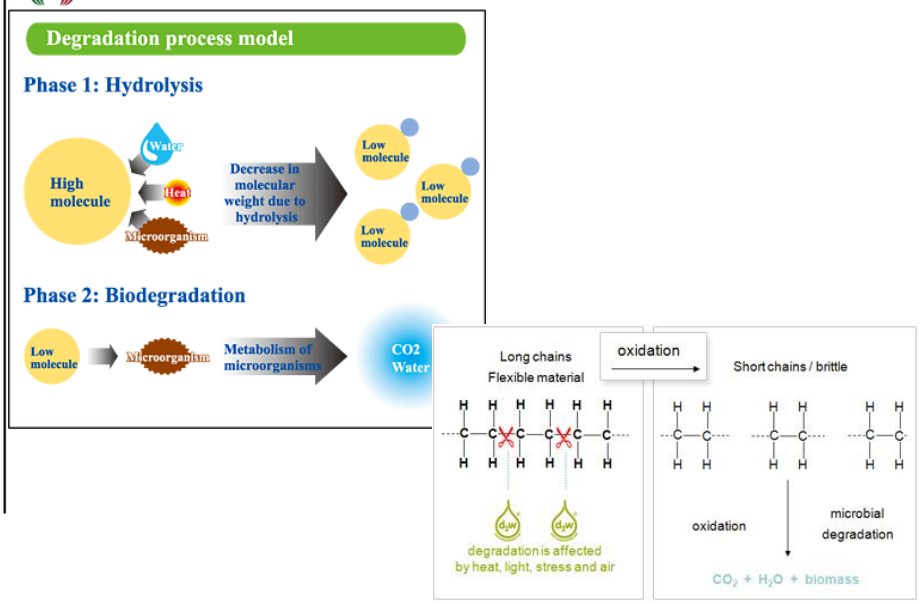
PET –poly(ethylene teraphtalate)
PTT–poly(trimethylene terephthalate)

PBAT – poly(butyrate adipate terephthalate)
PCL – polycaprolactone

Bioplastics - are materials that include both biodegradable plastics made from renewable raw materials, as well as biodegradable plastics made from renewable raw materials and biodegradable manufactured from petrochemical feedstocks (def. European Bioplastics)

http://polski-przemysl.bloog.pl/id,341585977,title,Tworzywabiodegradowalne,index.html?smoybbtticaid=613f41

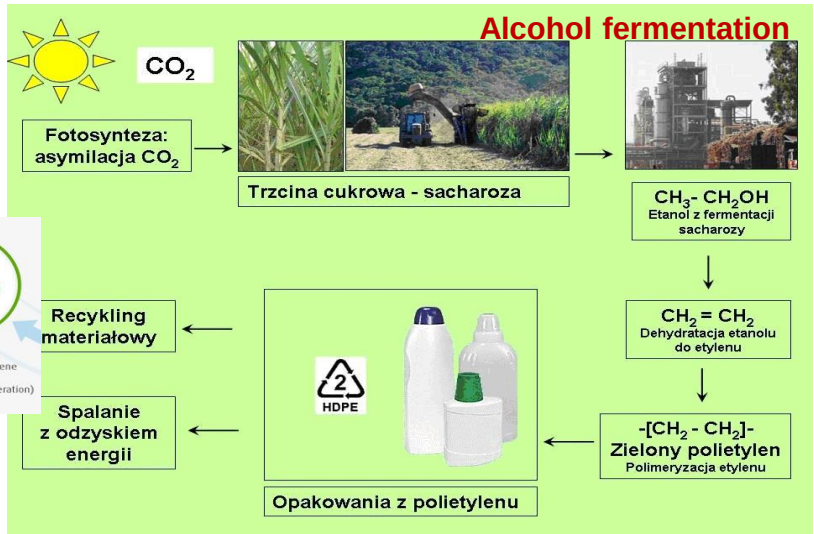
Classification of polymeric materials depending on the origin and degradability



www.agh.edu.pl

Green Polyethylene
Idea

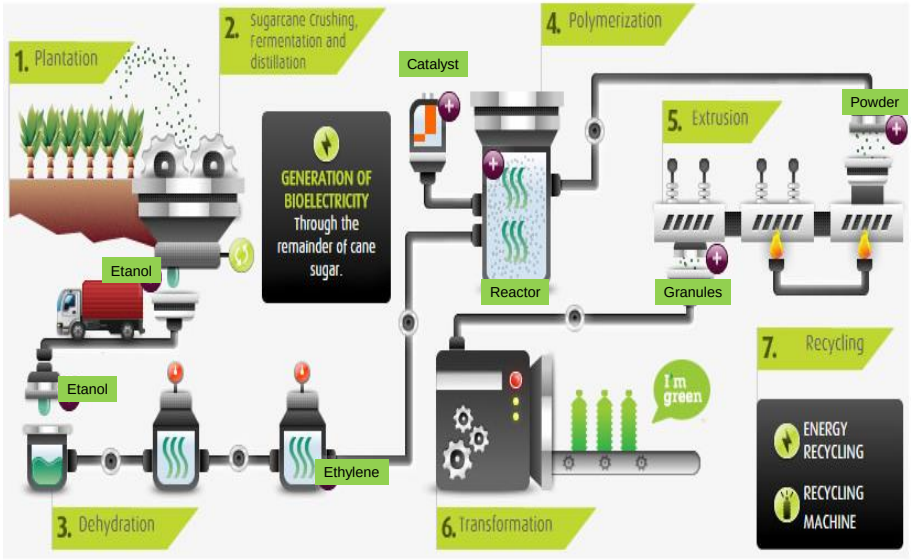
AGH



http://www.akademiaodpadowa.pl/444,a,11-alternatywne-materialy-opakowaniowe-z-surowcow-odnawialnych.htm

Green Polyethylene
Production

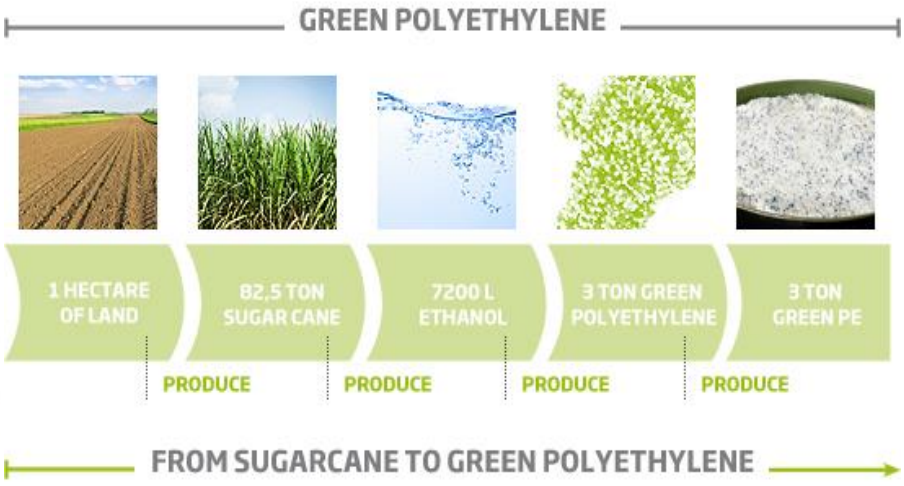
Braskem



www.agh.edu.pl

I'm green™ Polyethylene http://www.braskem.com.br/site.aspx/Where-it-is-produced

Green Polyethylene
Yield



www.agh.edu.pl

http://www.kobusch.com/en/we-innovate/rollstock/green-pe

Green Polyethylene
Advantages

- Produced from renewable resources
- recycling
- reduction of greenhouse gas emissions
- has the same properties, appearance as polyethylene from fossil raw materials
- the use of green PE does not require the use of other processing techniques

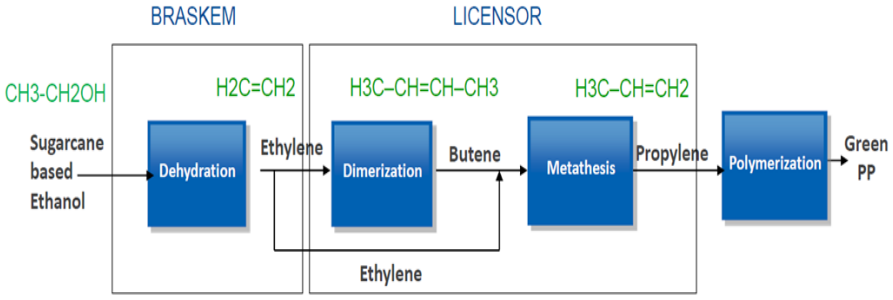
http://www.braskem.com.br/site.aspx/Where-it-is-produced

Green Polyethylene
Alternatine package material

I'm green™ Polyethylene
- HD-PE
- LLD-PE
- LD-PE

http://www.braskem.com.br/site.aspx/Where-it-is-produced

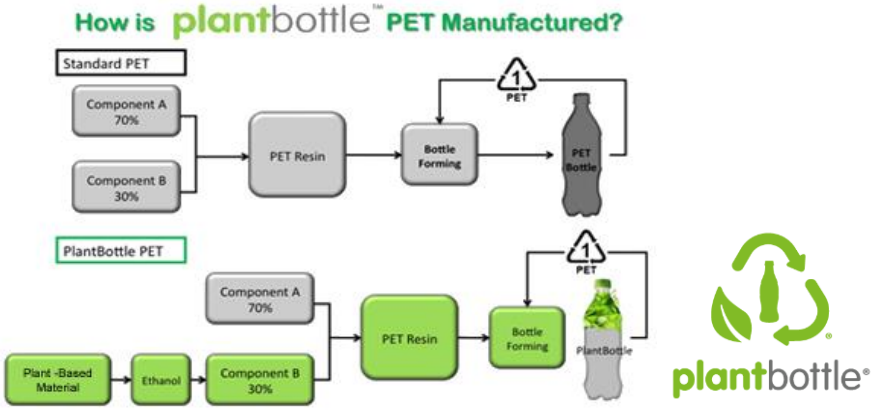
Green Polypropylene



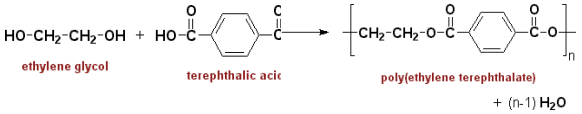
Enzymes are used in the fermentation process to convert sugars into ethanol and butene. Metathesis of ethylene and butene produces propylene monomer.

https://polymerinnovationblog.com/bio-based-polypropylene-multiple-synthetic-routes-under-investigation/

Green poly(ethylene terephtalate) PET *PlantBottle*



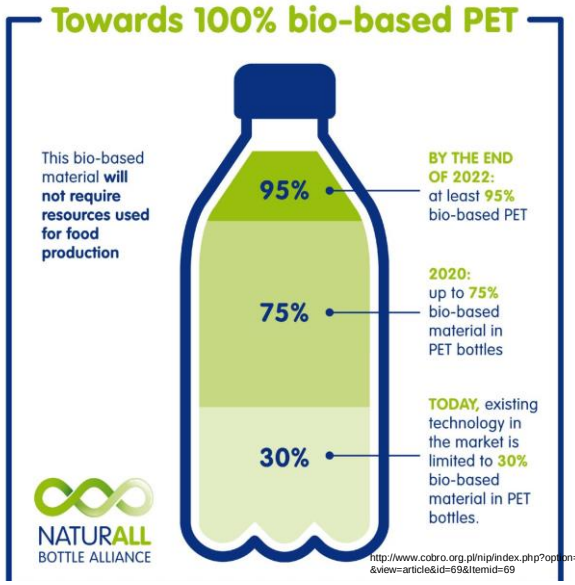
Alcohol fermentation



http://www.cobro.org.pl/nip/index.php?option=com_content&view=article&id=69&Itemid=69

Green poly(ethylene terephtalate) PET
PlantBottle

plantbottle®

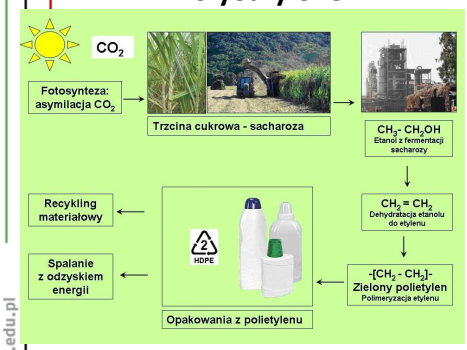


http://www.cobro.org.pl/nip/index.php?option=com_content&view=article&id=69&Itemid=69

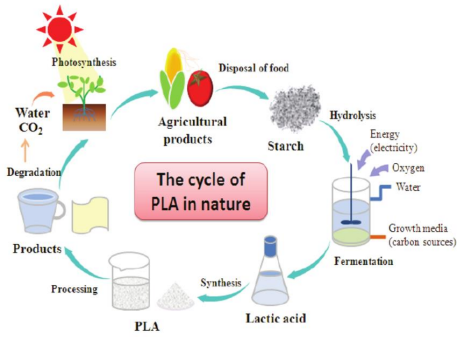
www.agh.edu.pl

Renewable resources
Biomass → processing into polymers

Polyethylene

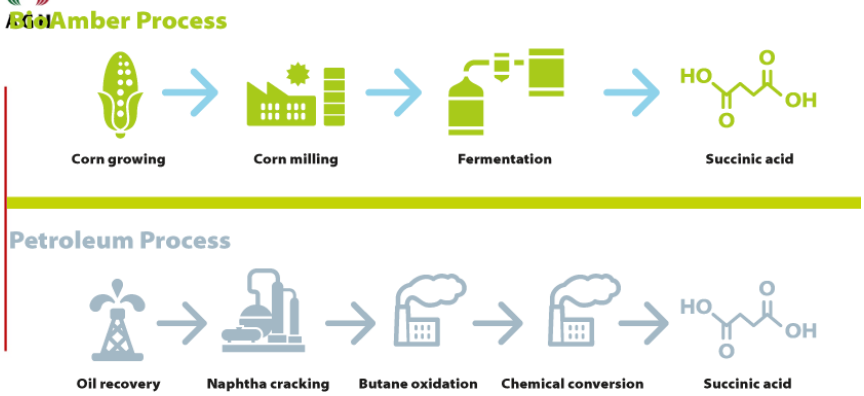


Polylactide



www.agh.edu.pl

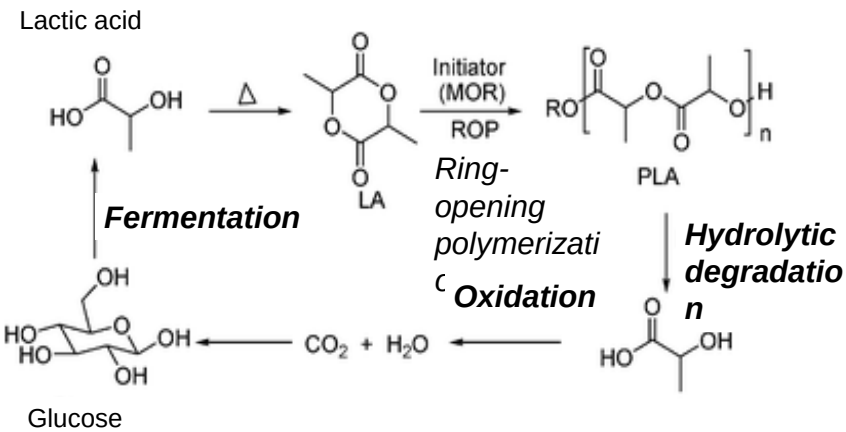
Succinic acid and its derivatives



Application (synthesis)
Polyuretanes - (butanodiol)
PBT - poly(butylene tereftalate) (butanodiol) – electrical insulator
PBS - poly(butylene succinate) – properties similar to PP; degradable packaging material

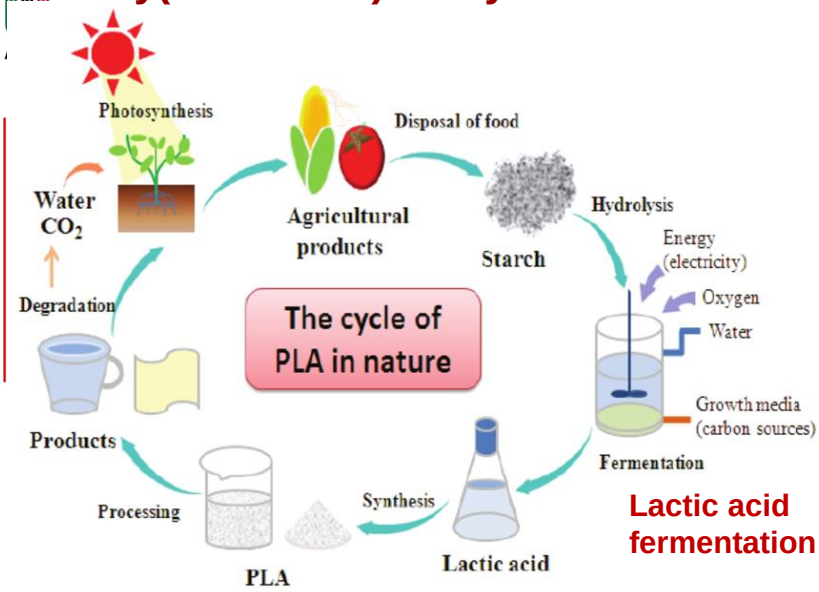
Poly(lactic acid) / Polylactide – PLA

Polylactide (polylactic acid, PLA) - a polymer belonging to the group of aliphatic polyesters. It is fully biodegradable. It is obtained from renewable natural resources such as maize.



Chem.Soc.Rev.,2010,39, 1724–1746

Poly(lactic acid) / Polylactide – PLA



Lactic acid fermentation

http://www.akademiaodpadowa.pl/444,a,11-alternatywne-materialy-opakowaniowe-z-surowcow-odnawialnych.htm

Poly(lactic acid) / Polylactide – PLA

AGH

Applications:

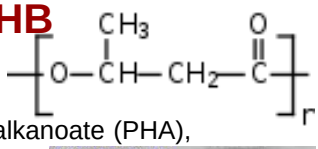
- implants (surgical sutures, screws)
- package
- foils for agriculture
- bottles
- clothings
- nonwovens
- fabrics
- disposable cutlery
- packaging cardboard

medicine

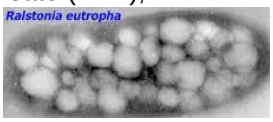
agriculture

http://www.natureworksllc.com

Polyhydroxybutyrate – PHB



Polyhydroxybutyrate (**PHB**) is a polyhydroxyalkanoate (PHA), a polymer belonging to the polyesters class



PHB is produced by bacteria (*Ralstonia eutropha*).

PHB-derived plastics are attractive because they are:
- compostable
- derived from renewables
- biodegradable

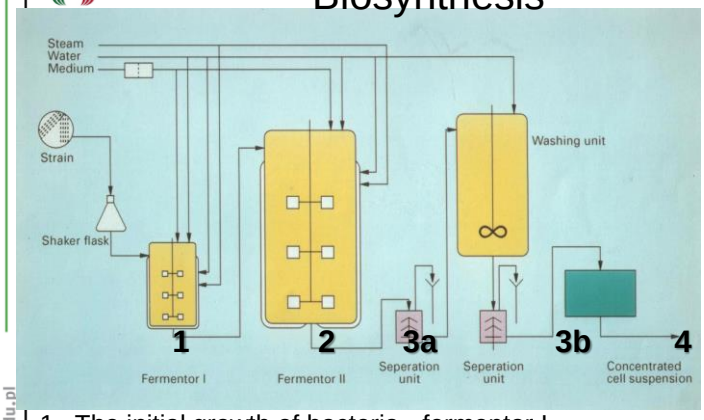
It is the first thermoplastic polymer produced by biosynthesis introduced into the market.

PHB slowly decomposes to hydroxybutyric acid and then to water and carbon dioxide under the influence of bacteria present in the soil, sewage or silt, especially in anaerobic conditions.

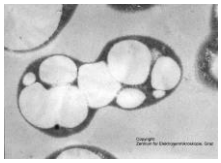
http://pl.wikipedia.org/

Production of polyhydroxybutyrate (PHB)

Biosynthesis



1. The initial growth of bacteria - fermentor I
2. Biosynthesis in a bioreactor (30°C, medium - sucrose) - fermentor II
3. Separation of bacteria from the broth
4. Concentration of bacteria suspension

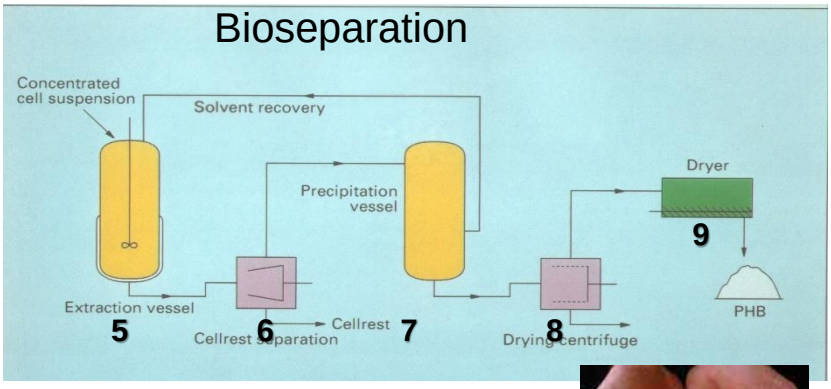


Ralstonia eutropha

Concentration of PHB in each cell of *Ralstonia eutropha* is 80%.

Yield: 100 kg PHB from 1 m^3 of broth

Production of polyhydroxybutyrate



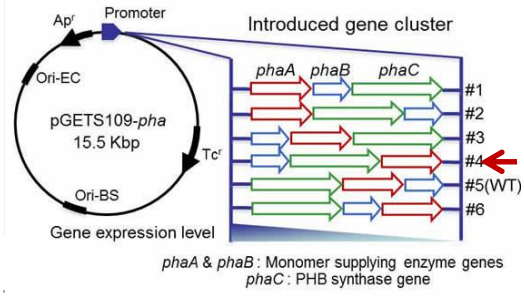
Isolation of PHB from bacteria:
5. Extraction
6. Cell separation by centrifugation
7. PHB precipitation (of purity 98%)
8. Drying
9. Granulation

PHB production

New method

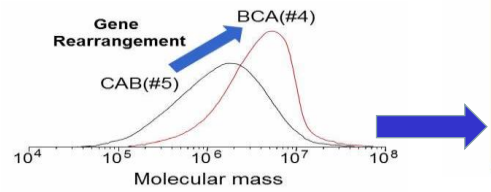
GMO

PHB - is produced in genetically modified bacteria *E. coli*



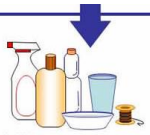
For PHB synthesis 3 genes are needed: phaA, phaB and phaC

Thanks to modification of the order of the genes used in the synthesis of PHB: sequence CAB – Wild type – (WT) – in sequence BCA PHB with high molecular mass was obtained



Application

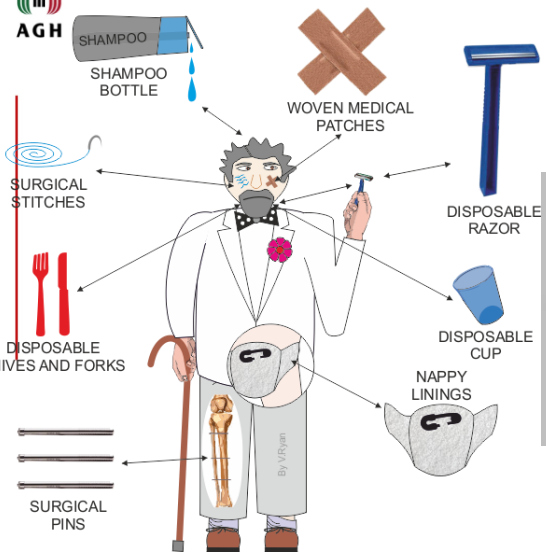
Biodegradable thermoplastics

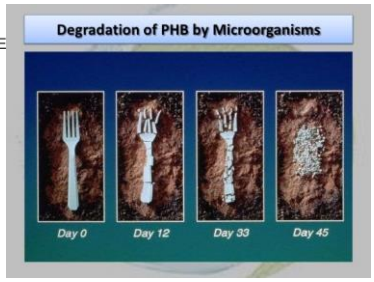


Strong fibers and films
(Mw>3,000,000)

http://www.iem.titech.ac.jp/tsuge/english.html

Application of polyhydroxybutyrate



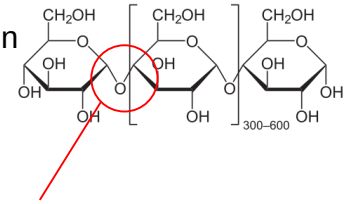


http://www.technologystudent.com/prddes1/biopola.htm

www.agh.edu.pl

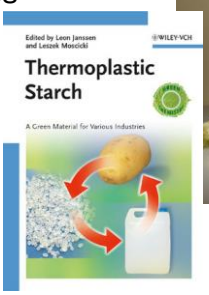
Starch

- Plant reserve material
- Stored in the forms of grains in plastids



α-glycosidic bond

Applications:
- food industry (thickener, stabilizer, emulsifier, carrier)
-paper industry
- production of adhesives
- packaging materials (thermoplastic starch)

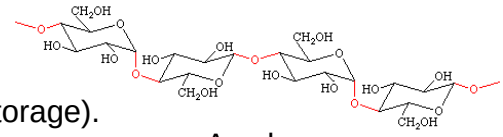


www.agh.edu.pl

Starch

Plant polysaccharide, consisting of glucose units connected by α-glycosidic bonds.

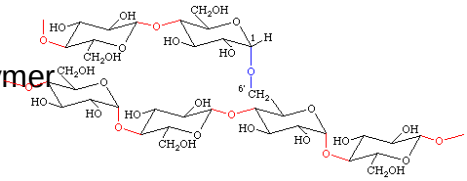
It plays the role of a backup substance in plants (energy storage).



Amylose

Starch consists of two fractions:
- **amylose** - linear polymer
- **amylopectin** - a branched polymer

The share of individual fractions differs depending on the origin.
Sources: potatoes, maize, cassava



Amylopectine

http://www.biodeg.net/biomaterial.html

Starch

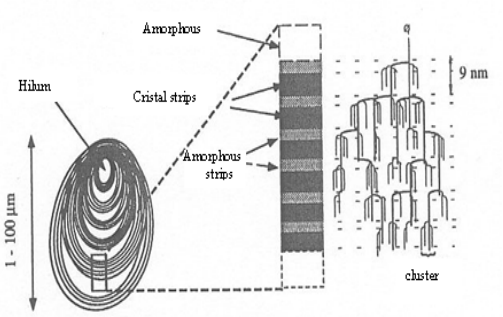
AGH

Starch occurs in the plant material in the form of grains, the size and shape of which are characteristic of individual plant species.

Starch grains have a diameter 0.5–100 μm

- Starch grains have a radial structure with alternating crystalline and amorphous regions.
- **Crystal regions** – amylopectin
- **Amorphous regions** - amylose and branches of amylopectin

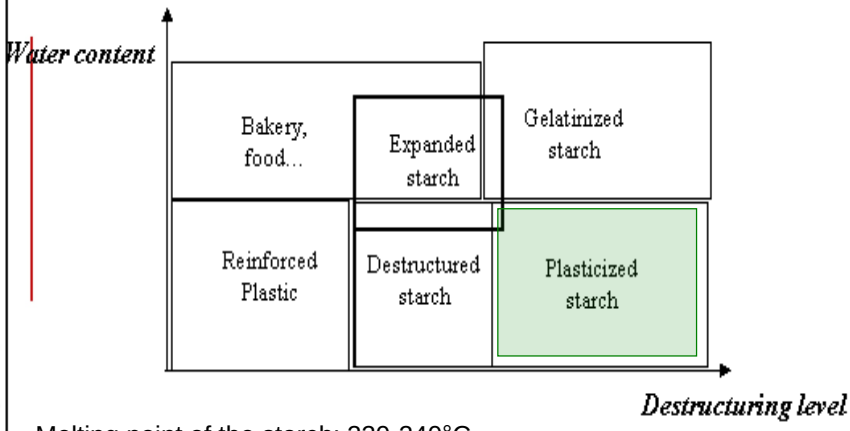
Starch grains derived from wheat



http://www.biodeg.net/biomaterial.html

Starch

Starch-based materials

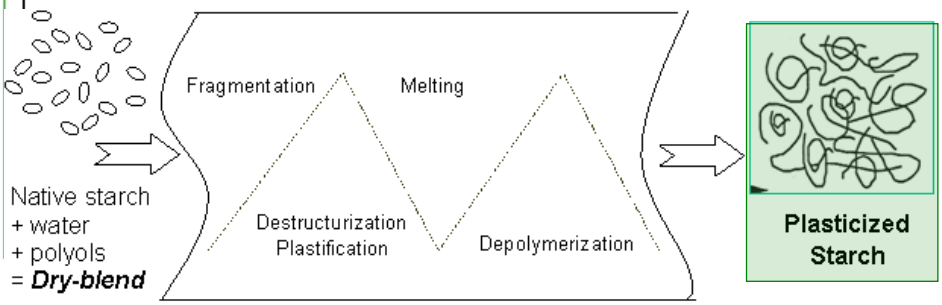


Melting point of the starch: 220-240°C
Decomposition temperature: 220°C
Presence of water and plasticizers necessary to obtain plasticised starch

http://www.biodeg.net/biomaterial.html

Starch

Processing



Thermoplastic plasticised starch (TPS) is obtained by extrusion. After mixing the starch granules with water and a plasticizer (polyol) and then extrusion, the crystal structure of the grains is destroyed - an amorphous polymer melts.

With time passing, it undergoes aging (retrogradation) due to the loss of water and ordering of the structure. http://www.biodeg.net/biomaterial.html

Starch

Application

Food stuff foils:

- odorless
- colorless
- non-toxic non-toxic
- biodegradable
- are characterized by low oxygen permeability and low humidity

- Trays for frozen food
  - for baking in ovens or processing in microwave ovens
  - similar properties as PP but lower tensile strength
  - lose their properties over time as well as in contact with food

BIONYL S TPS (thermoplastic starch)

Starch

Application

Biodegradable mulch from thermoplastic starch and polyester (PBAT), blow molded, decomposes in 90 days in contact with soil

Mulch - a protective cover of soil, placed on its surface mainly to offset the adverse effects of habitat factors.

http://bridgetrade.en.alibaba.com/product/1800313451-220600394/100_biodegradable_plastic_mulch_film.html

Starch

Application

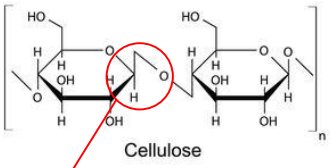
Figure 2. Products made with Mater-Bi® TPS bioplastic

Biodegradable starch-based pen

Cellulose

The main component of the cell wall of the plants.
The most widespread biopolymer on the Earth.

Linear polysaccharide built of 3,000 to 14,000 glucose molecules connected by β-1,4-glycosidic bonds



Cellulose

β-glycosidic bond

It is a raw material in the textile, paper and pharmaceutical industries, as well as in the production of explosives (nitrocellulose), varnishes and plastics.

Cotton

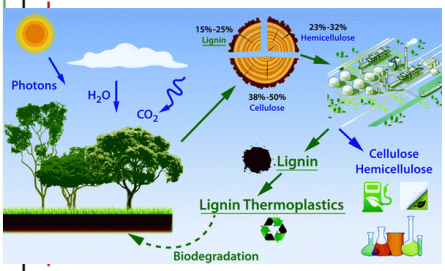
Paper

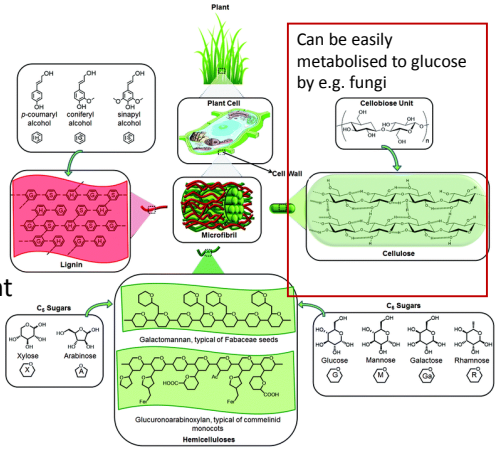
In average wood contains 45-50% cellulose

Renevable resources

Biomass → processing into polymers

Wood: lignin, cellulose, hemicellulose





Ligno-cellulose - the most abundant source of biomass
Complex raw material
Contains several fractions: lignin, cellulose, hemicellulose
Complex chemical structure – processing is a challenge

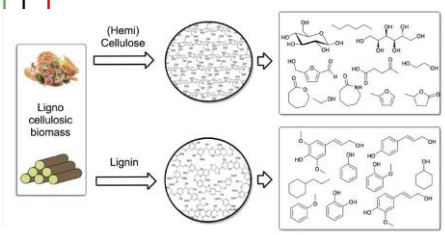
http://pubs.rsc.org/en/content/articlehtml/2015/py/c5py00263j

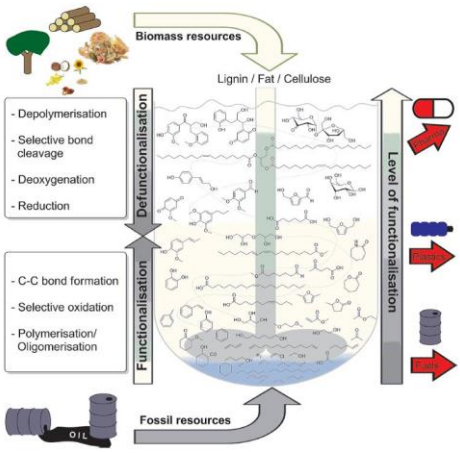
www.agh.edu.pl

Renevable resources

Biomass → processing into polymers

Wood: lignin, cellulose, hemicellulose





➢Wide range of chemicals can be obtained from wood.
➢They contain several, different chemical functionalities.
➢To process them into fuels they should be defunctionalised.
➢To produce chemicals (e.g. drugs) or polymers such high level of functionalization is beneficial.

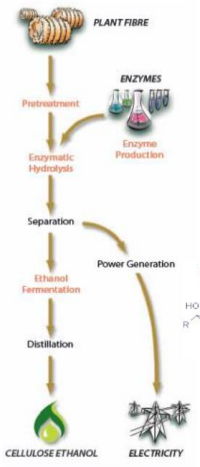
http://berc.berkeley.edu/homogeneous-catalysis-biomass-conversion/

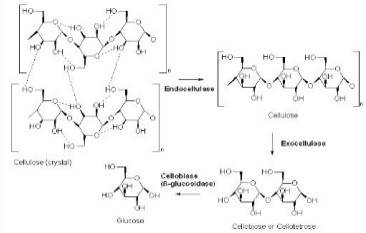
www.agh.edu.pl

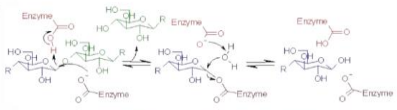
Renevable resources

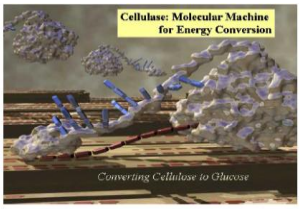
Biomass → processing into polymers

Wood: lignin, cellulose, hemicellulose









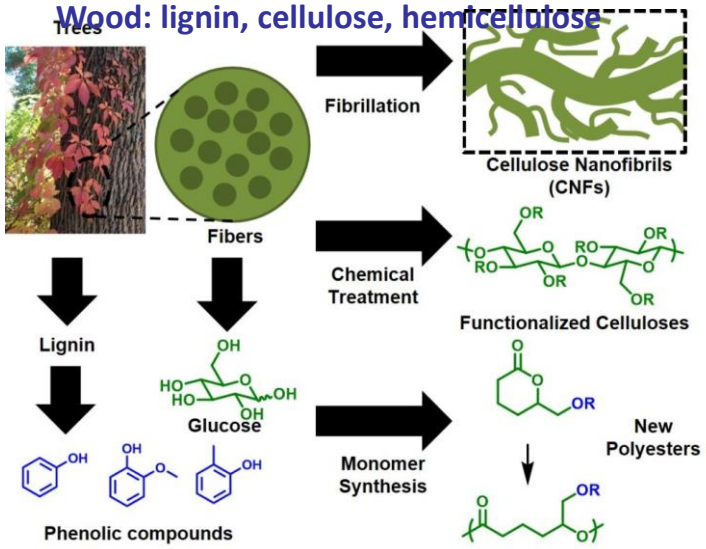
a class of enzymes produced chiefly by fungi, bacteria, and protozoans that catalyze the cellulolysis (or hydrolysis) of cellulose

Enzymes produced by fungi are used to degrade cellulose

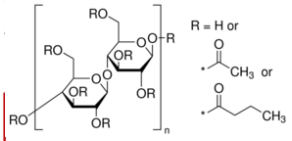
Renevable resources

Biomass → processing into polymers

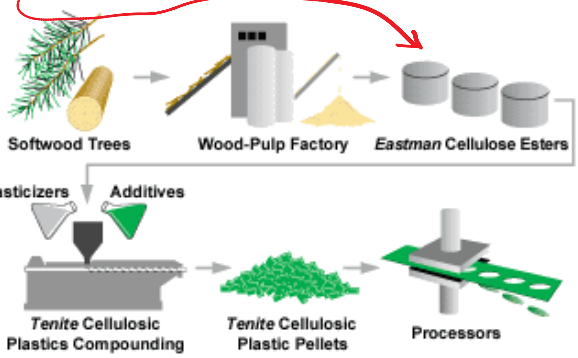
Wood: lignin, cellulose, hemicellulose



Cellulose – thermoplastic materials



Cellulose esters



5 kg wood = 1 kg cellulose plastic

http://www.mindfully.org/Plastic/Trees-Into-Plastic.htm

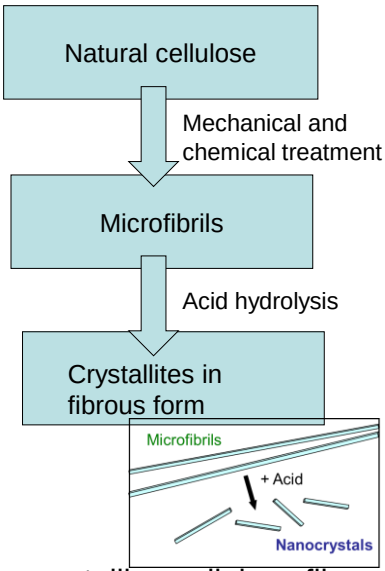
www.agh.edu.pl

Cellulose nanofibres

AGH

- Acquiring cellulose nanofibres requires (depending on the type of raw material)
  - Intensive machining
  - Chemical treatment (in the case of using wood as a substrate it is necessary to remove lignin and hemicellulose)
    - Acids (pH 2-6) decay of hemicellulose by hydrolysis
    - Bases (pH 8-10) dissolve lignin at elevated temperature

Young' modulus ~ 130 GPa
Strength ~ 60 GPa

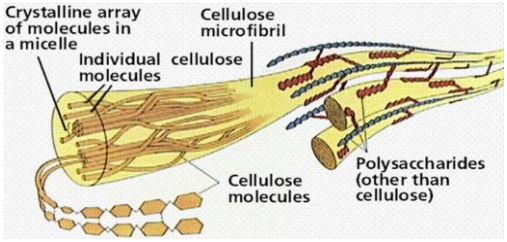


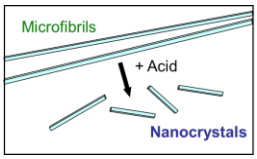
Whiskers, nanowhiskers, nanocrystals - crystalline cellulose fibers

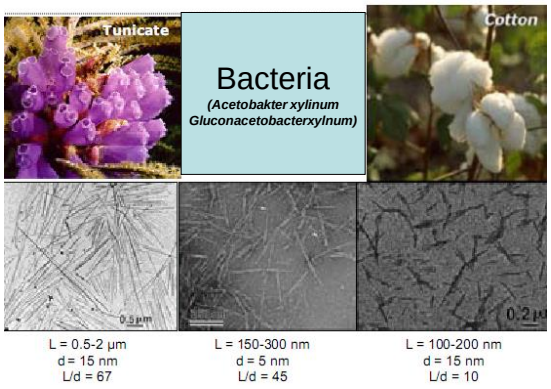
www.agh.edu.pl

Cellulose nanofibres

Nanocomposites with cellulose nanofibers in biodegradable matrices of synthetic, natural (also bacterial) origin







L = 0.5-2 µm d = 15 nm L/d = 67 | L = 150-300 nm d = 5 nm L/d = 45 | L = 100-200 nm d = 15 nm L/d = 10

Cellulose - derivatives

Material	Application
Cellulose acetate	Paints, varnishes, foils, filtration membranes
Nitrocelullose	Celluloid: first plastic, film films, everyday materials Withdrawn from production – flammable Target cotton - explosive
Metylocellulose	Thickener, lubricant, artificial saliva and artificial tears, adhesives, additive to mortars
Carboxymetylocellulose	Thickener, emulsifier, lubricant, chromatographic bed for protein separation

Materials from renewable resourcees for medicine

Collagen - structural protein, the basic component of the extracellular matrix (ECM)

Hyaluronic acid - a glycosaminoglycan (a kind of a polysaccharide) present in the extracellular matrix

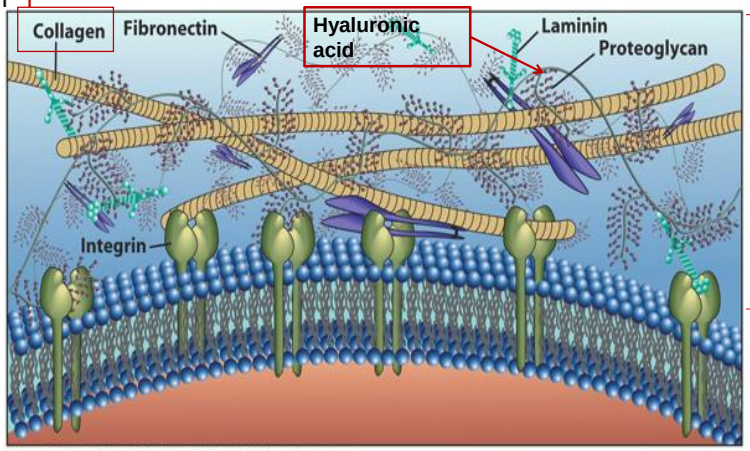


Figure 7-5 Cell and Molecular Biology, 4/e (© 2005 John Wiley & Sons)

Extracellular matrix ECM

Cell membrane

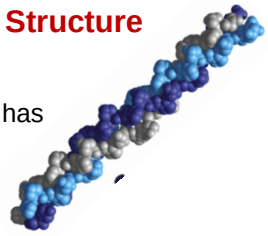
Collagen – structure

Collagen is a trimer (3 coiled α-helices)

To associate with the trimer, i.e. a functional protein has been created, post-translational processing (modification of individual amino acids) is necessar
- proline → hydroxyproline
- lysine → galactose-, hydroxy-, glucosolysine

Collagen is used in cosmetics, pharmaceuticals, as sutures, dressings, fillers and tissue reconstruction

Structure



Application of Natural Collagen on wet skin

Collagen – manufacturing
Animal derived resources

Collagen sources:

- connective tissue of slaughter animals (skin, tendons, intestines)
- fish skins, spines, bladders, strings, scales
-

Manufacturing

Mechanical desintegration of the raw material

Degreasing by soaking in hot water (fat <2%) and roasting (30 min, 100 oC)

Removal of the mineral fraction (bone) for 5 days of treatment in HCl (pH <1.5) / K_2CO_3 or Na_2CO_3

Extraction of collagen by boiling in distilled water

http://www.co-corngroup.com/products/gelatin

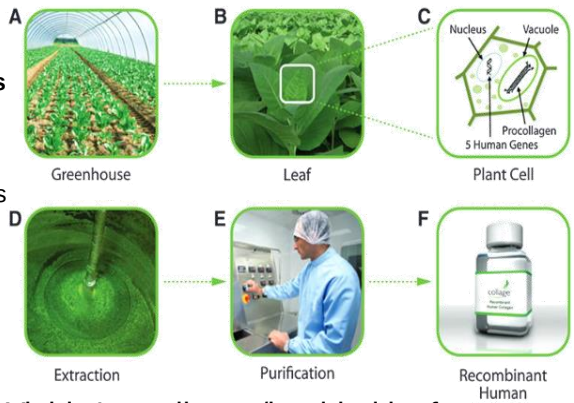
Collagen – manufacturing
Plants derived resources

Recombinant human plant-derived collagen (Plant-derived recombinant human collagen *Collage™ - CollPlant*) isolated from transgenic tobacco, enriched with 5 additional genes.

GMO

Transgenic tobacco contains 5 human genes:

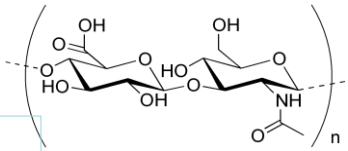
2 genes - responsible for the synthesis of polypeptide chains ***coll1, coll2***
P4Hα and **P4Hβ proline-4-hydroxylaseases** responsible for proline modification
LH3 lysine hydroxylase - a gene responsible for the modification of lysine



Yield: 1 g collagen/kg dried leafs

http://www.collplant.com/collage_brochure.pdf

Hyaluronic acid - application



Application

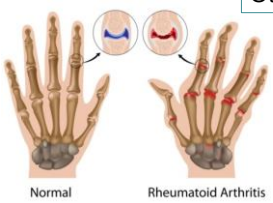
Pharmacology

Drug delivery systems

Medicine and Biomedicine

Ortohopedics
Reumatology
Ophtamology
Otolaryngology

Dermatology and plastic surgery
Wound dressing
Tissue regeneration



Production Methods for Hyaluronan - Review Article,
Carmen G. Boeriu, Jan Springer, Floor K. Kooy, Lambertus A. M. van den Broek,Gerrit Eggink,
International Journal of Carbohydrate Chemistry *2013*

www.agh.edu.pl

Hyaluronic acid - manufacturing

Manufacturing

Extraction from animal tisssues

Rooster combs, umbilical cord, bovine ointment from the joint capsule bovine lymph

Bacterial fermentation

Streptococci, Enterococcus feccalis
Agrobacterium sp.

Biocatalysis

Enzymes extracted from *Streptococcus puogenes*
Pasteurella multocida

Production Methods for Hyaluronan - Review Article,
Carmen G. Boeriu, et al.
International Journal of Carbohydrate Chemistry *2013*

www.agh.edu.pl

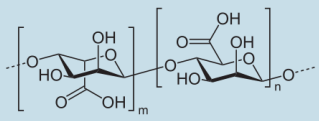
Hyaluronic acid - manufacturing

Technology	Pros	Cons
Extraction from animal tissues	Well-established – technology Simple raw materials, low cost of acquisition M_w ~20 MDa	The product requires advanced purification (low efficiency), no standard - tissue-dependent, low yields, risk of contamination with proteins, nucleic acids and zoonotic viruses
Bacterial frermentation	Advanced technology M_w ~1 – 4 MDa High yield	GMO application The risk of bacterial infections with endotoxins, proteins, nucleic acids
Enzymatic biocatalysis	The possibility of very good bioprocess parameters control M_w ~0.55 – 2.5 Mda No risk of infection A high quality product, very standarised	A very promising technology at the initial stage of development Low economic justification so far

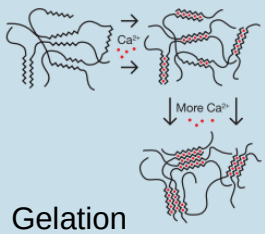
Production Methods for Hyaluronan - Review Article, Carmen G. Boeriu, et al. International Journal of Carbohydrate Chemistry *2013*

Alginates

- Component of the cell walls of many algae and seagrass
- Alginic acid is a linear copolymer composed of D mannuric and L-guluronic acid blocks
- Ability to form hydrogels crosslinked by Ca^{2+} ions



Alginic acid

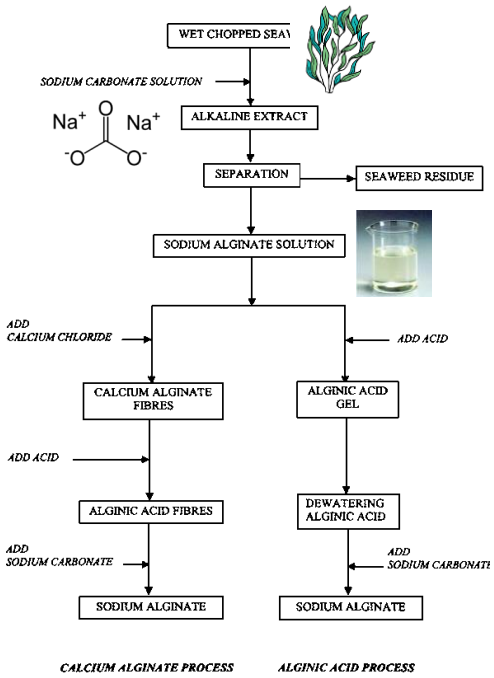


Gelation

Alginates

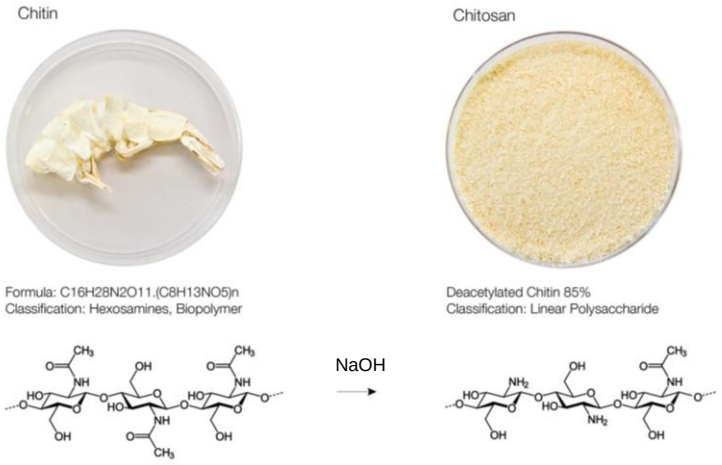
Manufacturing and application

- Thickening agent
- Food additive (E400) - emulsifier, gelling agent
- Cosmetics ingredient - shower gels, toothpastes
- Dressing material
- Rubber modifier in tire production - improves flexibility

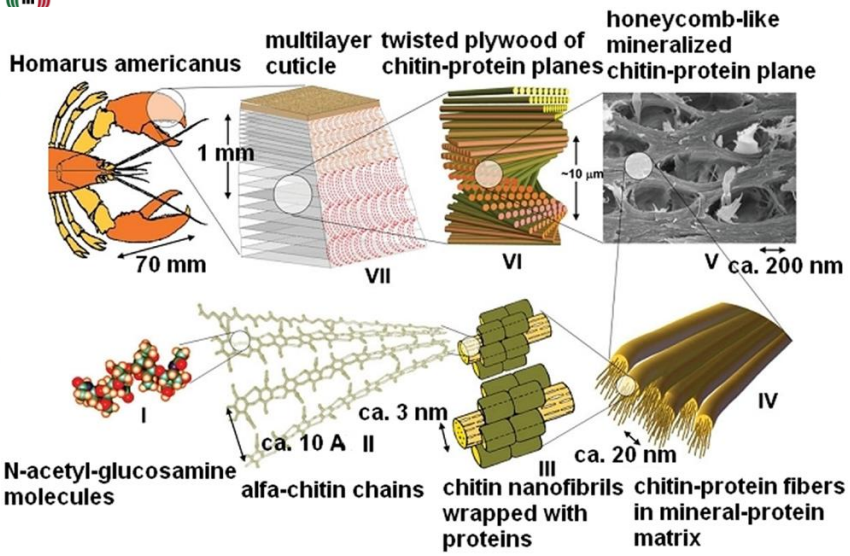


Chitin/Chitosan

Chitin - biopolymer obtained from crustaceans' shells, the second (after cellulose) the most common biopolymer
Chitosan - a product of deacetylation of chitin, soluble in acids



Chitin/Chitosan

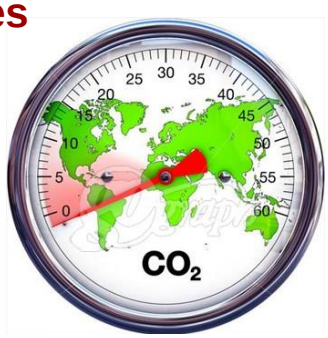


Front. Mater., 16 March 2015 | http://dx.doi.org/10.3389/fmats.2015.00020

Chitin/Chitosan - application

- Natural pesticide (induces defense reactions in plants)
- Water filtration (precipitation of pollutants)
- Varnishes (self-healing materials)
- Dressings (good blood staining and clotting properties, antibacterial)
- Drug delivery (pH-sensitive)
- Foils for food storage
- Slimming preparations

Polymers from renewable resources - advantages



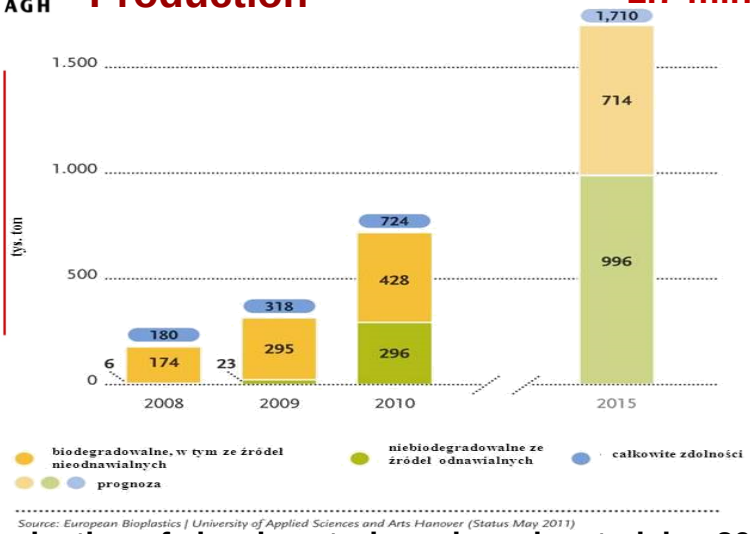
Reduction in CO_2 emission

Reduction of oil consumption

Reducing the amount of waste

Polymers from renewable resources - Production

1.7 mln tonnes



Source: European Bioplastics | University of Applied Sciences and Arts Hanover (Status May 2011)

Production of classic petroleum-based materials - 265 mln t.

Interdisciplinary Aspects of Materials Engineering
Materials from renewable

- Introduction - resources, raw materials and fossil fuels
- Materials obtained from nonrenewable fossil raw materials
- Biobased materials and recycled materials
- Material life cycle, sustainable materials and carbon footprint
- Bioplastics

Thank you!

Elżbieta Pamuła
epamula@agh.edu.pl