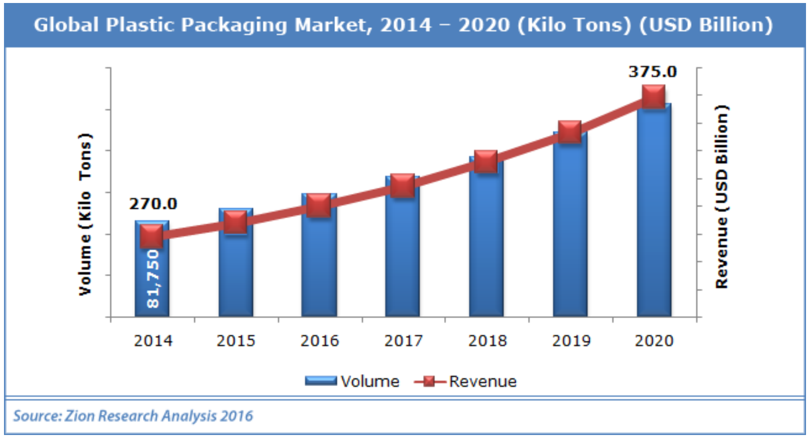
Bio-plasticizers, bio-lubricants and CARDIGAN project

GLOBAL DEMAND FOR PLASTICS AND BIOPLATICS

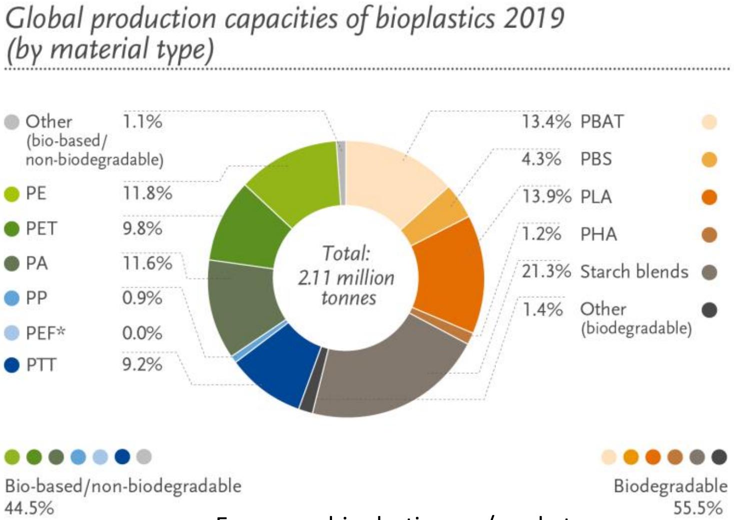
The plastic demand is continuously growing



Source: Zion Research Analysis 2016

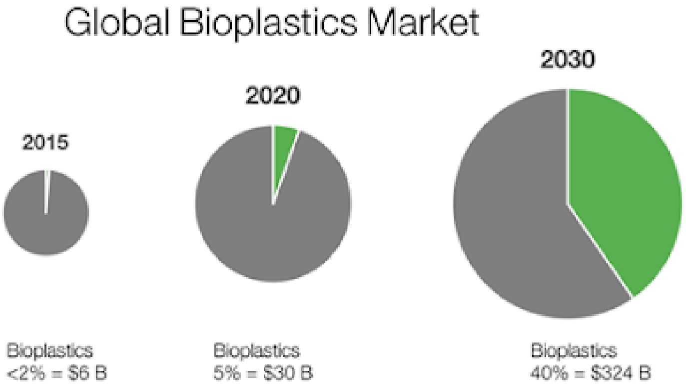
https://www.plasticstoday.com/

Only a small percentage of plastics is novaday bio-based or biodegradable



www.European-bioplastics.org/market

The global bioplastics market is expected to grow in the next decades



http://news.bio-based.eu/ 2017 prevision

GLOBAL DEMAND FOR PLASTICS AND BIOPLATICS

PETROL BASED

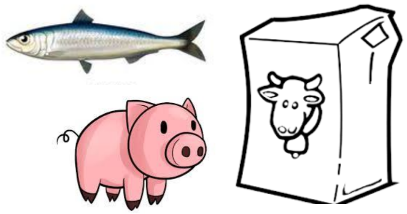
↓

PVA, PVB, PVC, NYLON

POLYSACCHARIDE-BASED

↓

STARCH, ALGINATE, CELLULOSE, CHITOSAN



PROTEIN BASED

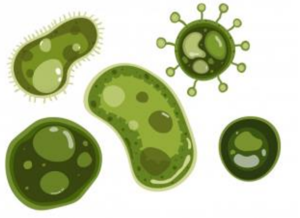
↓

FISH MINCE, B-LACTOGLOBULIN, GELATIN

NATURAL RUBBER

↓

POLYISOPROPENE



MICROBIAL DERIVED

↓

PLA, PHA

Bio-based polymers: «sustainable materials for which at least a portion of the polymer consists of materials that are produced from renewable raw materials».

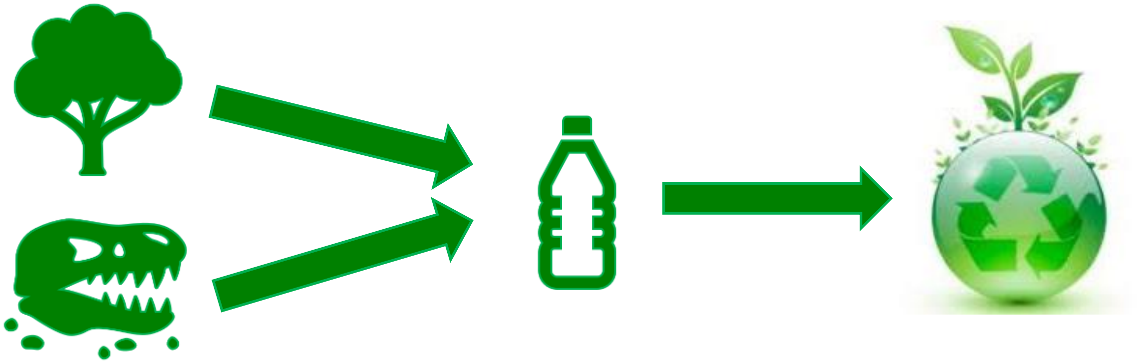
1) natural polymers, or chemically and physically modified natural polymers;
2) biobased molecules deriving from biomass feedstocks mixed to obtain biobased polymers;
3) biobased monomers synthetized in polymers.

As the plastic industry grows, the demand for plasticizers and lubricant increases.

DEFINITIONS OF PLASTICIZER AND LUBRICANTS

Plasticizer: «Substance or material incorporated in a material (usually a plastic or elastomer) to increase its flexibility, workability or distensibility» IUPAC
Bio-plasticizers are based on renewable sources and product from vegetable raw material.

Lubricants: «Substance introduced between two moving surface to reduce the friction between them and facilitate the relative motion »
All lubricants that are non-toxic and biodegradable are **bio-lubricants**.



PLASTICIZERS

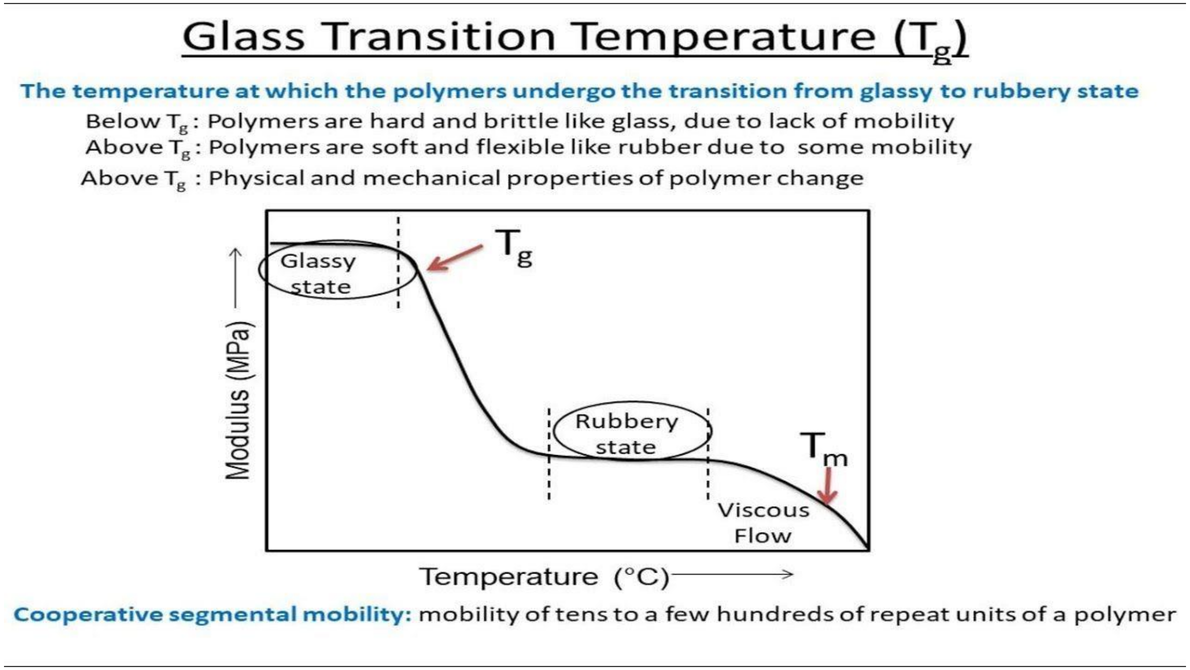
Most common plastic additives.
Low molecular weight, non-volatile substances that:

REDUCE **glass transition temperature T_g**, tension of deformation, hardness, density, viscosity, electrostatic charge

INCREASE polymer chain flexibility, resistance to fracture, dielectric constant

AFFECT degree of crystallinity, optical clarity, electric conductivity, fire behaviour and resistance to biological degradation

Do not only MODIFY the physical properties but also the processing characteristics such as viscosity and heat generation



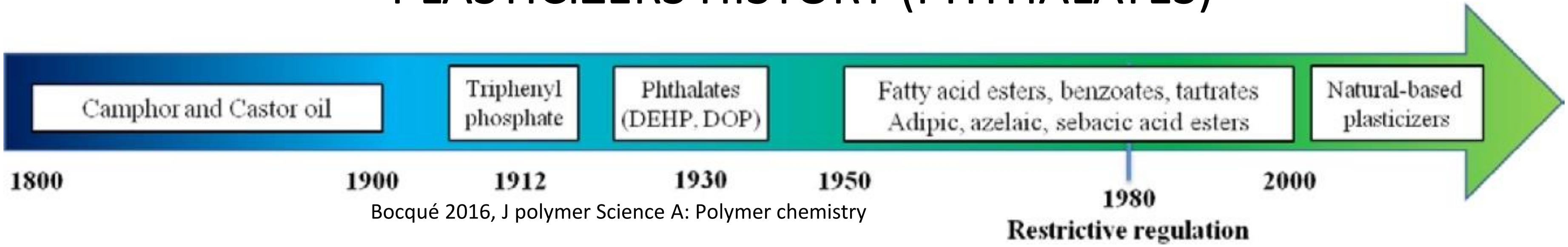
Glass Transition Temperature (T_g)

The temperature at which the polymers undergo the transition from glassy to rubbery state

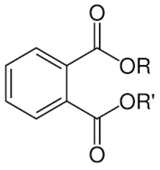
Below T_g : Polymers are hard and brittle like glass, due to lack of mobility
Above T_g : Polymers are soft and flexible like rubber due to some mobility
Above T_g : Physical and mechanical properties of polymer change

Cooperative segmental mobility: mobility of tens to a few hundreds of repeat units of a polymer

PLASTICIZERS HISTORY (PHTHALATES)

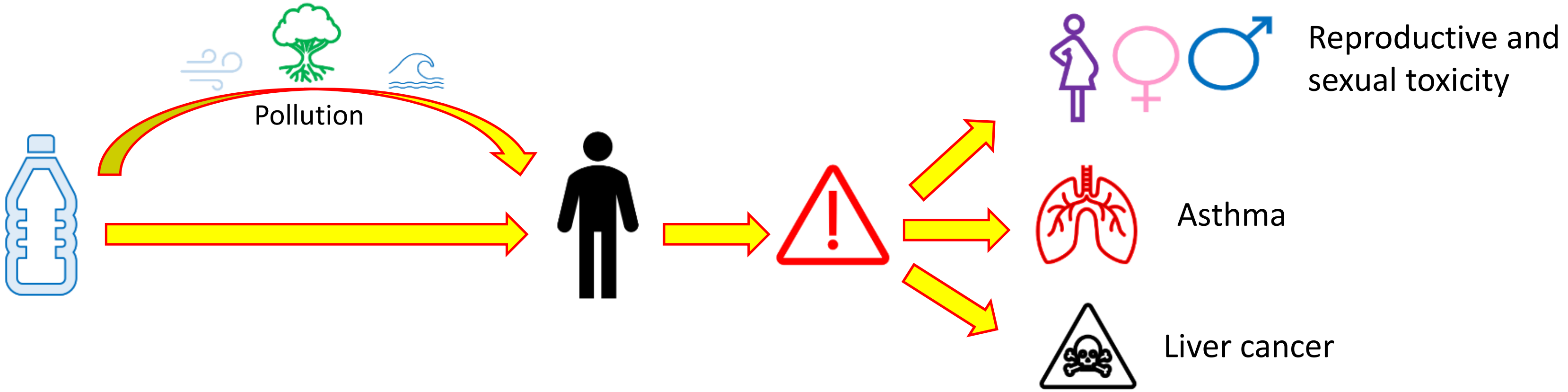


Bocqué 2016, J polymer Science A: Polymer chemistry



Phthalate

Phthalates were introduced in 1930 as plasticizers, but since 1980 there have been concerns about their effects on human health and on the environment. Diethylhexil phthalate DEHP, dibutyl phtalate, benzyl butyl phthalate, diisobutyl phthalate DIBP, di-isodecyl phthalate and di-n-octyl phtalate have been banned in Europe and USA for a content above 0.1% wt, being thus replaced with DINP or DIDP (phthalates at higher molecular weight, therefore less prone to migration). Used for PVC, PVB, PVA, cellulose and nylon.



Increasing interest in the use of natural-based plasticizers with low toxicity and low migration capacity (polysaccharides, lipids and sugars as they are or after modification)→ better if biodegradable

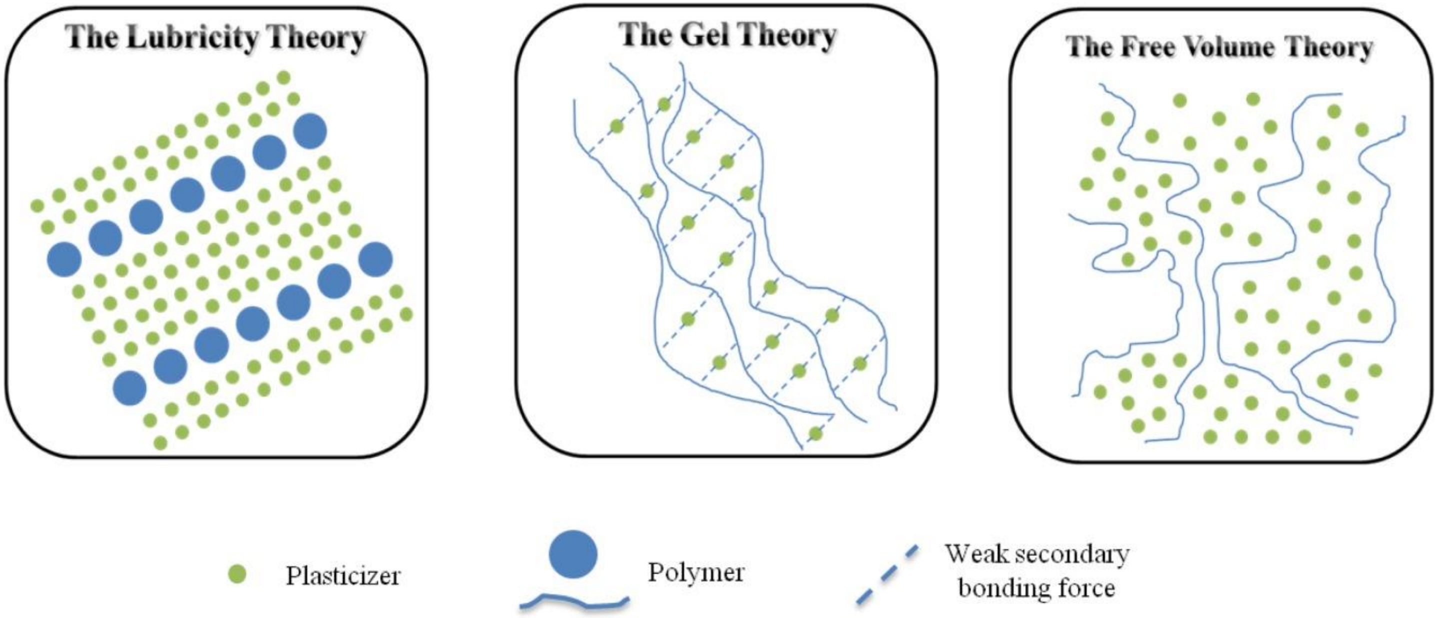
PLASTICIZERS

How do plasticizers work?

LUBRICITY THEORY: plasticizer acts as lubricants between layers of polymers

GEL THEORY: plasticizer reduces points of attachment of polymer to polymer

FREE VOLUME THEORY: plasticizer increases the free volume inside the polymer. Most accepted theory.



Bocqué 2016, J polymer Science A: Polymer chemistry

PLASTICIZERS

CLASSIFICATION

EXTERNAL
Low volatile substances, interact with the polymer chains but not with primary bonds, lost by evaporation, migration or extraction BUT most used on the market

OR

INTERNAL
Inherent parts of the polymer, primary bonds, co-polymerization or reaction with already-formed polymer

PRIMARY
Soluble in the polymer, sole or main element of the plasticizer, should not exude from the material

OR

SECONDARY
Limited compatibility with the polymer, added to primary plasticizers to improve product properties and reduce costs

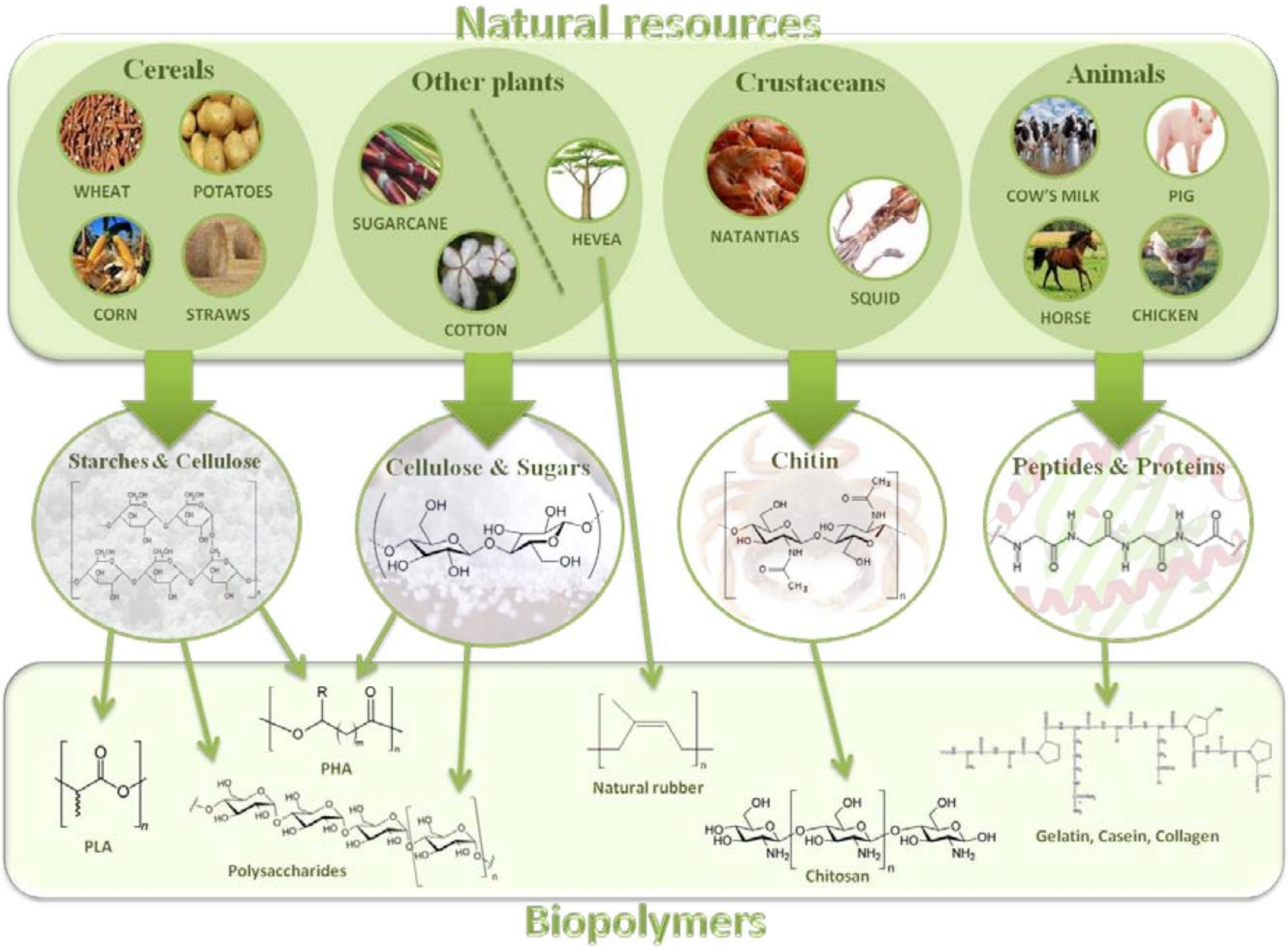
WATER SOLUBLE
Increase water diffusion

OR

WATER INSOLUBLE
Decrease water uptake

Problem of the compatibility between plasticizers and polymers.

BIOPLASTICIZERS



Bocqué 2016, J polymer Science A: Polymer chemistry

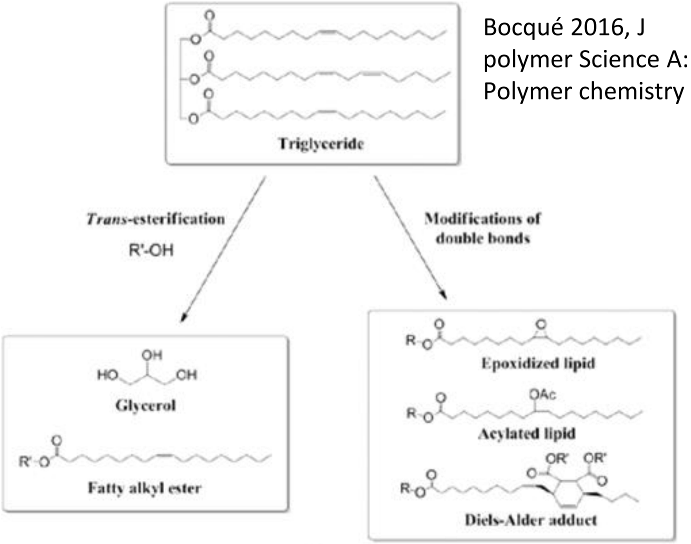
BIOPLASTICIZERS

Most natural? **Water!**

Most used: **Polyols (Glycerol, ethylene, PEG, sorbitol, mannitol), Oligosaccharides, vegetable oils.**

BIOPLASTIC	CHARACTERISTICS	PLASTICIZERS
PETRO-BASED POLYMERS (PVA, PVB, PVC, NYLON)	Inert, high transparency, facility of sterilization	Addition of phthalates, Epoxidized soybean oil (ESBO), (80% for PVC)
POLYSACCHARIDE-BASED FILMS: (STARCH, ALGINATE, CELLULOSE ESTERS, CHITOSAN, PECTINS)	Transparent, resistant to oils and fats but low water vapor resistance	Addition of Glycerol, sorbitol, triacetin, vegetable oils, fatty acids, poly ethylen oxide (PEO), citrates, polyadipates, polysuccinates
PROTEIN OR LIPID-BASED FILMS (ZEIN, FISH MINCE FROM SARDINES, B-LACTOGLOBULIN, SUNFLOWER PROTEIN, PIG-SKIN GELATINE)		Addition of Oleic and linoleic acid, Glycerol, PEG, polyols, PEO
NATURAL RUBBER		Modified with lipidic derivatives, mainly epoxidized soybean oil, linseed oil, coconut oil, castor oil, sunflower oil and esterified fatty acids
MICROBIAL-DERIVED FILMS: POLYESTERS PLA, PHA (PHB)	PLA excellent optical properties and tensile strength (derives from starch)	Addition of soybean oil, ESBO, fatty acids, Glycerol

Bioplasticizers



Bocqué 2016, J polymer Science A: Polymer chemistry

VEGETABLE OILS

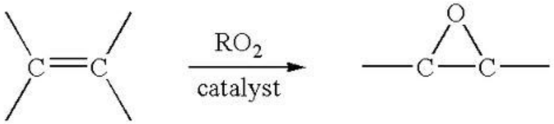
From vegetable oils: biodegradable and low toxic. Glycerol+ fatty acids. Via trans-esterification it is possible to change TG chains obtaining oils with different characteristics.

Epoxidation of vegetable oils (olive, corn, cottonseed, palm, sunflower)

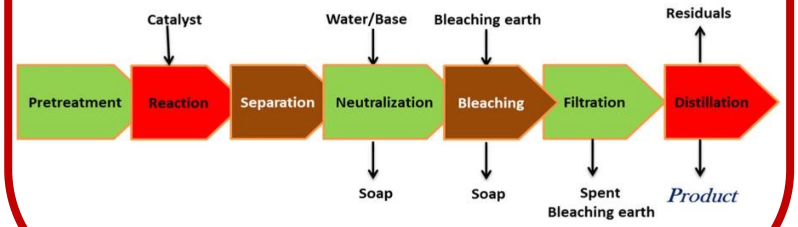
Acetylation after ring-opening of the epoxidized vegetable oils leads to plasticizers with properties similar to phthalates.

TOO EXPENSIVE

CHEMICAL PROCESS

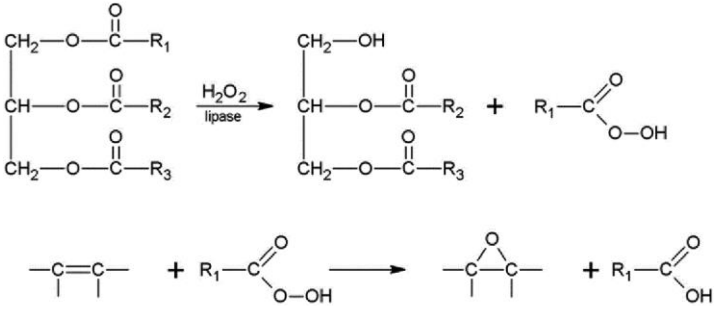


Reduction in epoxides selectiveness that results in **ring opening, instability** and **explosiveness** of peroxy acids, **corrosion** problems due to acidic byproducts, **conversion < 80%, high T.**


Catalyst
Water/Base
Bleaching earth
Residuals
Pretreatment
Reaction
Separation
Neutralization
Bleaching
Filtration
Distillation
Soap
Soap
Spent Bleaching earth
Product

Hosney 2018, J apll polymer

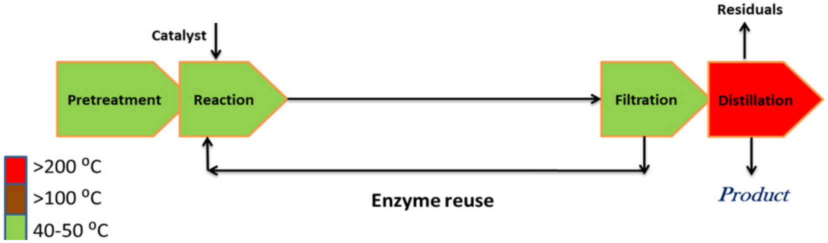
CHEMOENZYMATIC PROCESS



Way 2019, RSC Advanced

Low T, neutral pH, reusability enzyme

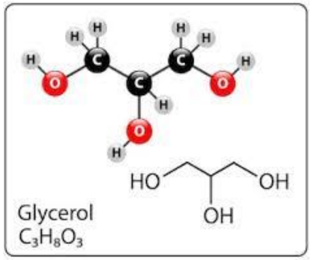
Ex: Oleic acid and linoleic acid with *Candida antarctica* lipase, Soybean oil with Novozyme 435.


Catalyst
Residuals
Pretreatment
Reaction
Filtration
Distillation
Enzyme reuse
Product

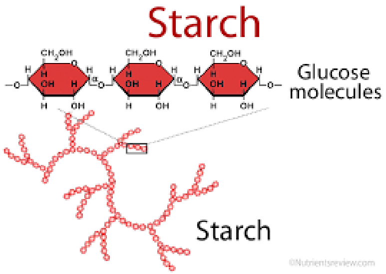
🟥 >200 °C
🟫 >100 °C
🟩 40-50 °C

GLYCEROL

Glycerol: used in plasticization of edible and biodegradable films (FDA approved). Together with starch gives «**thermoplastic starch**».



+



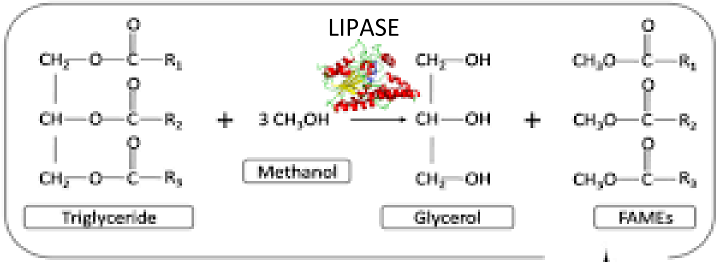
http://www.nutrientsreview.com/

THERMOPLASTIC STARCH

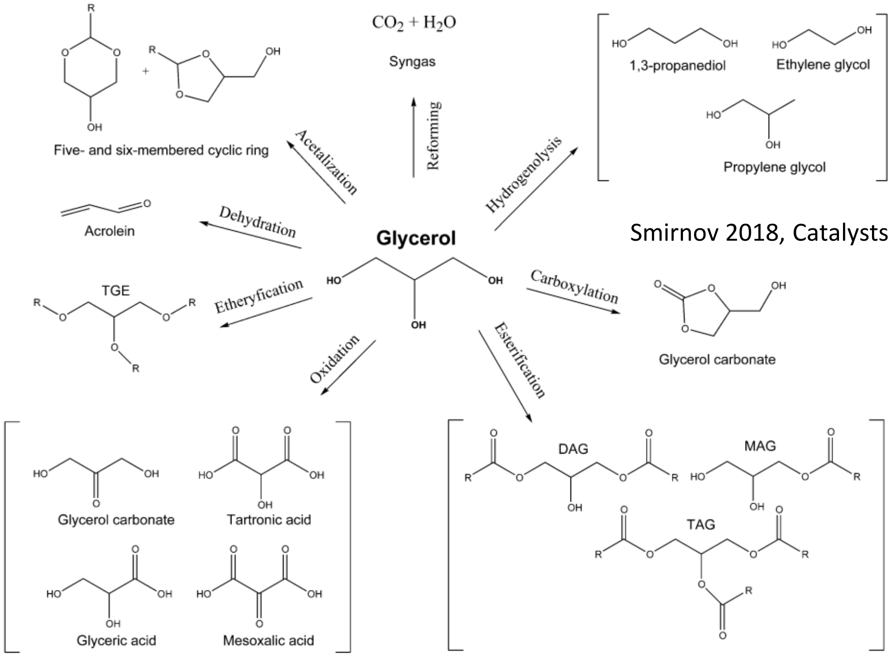
https://www.ecoproducts.com/

Glycerol is a by-product in biofuel production (chemo or enzymatic). It can be modified to obtain fuel additives that increase viscosity and stability to oxidation.

ENZYMATIC PRODUCTION OF BIOFUEL AND GLYCEROL



Cesarini 2015, Sustainibility

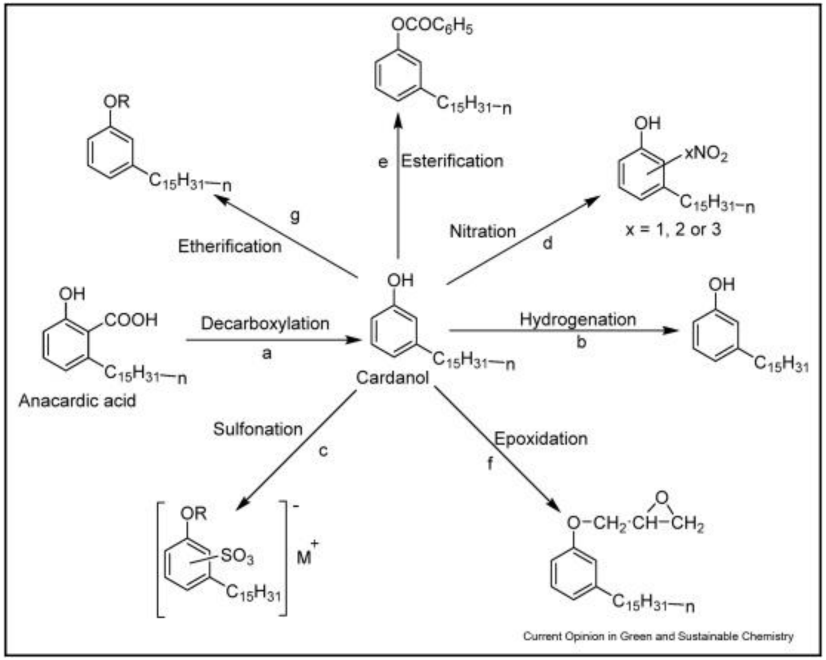


Smirnov 2018, Catalysts

CARDANOL

Cardanol: obtained by distillation of cashew nutt shell liquid

Caillol 2018, Curr Opin Green Sust Chem



Caillol 2018, Curr Opin Green Sust Chem

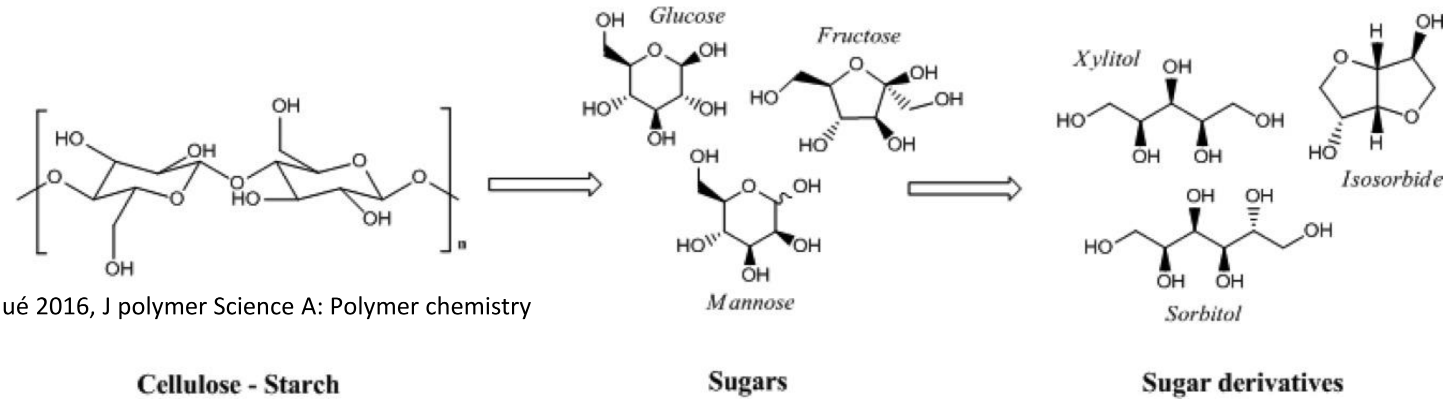
ENZYMATIC PRODUCTION OF CARDANOL BIOPLASTICIZERS

LIPASES → **EPOXIDATION**

PEROXIDASES → **POLYMERIZATION**

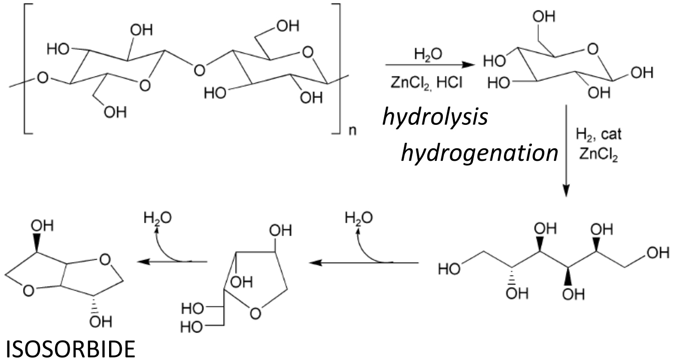
STARCH AND CELLULOSE

From hydrolysis of starch and cellulose it is possible to obtain polyols such as sugar alcohols and isosorbide esters (diols derived from glucose) used as plasticizers for PVC.



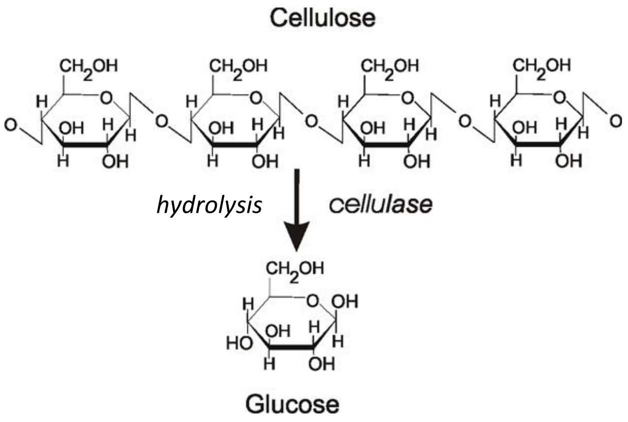
Bocqué 2016, J polymer Science A: Polymer chemistry

CHEMICAL PROCESS



Menegassi de Almeida 2010, ChemSusChem

ENZYMATIC PRODUCTION OF GLUCOSE

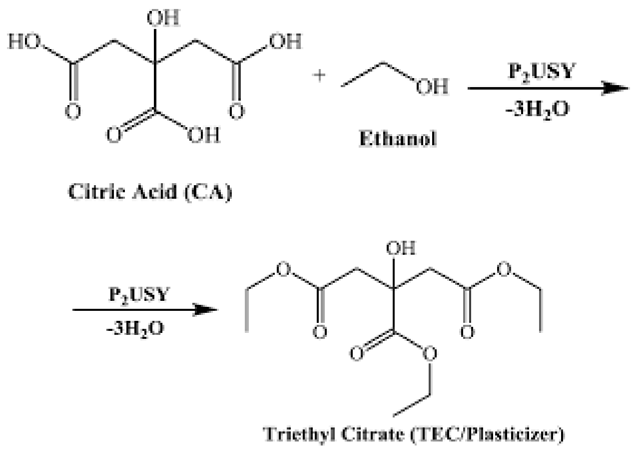


CITRIC ACID

After esterification of citric acid (extracted from citrus fruit, sugarcane and beetroots), it is possible to obtain tri or tetra-esters that are used as plasticizers for PVC for medical products and toys (FDA approved as food additives).

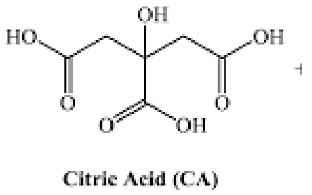
TOO EXPENSIVE

CHEMICAL PROCESS



Fattahi 2019, Catalysts

ENZYMATIC PROCESS

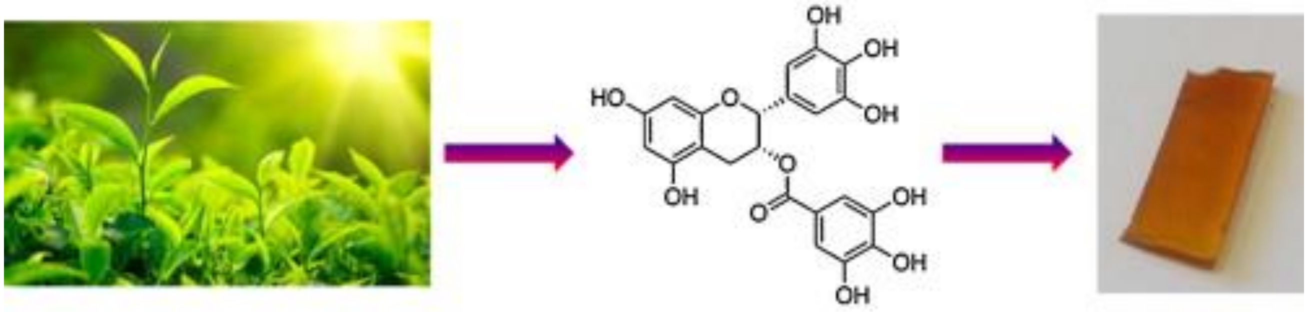


LIPASE

CITRIC ACID ESTERS

BIO-BASED WASTE PLASTICIZERS

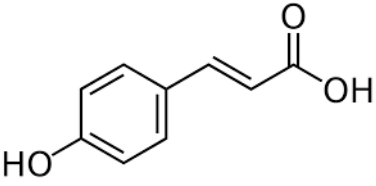
Tannins behave as super-plasticizers. Phenols such as tannic acid are used as plasticizers in protein materials.



Benyahya 2014, Ind Crops Products

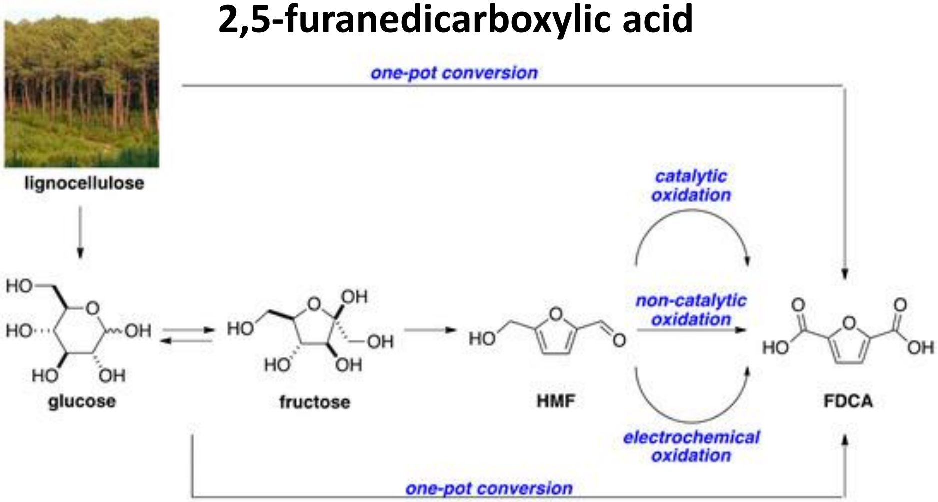
FUTURE CANDIDATES

p-coumarate



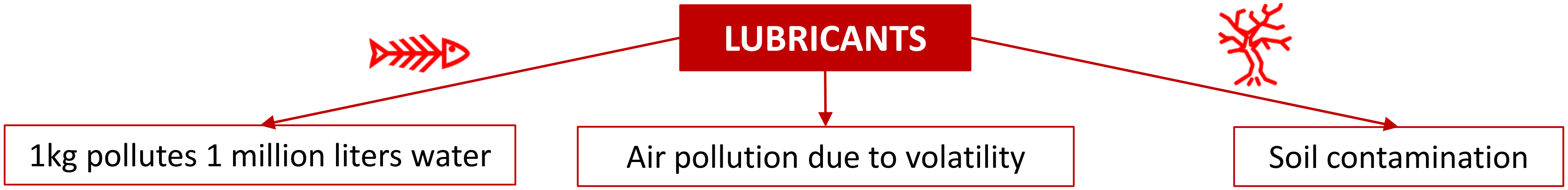
p-coumaric acid

2,5-furanedicarboxylic acid



Zhao 2019, Molecules

BIO-LUBRICANTS



LUBRICANTS

- 1kg pollutes 1 million liters water
- Air pollution due to volatility
- Soil contamination

BIOLUBRICANTS are **renewable, biodegradable and non-toxic** industrial fluids from oils and fats for non-edible purpose, with minimal impact on human health/environment. They are used in INDUSTRIAL and BIOMEDICAL applications.

Functions:

- minimize friction
- facilitate motion
- remove heat
- prevent corrosion
- power transfer
- remove particles

Requisites:

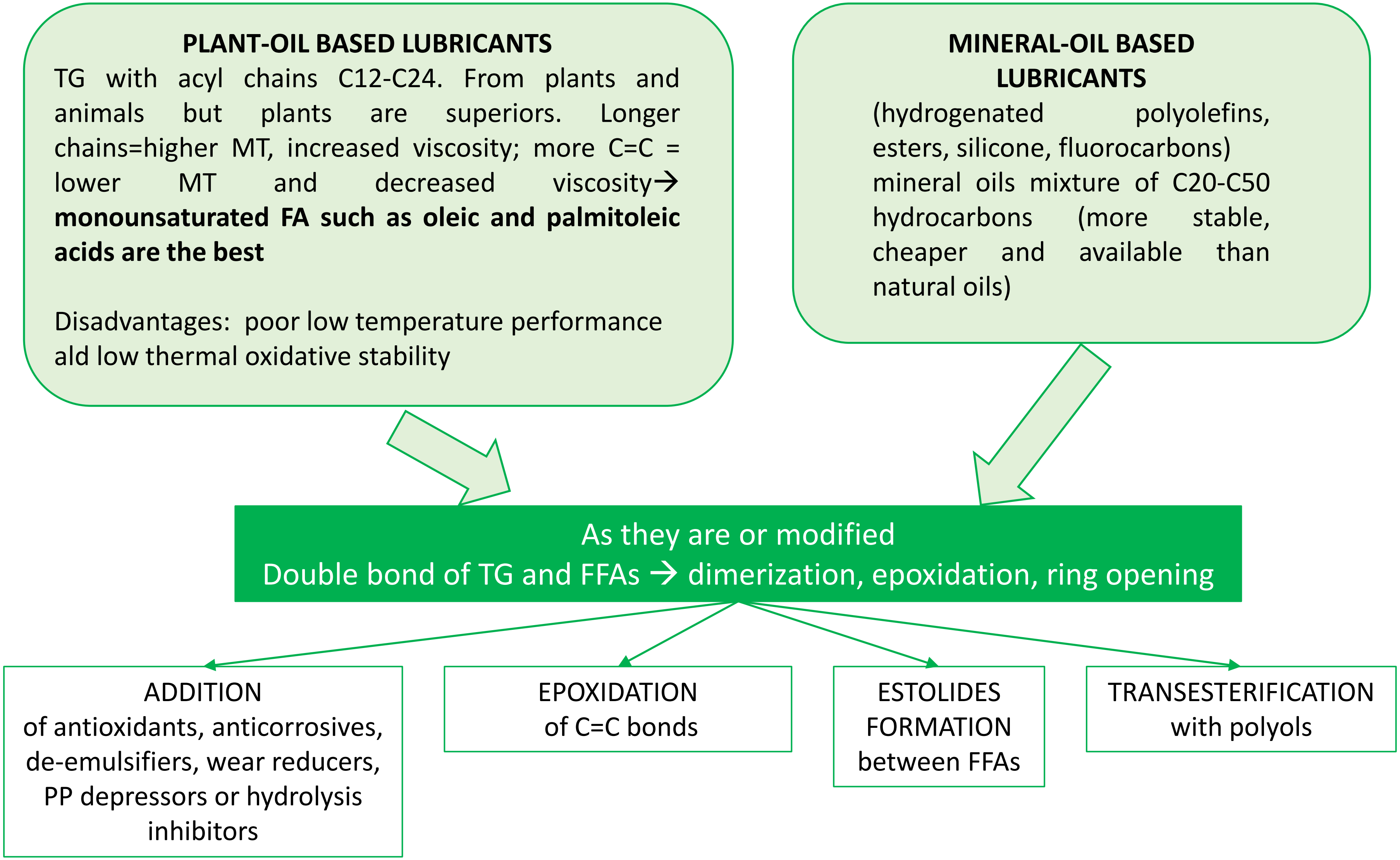
- Low Pour Point PP
- High flash point (safe and non-volatile)

PLANT-OIL BASED LUBRICANTS

MINERAL-OIL BASED LUBRICANTS

WASTE COOKING-OIL BASED LUBRICANTS

BIO-LUBRICANTS



PLANT-OIL BASED LUBRICANTS

TG with acyl chains C12-C24. From plants and animals but plants are superiors. Longer chains=higher MT, increased viscosity; more C=C = lower MT and decreased viscosity→ **monounsaturated FA such as oleic and palmitoleic acids are the best**

Disadvantages: poor low temperature performance ald low thermal oxidative stability

MINERAL-OIL BASED LUBRICANTS

(hydrogenated polyolefins, esters, silicone, fluorocarbons) mineral oils mixture of C20-C50 hydrocarbons (more stable, cheaper and available than natural oils)

As they are or modified
Double bond of TG and FFAs → dimerization, epoxidation, ring opening

ADDITION
of antioxidants, anticorrosives, de-emulsifiers, wear reducers, PP depressors or hydrolysis inhibitors

EPOXIDATION
of C=C bonds

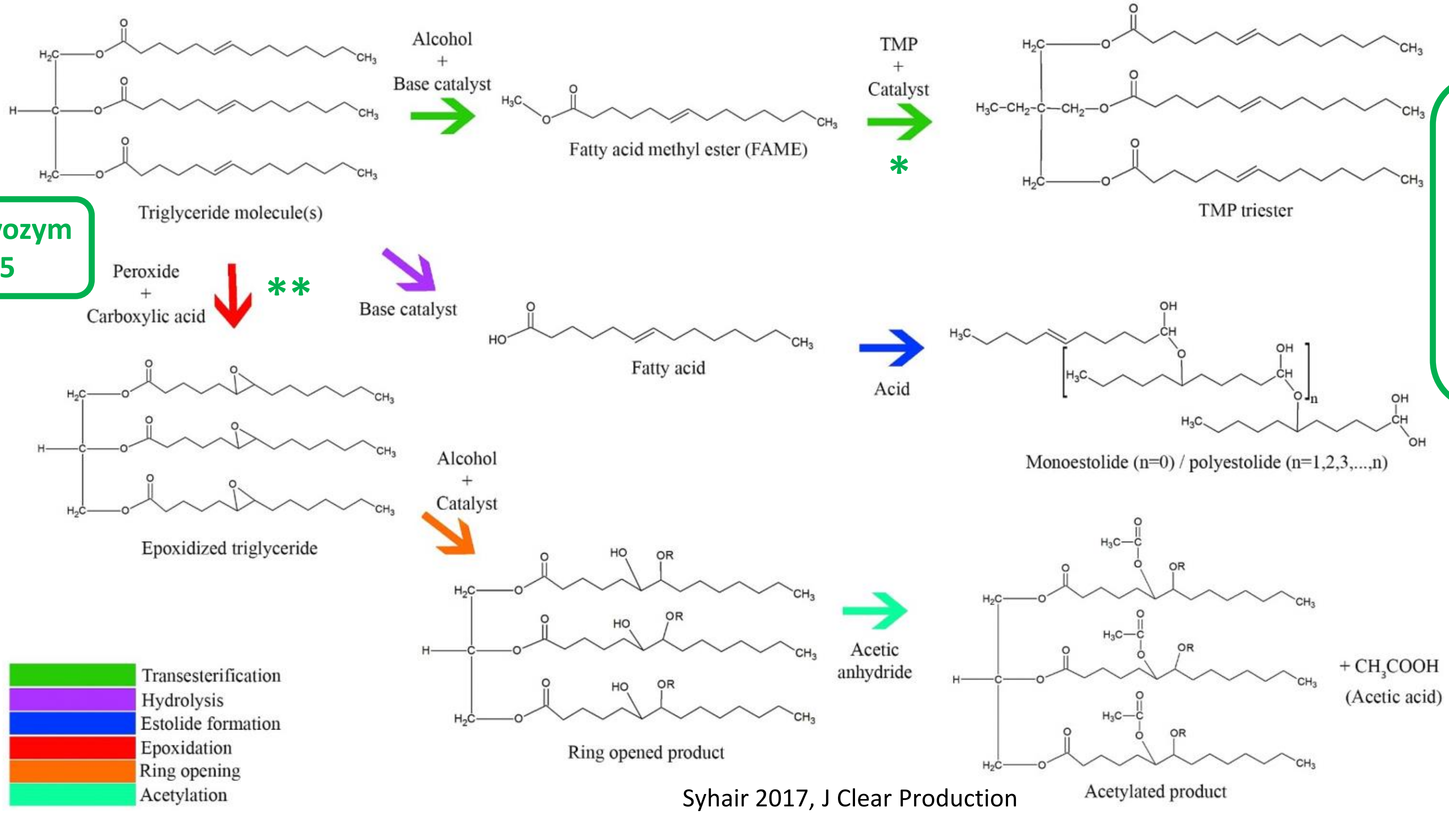
ESTOLIDES FORMATION
between FFAs

TRANSESTERIFICATION
with polyols

OILS MODIFICATION TO PRODUCE BIO-LUBRICANTS

1) Rearrange acyl moieties to form new TG through **ESTERIFICATION/TRANSESTERIFICATION** → formation of esters with improved physical properties (metyl esters + TMP).
2) Modify acyl groups through **FORMATION OF ESTOLIDES** after hydrolysis of TG→ bonding of FFAs carboxylic acid to the C=C of another FFA. Done on sinflower oil, olive oil, oleic acid, ricinoleic acid, castor oil and tallow.
3) Acyl chains **EPOXIDATION of C=C bonds**: Increases oxidative stability, better lubricity, increased viscosity index, increased PP. After epoxidation, often oxirane-ring opening followed by esterification and/or acetylation. Done on canola oil, Jatropha oil, oleic and ricinoleic derivatives, castor oil, sunflower oil and waste cooking oil.

**** Novozym 435**



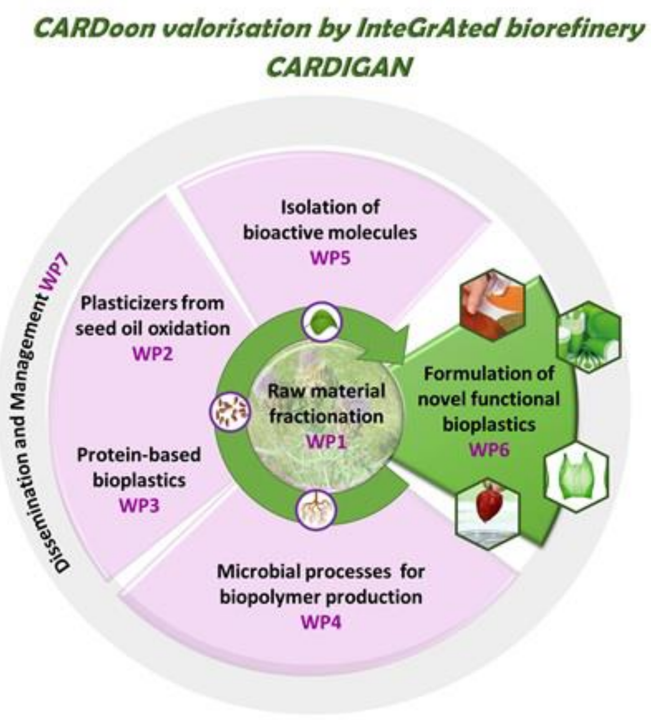
*** *Candida rugosa* lipase, or immobilized *Rhizomucor miehei* lipase with rapseed oil Or Novozym 435 with oleic acid**

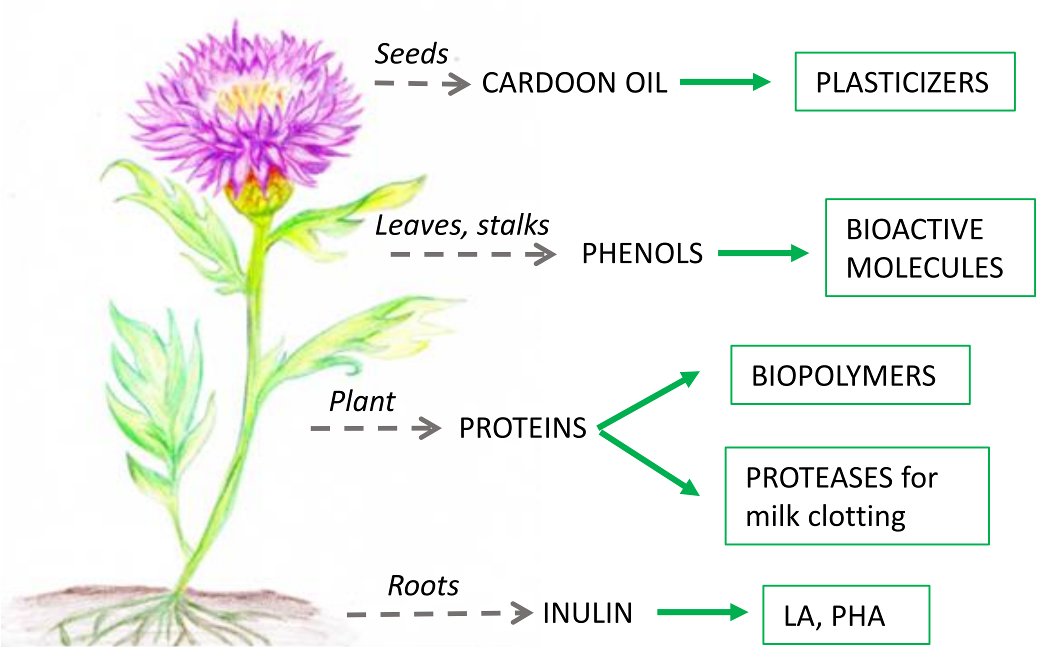
Syhair 2017, J Clear Production

THE CARDIGAN PROJECT

CARDoon valorisation by InteGrAted biorefiNery

Valorization of non-edible parts of cardoon (seeds, leaves and roots) to obtain biopolymers, bioplasticizers and bioactive molecules.





Seeds → CARDOON OIL → PLASTICIZERS

Leaves, stalks → PHENOLS → BIOACTIVE MOLECULES

Plant → PROTEINS → BIOPOLYMERS

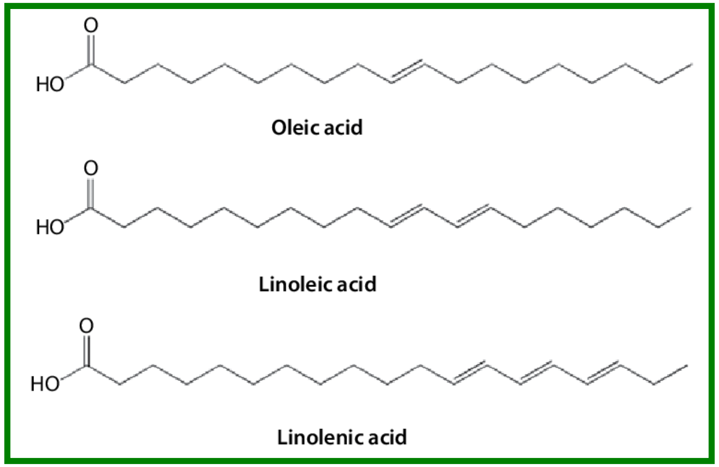
Plant → PROTEINS → PROTEASES for milk clotting

Roots → INULIN → LA, PHA

Cynara cardunculus

CARDIGAN PROJECT & BIOPLASTICIZERS

Through the epoxidation of cardoon oil, several plasticizers will be obtained.



Oleic acid

Linoleic acid

Linolenic acid

Cardoon oil →High content of linoleic acid and oleic acid

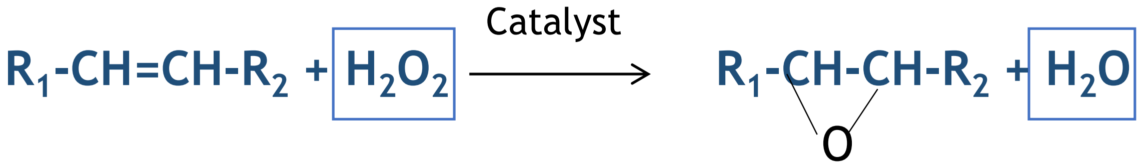
Epoxidizable C=C bonds

Cardoon oil plasticizers and lubricants will be tested in addition to commercial polymers such as polybutylene succinate (PBS) and polybutylene adipate terephtalate (PBAT) to change their properties.

In addition, bioactive compounds from cardoon leaves will be included in the optimized formulations, aimed to the development of functional packaging materials and mulching films.

CARDIGAN PROJECT & BIOPLASTICIZERS

Chemical and enzymatic epoxidation of cardoon oil will be tested to obtain plasticizers and lubricants.



$$R_1\text{-CH=CH-}R_2 + \boxed{H_2O_2} \xrightarrow{\text{Catalyst}} R_1\text{-}\underset{\text{O}}{\text{CH-CH}}\text{-}R_2 + \boxed{H_2O}$$

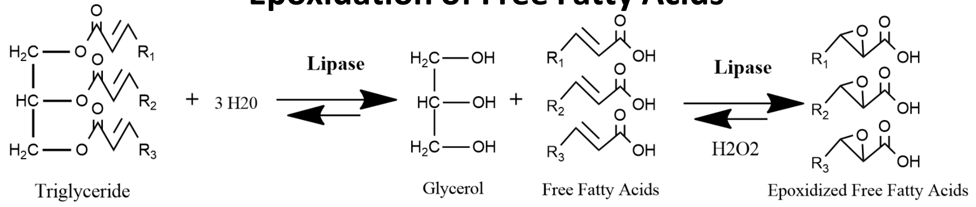
CHEMICAL PROCESS
epoxidation of Free Fatty Acids using peracids and catalysts

ENZIMATIC PROCESS

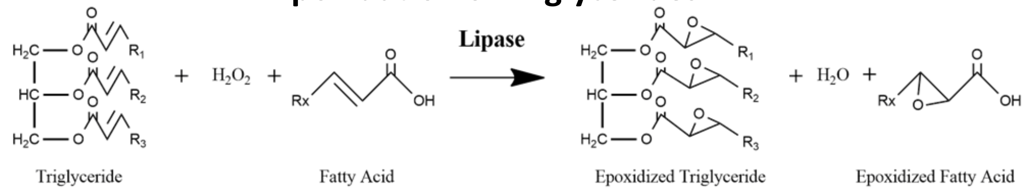
Epoxidation of Triglycerides and Free Fatty Acids using lipases.

SOLVENT FREE!

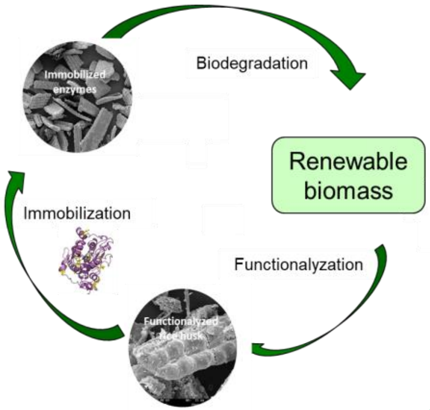
Epoxidation of Free Fatty Acids



Epoxidation of Triglycerides



IMMOBILIZATION of lipases on Rice Husk (from renewable biomass)

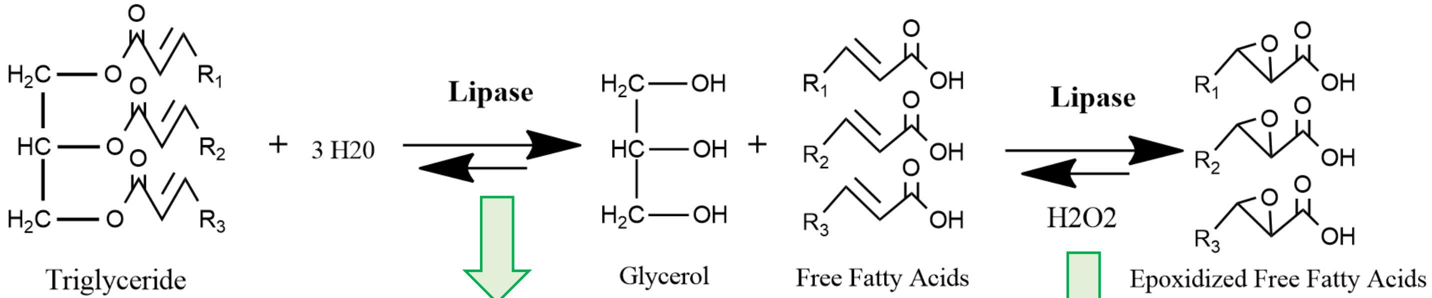


CARDIGAN PROJECT & BIOPLASTICIZERS

The epoxidation enzymatic process will be performed with different lipases, testing different conditions.

LIPASE	FATTY ACID LENGTH	SATURATION	REGIOSELECTIVITY
RmL	Medium-Long (C12, Oleic acid, α-linolenic)	Saturated, monounsaturated, tri-unsaturated	sn1-3
TlL	Medium-Long (C12, Oleic acid)	Saturated, monounsaturated	sn1-3
CaLB	Short-medium-long	Saturated, unsaturated, **polyunsaturated**	Nonspecific (or sn1-3)
PS Amano	Medium (if saturated), long (if unsaturated)	Saturated and unsaturated	Nonspecific

ENZIMATIC PROCESS



Cardoon seed oil→ obtained from pressed bio-waste material

HYDROLYSIS
~Neutral pH
T ≅ 40-50°C
TlL and CalB

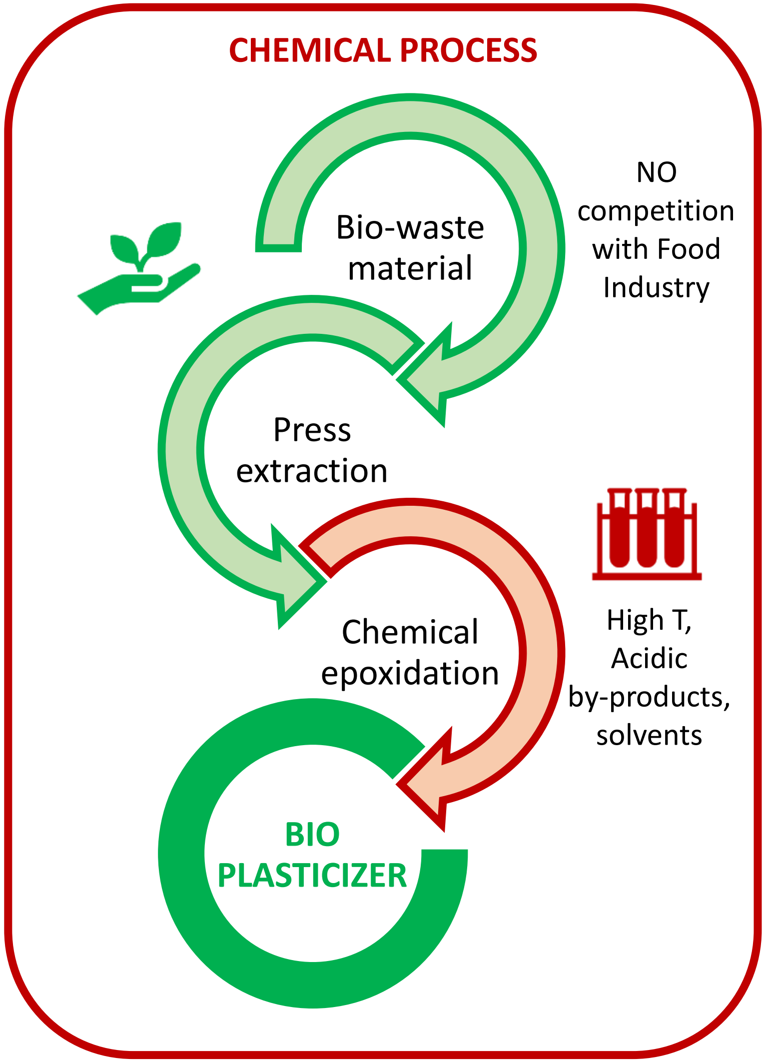
SEPARATION
aqueous from hydrophobic phases → easy

EPOXIDATION
Solvent free
T ≅ 40-50°C
CalB

Easy reaction control:
TLC

CARDIGAN PROJECT & BIOPLASTICIZERS

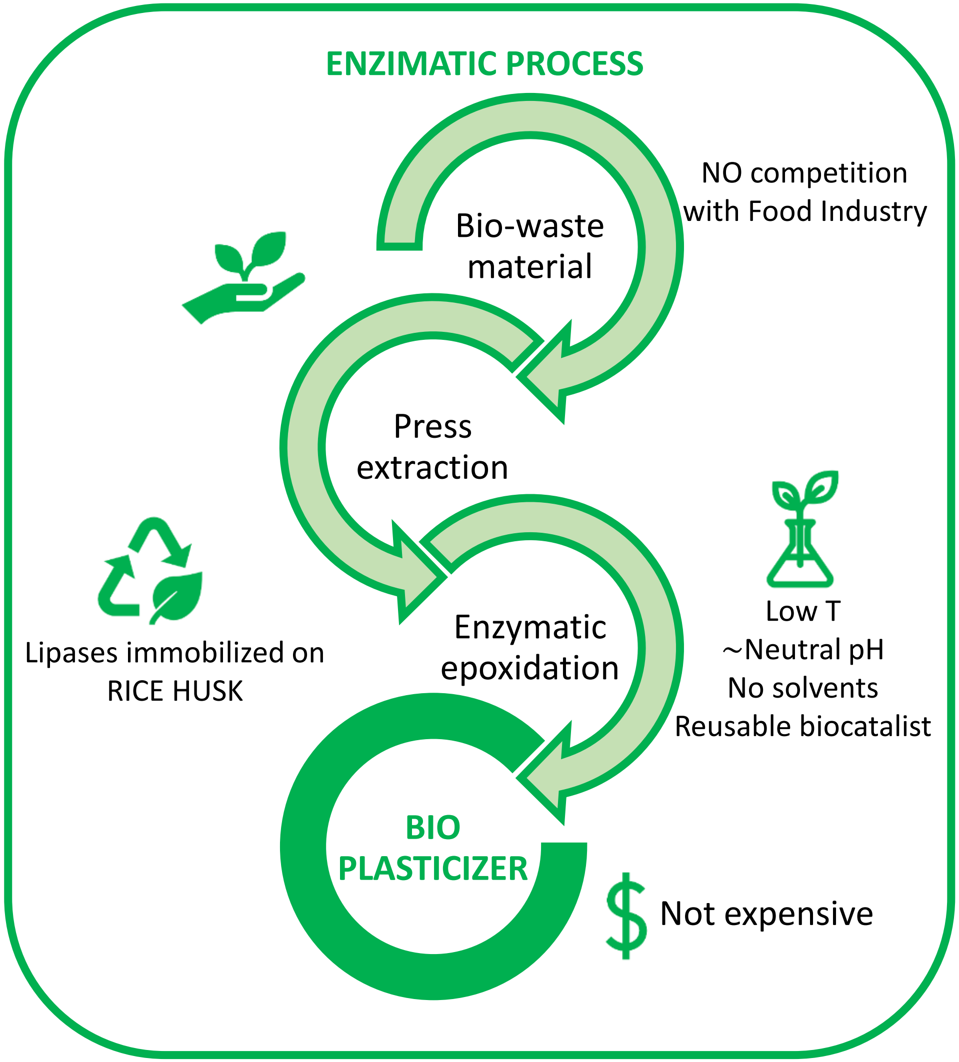
Through the epoxidation of cardoon oil, several plasticizers will be obtained.



CHEMICAL PROCESS

NO competition with Food Industry

High T, Acidic by-products, solvents



ENZIMATIC PROCESS

NO competition with Food Industry

Lipases immobilized on RICE HUSK

Low T
~Neutral pH
No solvents
Reusable biocatalist

$ Not expensive

References (review):

- Y. Jiang and K. Loos; Polymers 8 (2016) 243
- M.G.A. Vieira et al; European Polymer Journal 47 (2011) 254-263
- M. Bocqué et al; J polymer Science A: Polymer chemistry 54 (2016) 11-33
- J. Salimon et al; Eur J Lipid Sci Technol 112 (2010) 519-530
- J. McNutt and Q. He; J Ind Eng Chem 36 (2016) 1-12