Rethinking **flame retardants**: *biobased routes and case studies*

AddBIO | Centexbel | Brecht Demedts | Myriam Vanneste

Fire facts

- 0,22 % of deaths in the world are due to a fire
- 30 % of all fires are residential home fires
- Main causes of accidental fires in Europe
  - Smoking
  - Electrical faults
  - Cooking
  - Carelessness with sources of ignition, such as matches or candles
- Most fatal residential fires ignite upholstered furniture, beds, mattresses and textiles, including clothes and start in living room, bedroom and kitchen

Fire safety


PREVENTION
DETECTION
EARLY SUPPRESSION
EVACUATION
COMPARTMENTATION
STRUCTURAL SAFETY
FIREFIGHTING
EU FIRE SAFETY GUIDE - THE 7 LAYERS OF FIRE SAFETY IN BUILDINGS

Flame retardants



- Goal flame retardants
  - slow down or suppress ignition
  - once ignition: reduce spread of fire, smoke density and smoke toxicity
  - save lives
  - reduction of material losses
- Flame retardants are an essential element of fire protection

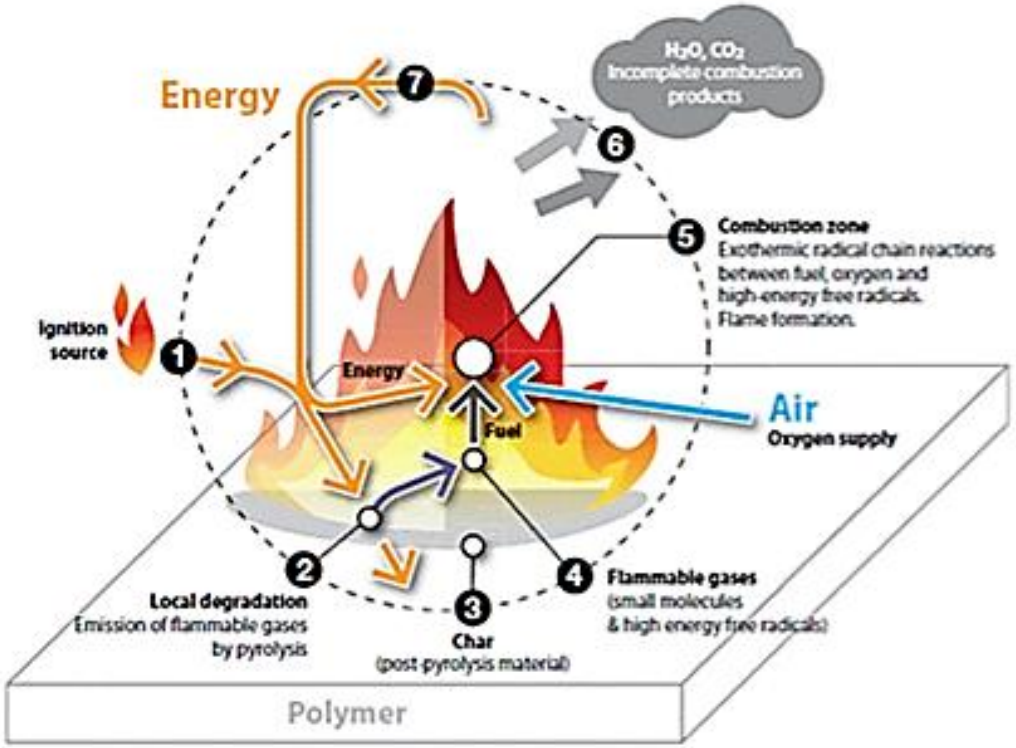
Flame retardants

- Big variety of products/chemicals
  - Each with specific physico-chemical interaction with fire
  - Different physical / chemical properties, environmental fate, toxicology, regulatory status

About fire



- Need for oxygen
- Need for heat
- Need for fuel



LOI values

Matrix	Limited oxygen index (LOI)
Cotton	19
Flax	20
PP	20
PA	22
PET	22
Wool/Silk	26

LOI = the amount of oxygen in the athmosphere (in %) required to sustain burning

Flame retardants

Halogenated (Br, Cl, F)

- Radical quenching (substitution of high-energy free-radicals by low-energy free-radicals)
- Avoid fire cycle to establish or to sustain itself
- High efficiency – low loadings (12 %wt)

Oxidated metals (Mg(OH)2, ATH)

- Endothermic decomposition (energy capture)
- Dilution of combustion zone with inert gases (water)
- Non flammable layer material surface
- Low efficiency – high loadings (60 %wt)

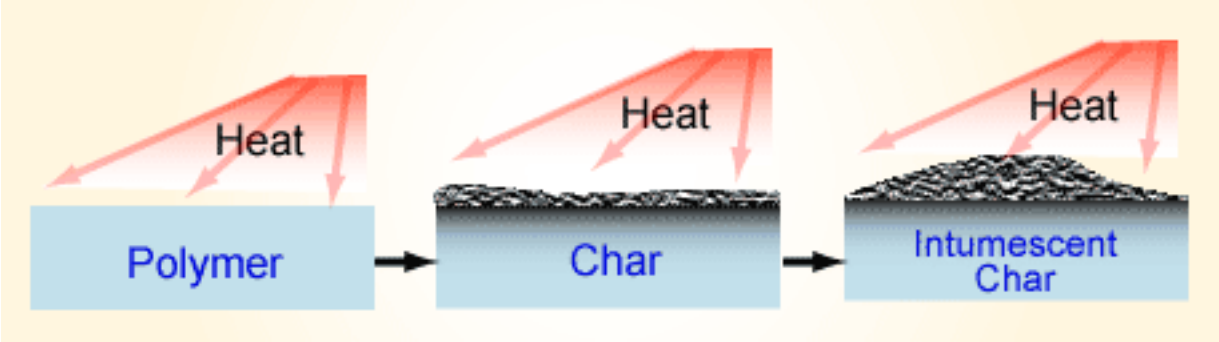
Phosphorus

- Powerful char promoter
- Char hinders the passage of flammable gases
- Char shields polymer from energy (heat) supply
- Varying efficiency & loadings (10-30 %wt)

Nitrogen

- Enhancing formation of cross-linked stable compounds at high temperatures, which inhibits pyrolysis
- Dilution of combustion zone with inert gas (nitrogen)
- Low efficiency alone, good synergist

Intumescent charring



Char blocks heat & passage of combustible gasses

Catalyst (acid)	Charring agent	Blowing agent
Phosphate sources Sulfate sources	Pentaerithritol Polyphenols (tannin, lignin,…) Organic acids (citrate, tartrate,…) Usually the matrix itself (PP, PU, PA,…)	Nitrogen sources

http://fr.polymerinsights.com/home/mechanisims

Flame retardants

Halogenated (Br, Cl, F)

- Radical quenching (substitution of high-energy free-radicals by low-energy free-radicals)
- Avoid fire cycle to establish or to sustain itself
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Never biobased

Phosphorus

- Powerful char promoter
- Char hinders the passage of flammable gases
- Char shields polymer from energy (heat) supply
- Varying efficiency & loadings (10-30 %wt)

Some biobased options

Metals (Mg, Al, …)

- Endothermic decomposition (energy capture)
- Dilution of combustion zone with inert gases (water)
- Non flammable layer material surface
- Low efficiency – high loadings (60 %wt)

Nitrogen

- Enhancing formation of cross-linked stable compounds at high temperatures, which inhibits pyrolysis
- Dilution of combustion zone with inert gas (nitrogen)
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Many biobased options

What about minerals in biobased materials?

- Avoid heavy metals (Sb, Zn) as especially for biodegradability they are not allowed
- Aluminium and Magnesium hydrates are allowed
  - No influence on C14 dating → 100% biobased label is possible
  - Influence on LCA
  - >50% of your product must be carbon! (relevant in the context of FR)



Relevant products

- Aluminium trihydrate (ATH)
- Magnesium hydroxide (Mg(OH)2)
- High loadings needed – do not put > 50% or biobased certification is compromised

The need for alternatives often come when triggerd by the **price**

Price of antimony over time



- ATO (antimony trioxide) highly relevant for FR
- Very common synergist with halogens
- PVC, brominated, etc.

Phosphates & phosphinates



HIGHLY STABLE PHOSPHINATE FLAME RETARDANT

Exolit™ OP 1230 Terra

Exolit OP 1230 Terra is a white, fine-grained powder based on an organic phosphinate. The product is non-hygroscopic and it is insoluble in water and organic solvents. Clariant's Exolit OP flame retardants for polyamides are all based on aluminum diethyl-phosphinate (= DEPAL). The pure substance DEPAL is sold as Exolit OP 1230 and in combination with synergists as Exolit OP 13xx & Exolit OP 14xx types. Exolit OP 1230 is the first non-halogenated flame retardant which can withstand the demanding requirements of this high end segment of engineering plastics.

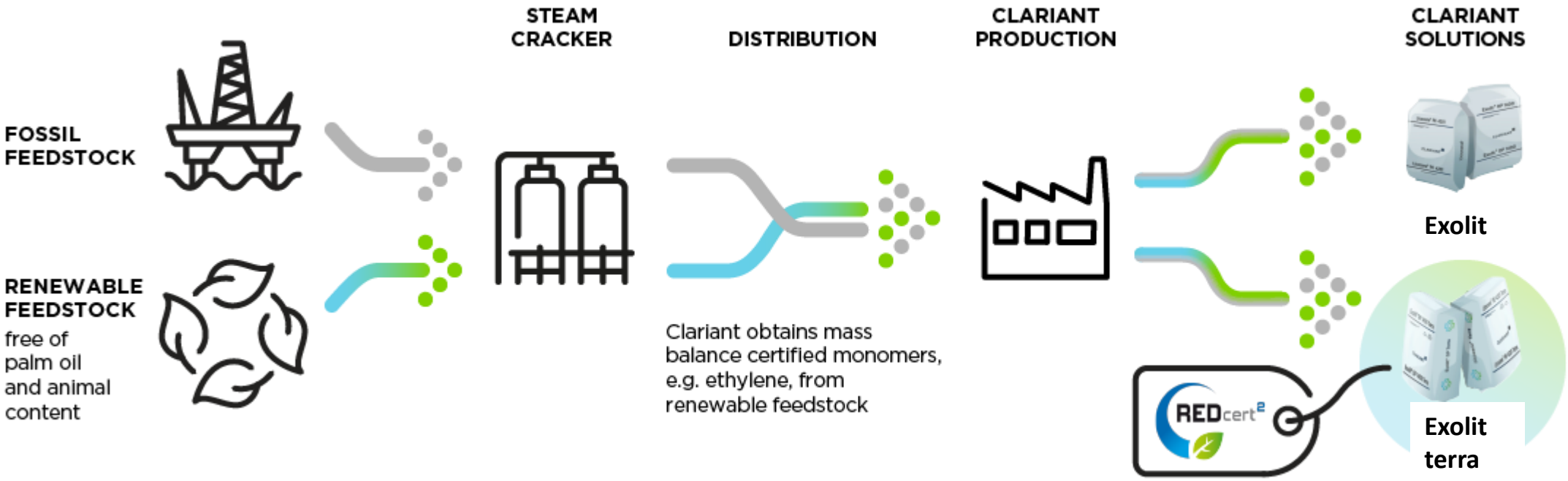
Exolit OP 1230 Terra is chemically and from its composition equivalent to Exolit OP 1230, but comes with a mass balance certificate as for its production, renewable based Ethylene was sourced.

Therefore we assume that for Exolit OP Terra products no additional performance testing and qualification compared to the standard grade are necessary.

For more details see our Innovation Spotlight video.

CLARIANT

What is mass balance?



Very dependent on excellence in certification!

Another relevant example for FR

Reduce your carbon footprint with renewable Penta

Perstorp

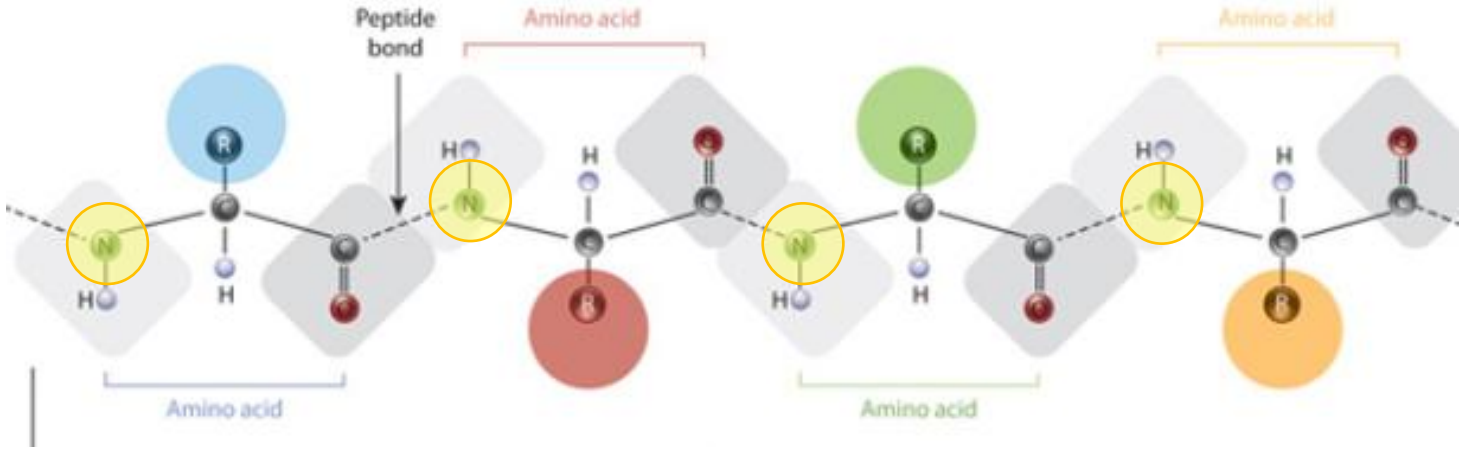
Voxtar™ is our renewable counterpart to Penta (pentaerythritol). Based on a traceable mass balance concept, Voxtar™ is designed to reduce the carbon footprint throughout the value chain and to support sustainable sourcing of renewable and recycled raw materials.

Voxtar™ was launched in 2010 as the world's first renewable pentaerythritol. It comes in grades of 40% and 100% renewable carbon content and carries the ISCC PLUS certification. This ensures that all raw materials used are sourced responsibly and sustainably from cradle to gate. The certification includes a calculation of mass balance and greenhouse gas values.

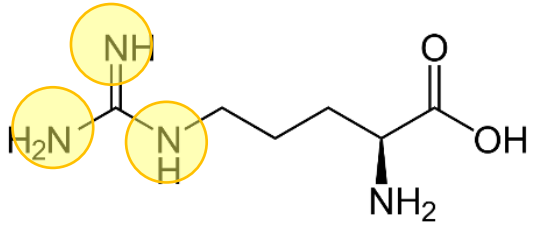
Very dependent on excellence in certification!

The ***biobased*** ingredients for FR

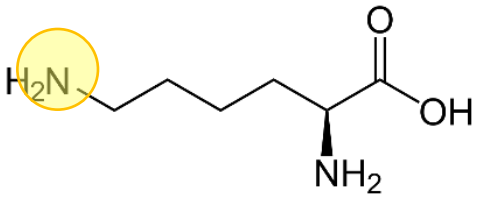
Proteins & peptides



Arginine



Lysine

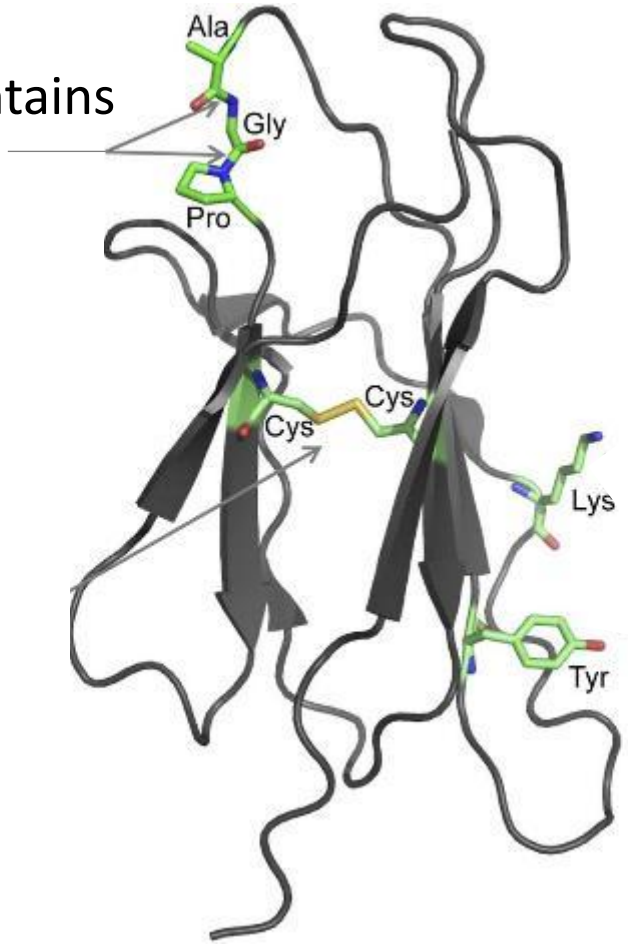


Arginine, lysine rich proteins

Be aware of smoke toxicity → HCN, H_2O, SO_2 from burning wool & silk

Proteins & peptides

1/3th of the backbone contains **nitrogen**



Lysine + Arginine provide extra nitrogen

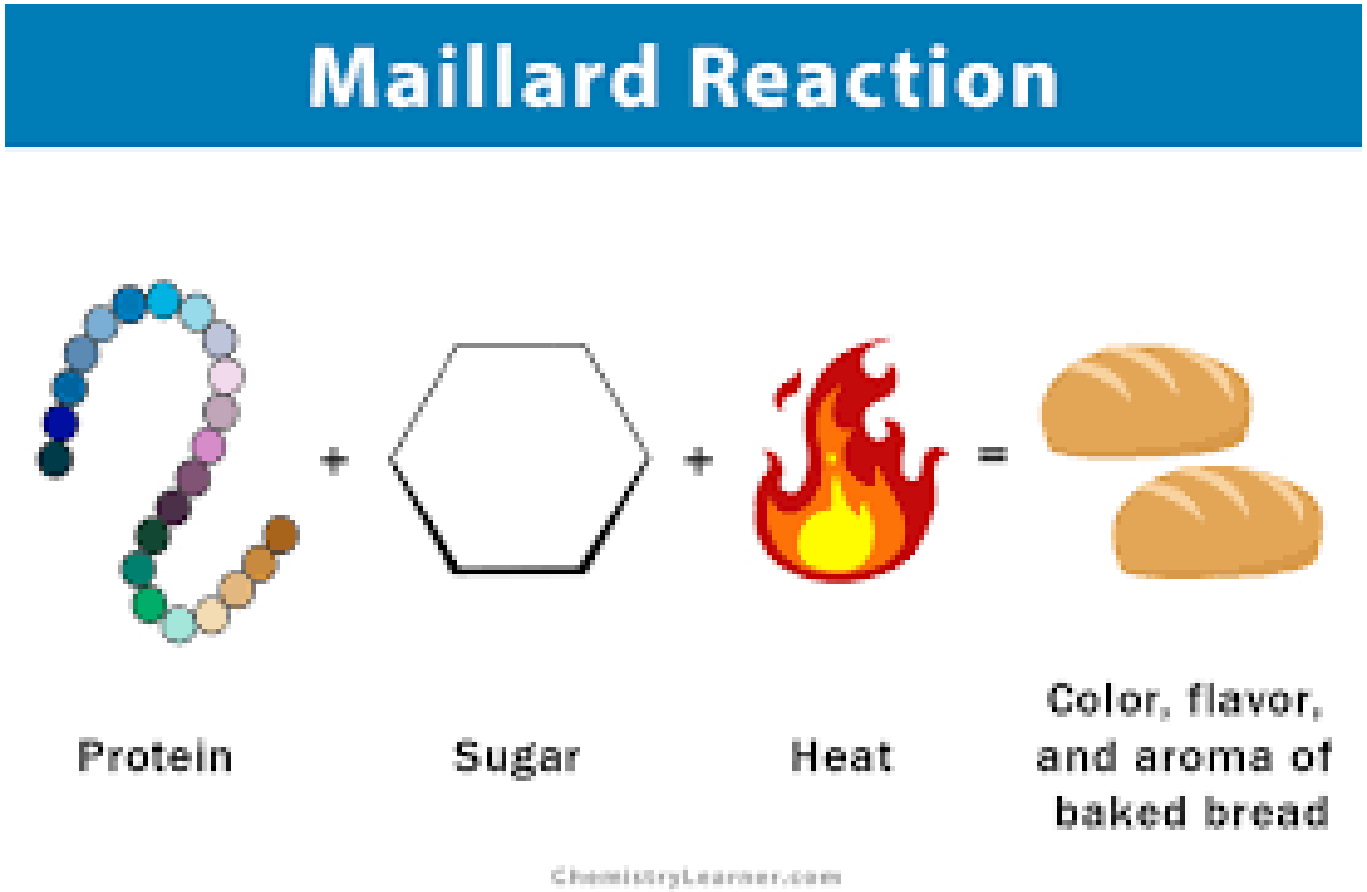
Cystein + Methionine contain sulfur (smoke tox?)

Tyrosine + Serine provide sites for phosphorylation

Proteins & peptides

- Huge variety
- Good availability
- Stiff
- Inherently biodegradable
- Hydrophylic (e.g. gelatin) & hydrophobic (e.g. keratin)
- Can be phosphorylated (mainly in bulk available for storage (seeds) and feed (milk))
- May contain sulfur (methionine, cystein) → smoke toxicity
- Seldomly sufficient when used alone
- Can be biochemically modified (phosphorylated)

Beware the maillard reaction!



Processing proteins often leads to brown color, smell and unwanted by-products

Proteins - conclusions

- Seldomly suffient to be a highly potent FR
- Needs to be formulated with phosphorus components
- Often does not withstand processing temperatures
- Are pricy
- May be animal derived
- May be in competition with food chain

Organominerals

Biologically occuring in bone



Ossein (collagen = gelatin)

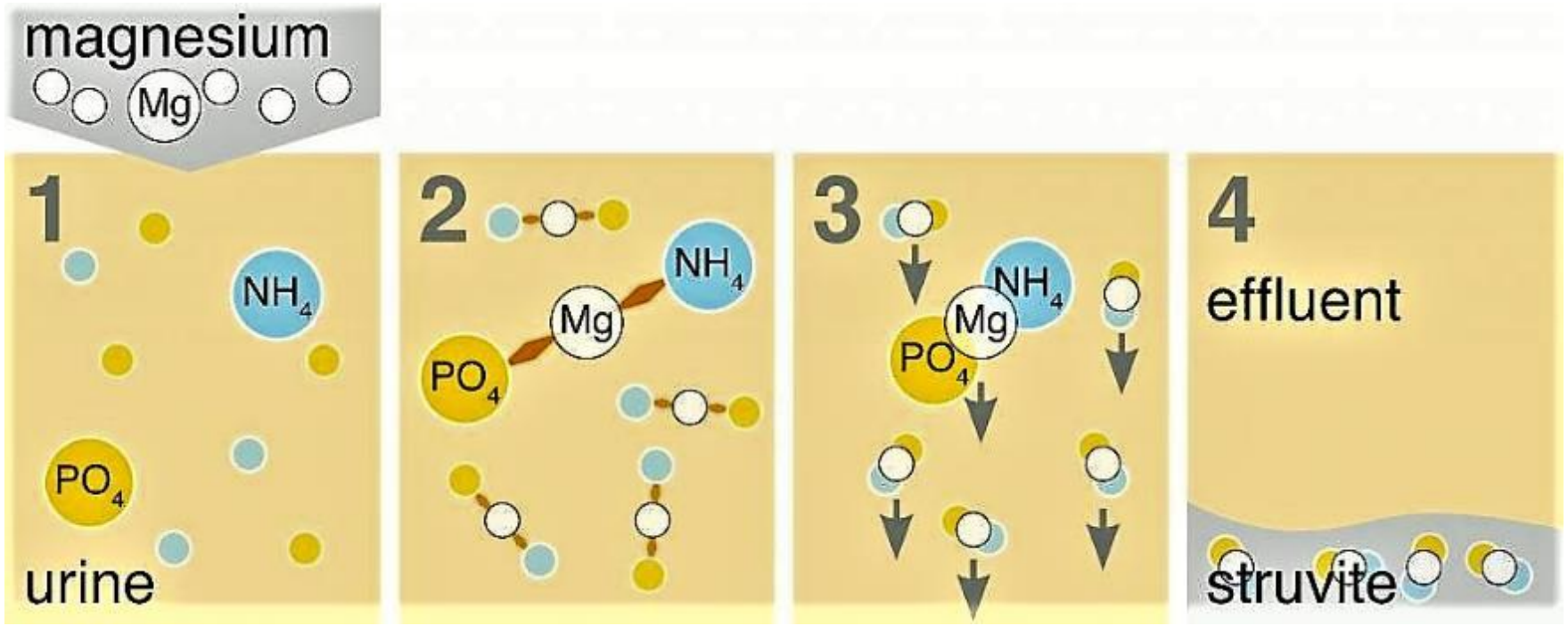
Gelatin **Hydro-P** & **collagen** do not increase viscosity

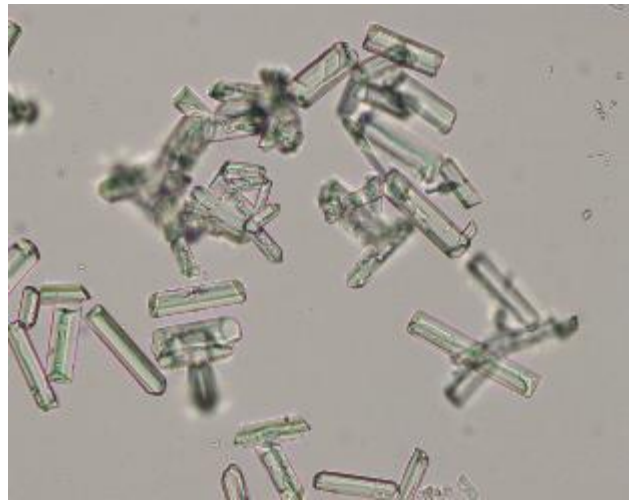
Hydroxyapatiet ($Ca_{10}(PO_4)6(OH)_2$)

Insoluble, large particles

No contribution to organic carbon (certification)

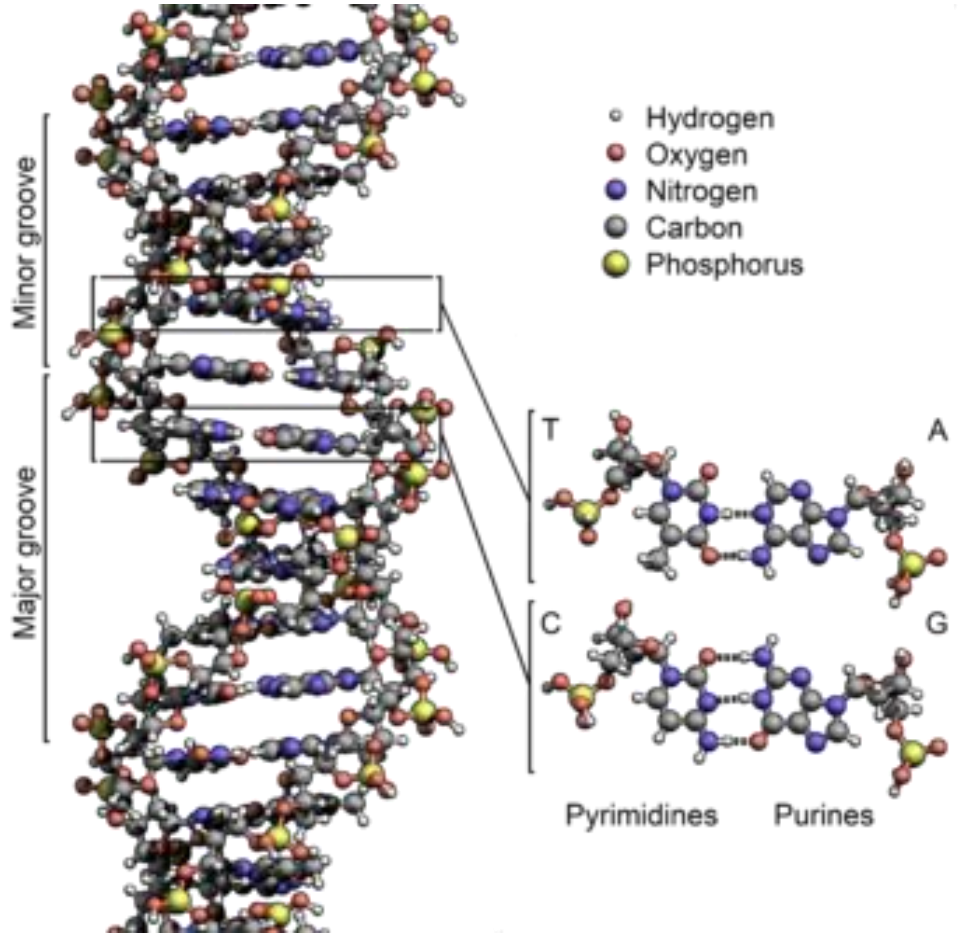
Struvite ($MgNH_4PO_4.6H_2O$)





- Massive by-product from water purification
- We sourced from local potato processor

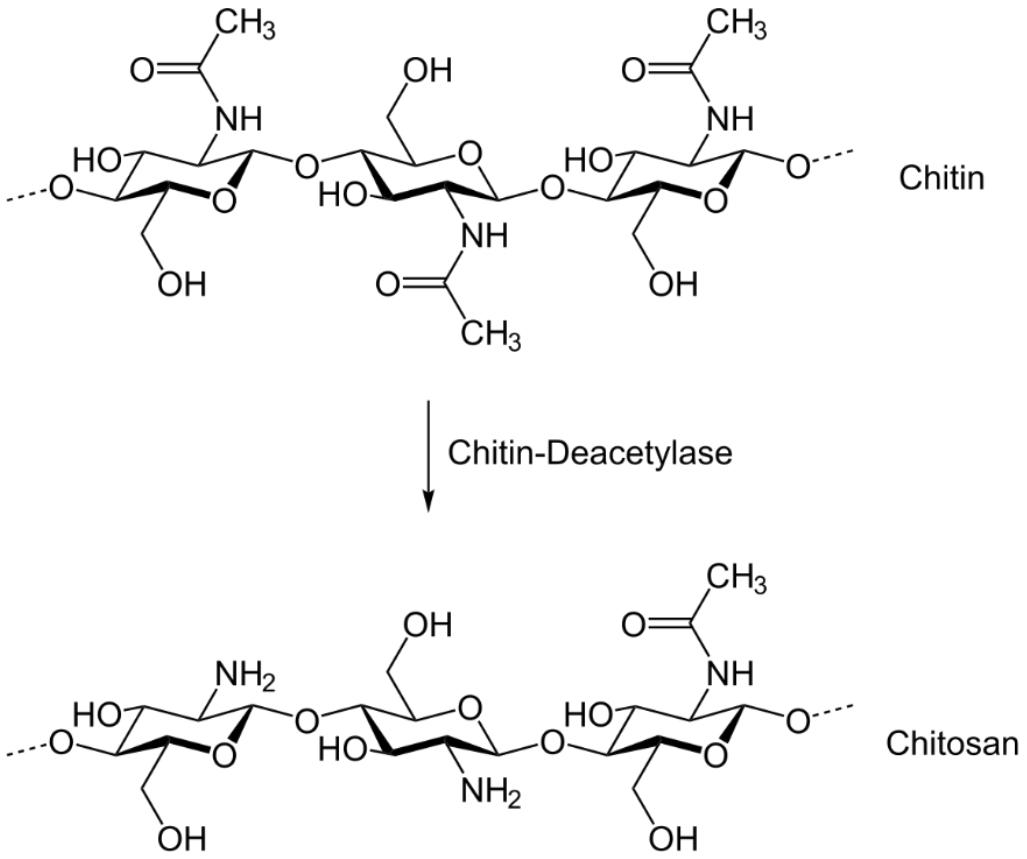
DNA



Rich in phosphor & nitrogen
Low availability
ATP (adenosine triphosphate)

Is this really available?

Chitosan

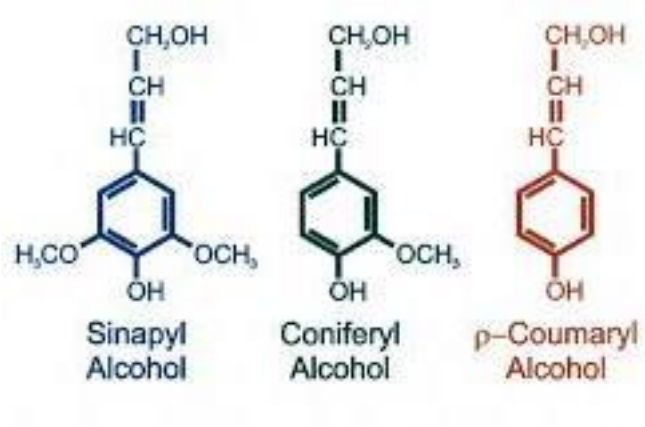




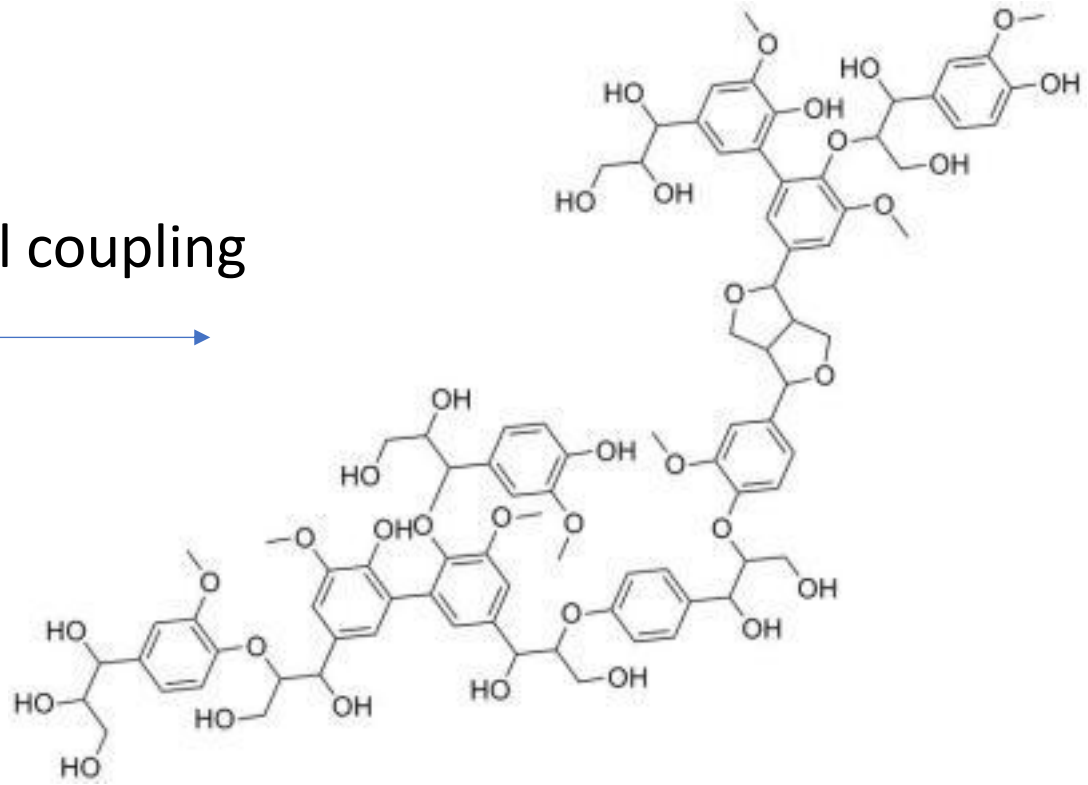
Exoskeleton

Polyphenols

Building blocks (lignin)



Radical coupling



Very random polymers!!! biovariation

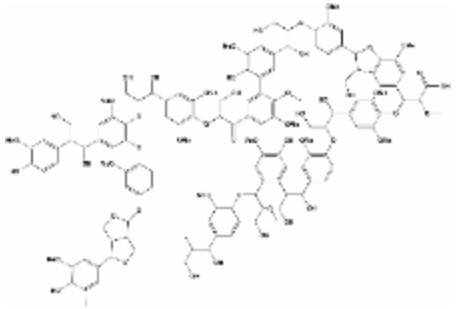
Tannin

Ajinomoto omnichem



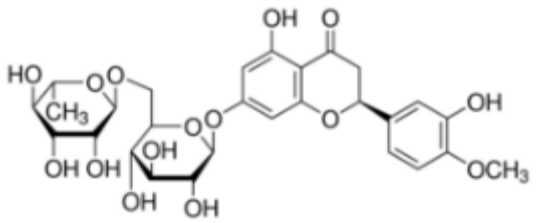
- Seeds, bark, stem
- Extractable (not coupled to cellulose)
- Sometimes clear streams (grape pits)
- Creates color with metal ions (Sn, Fe, Cu)

Lignin



- Wood (coupled to cellulose)
- Very variable in composition
- Paper industry
- Sulfonated lignin, tar & chemical extracts

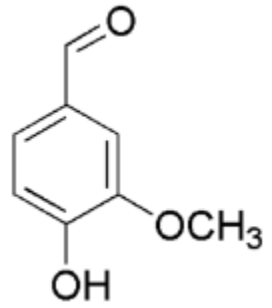
flavonoids





- Antioxidant
- Extract from wastestreams (Kaemferol/Hesperidin)
- Often glucosylated

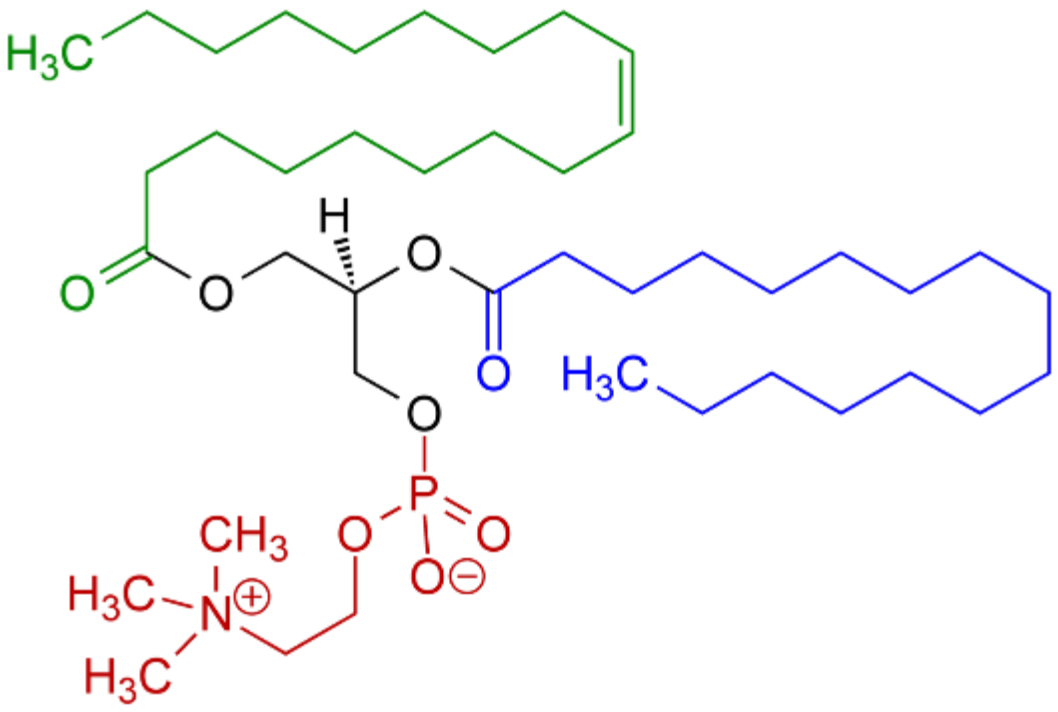
Mono/di lignols



e.g. vanilin

- Often functional (antimicrobial, color, odour,…)
- UV-protective
- Very often made synthetic

Select your coating system wisely



*Why not a **phospholipid** (e.g. lecithin)?*

*Replace a minor amount of the plasticizer by a **phosphate plasticizer** (non biobased – check toxicity)*

*Use a **PU as binder** rather than an acrylate*

***Replace** part of the TiO_2 by $MgOH_2$ and/or ATH*

Examples

“Waste” products from the food industry

product name	what?	content	possible use	form
binary salt 9/0/9	by-product chichory refining	potassium-ammonium sulfate	FR?	powder, brown
struvite	Precipitated salt	Mg-ammonium-phosphate	FR?	Coarse powder
Hydroxyapatite - calfos	organomineral	Ca10(PO4)6(OH)2	FR?	Coarse powder
beneofeed FB FBR	by-product of beans	fiber + protein	fiber reinforcement, FR, dyeing?	hulls unground
VWG pellets	gluten	insoluble protein	FR?	pellets
vital wheat gluten 82 feed	gluten	insoluble protein	FR?	powder, brown
maisvoermeel	By-product milling grains	certain protein content	FR?	powder
chicory vinasse	protein + ash	syrup	FR?	syrup, black

ISO 15025 as screening test for flame retardant

			pickup	LOI	afterburn	afterglow	molten parts	burning parts	flames till top	hole formation to sides	hole fo
T2404277	Addbio_03_00		0	20	116	579	N	N	Y	Y	Y
T2404278	Addbio_03_01	vinasse (low concentration)	6,80%	19	100	0	N	N	Y	Y	Y
T2404279	Addbio_03_03	vinasse (low concentration) + AmPO4	5,70%	23	102	0	N	N	Y	Y	Y
T2404280	Addbio_03_05	vinasse (low concentration) + binary salt	6,30%	19	152	0	N	N	Y	Y	Y
T2404281	Addbio_03_07	vinasse (high concentration)	8%	19	133	0	N	N	Y	Y	Y
T2404282	Addbio_03_09	vinasse (high concentration) + AmPO4	10%	25	92	0	N	N	Y	Y	Y
T2404283	Addbio_03_11	vinasse (high concentration) + binary salt	9,80%	21	95	36	N	N	Y	Y	Y
T2404284	Addbio_03_13	gluten protein	2,80%	20	142	0	N	N	Y	Y	Y



15 second ignition with bunsen

- Fast screening test
- Information on afterburn, afterglow, molten parts, burning parts & hole formation
- Vinasse has a bad smell & is brownish

Combination of acids with organic salt

Formulation

- Bio-based acid + inorganic salt
  - ISO 15025 ***V***
  - NFPA 701 ***V***
  - M1 ***V***

- Compatible with glycerol and amino acids (ISO 15025 and NFPA 701)

- Washability is poor

Combination of ATP with acid

Formulation

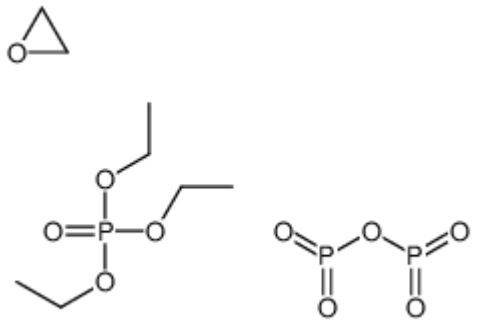
- ATP (adenosine triphosphate) + inorganic salt or bio-based acid
  - ISO 15025 ***V***
  - NFPA 701 ***V***

- Only for cellulosic fabrics

Combination of biobased 2K PU with phosphinate

2K PU formulation

- Bio-based isocyanate and bio-based polyols
- Exolit OP as FR polyol additive
- 2 layers of 50 µm



2K PU formulation

- Complying to ISO 15025
- Waterproof even after 3 weeks hydrolysis, but not after washing

Combination of chitosan & struvite

It is important to dissolve the struvite

- Powdered struvite in thick coatings → fail
- Struvite dissolved in mild acid + chitosan → pass
- Remark: chitosan has a color!

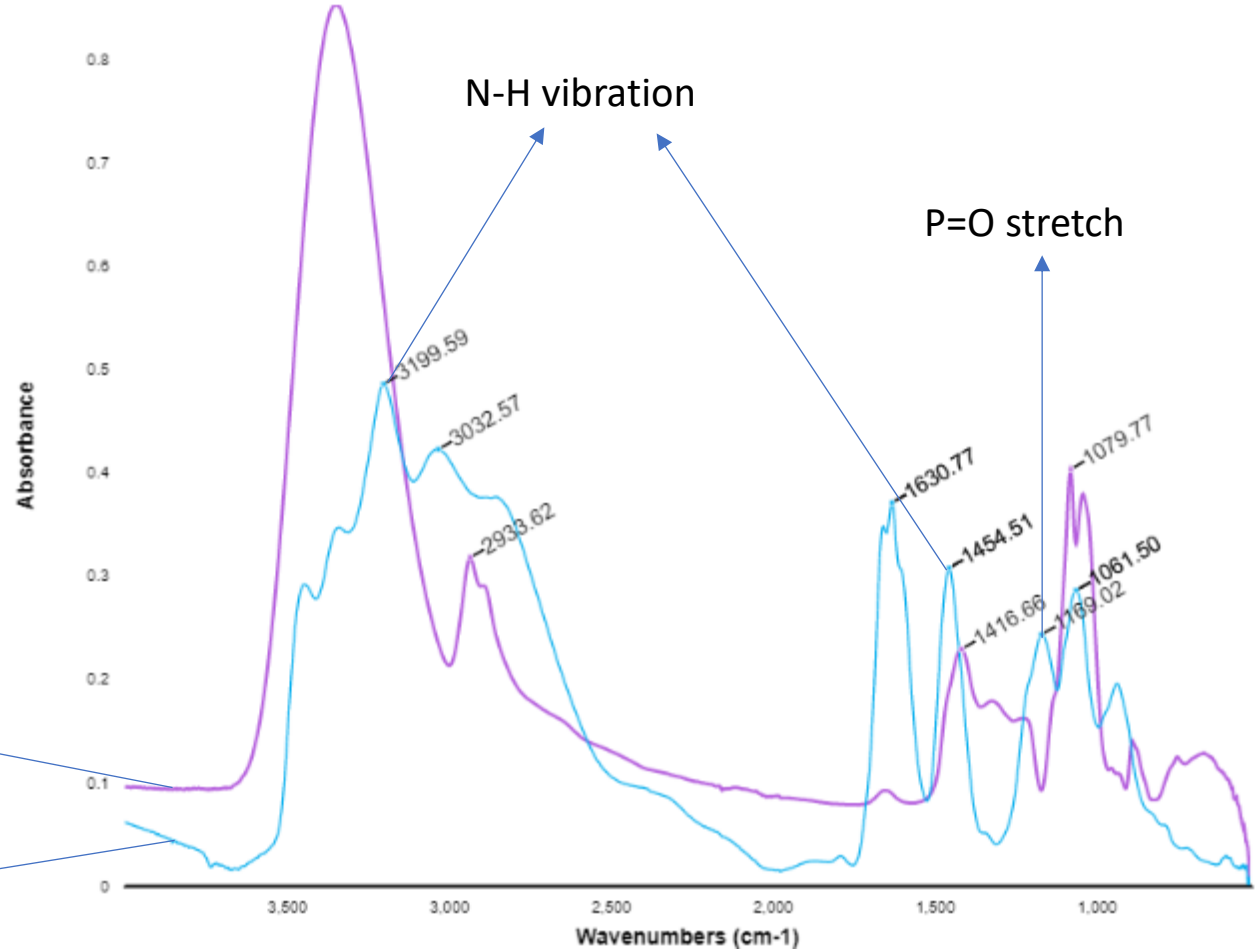
Synthesis of FR from polyols

Synthesis 1

- Modification of hydroxyl groups to introduce phosphate and ammonia groups
  - Step 1: esterification of OH-groups into phosphates
  - Step 2: ammonium complexation

- Application on cotton fabrics in dye bath

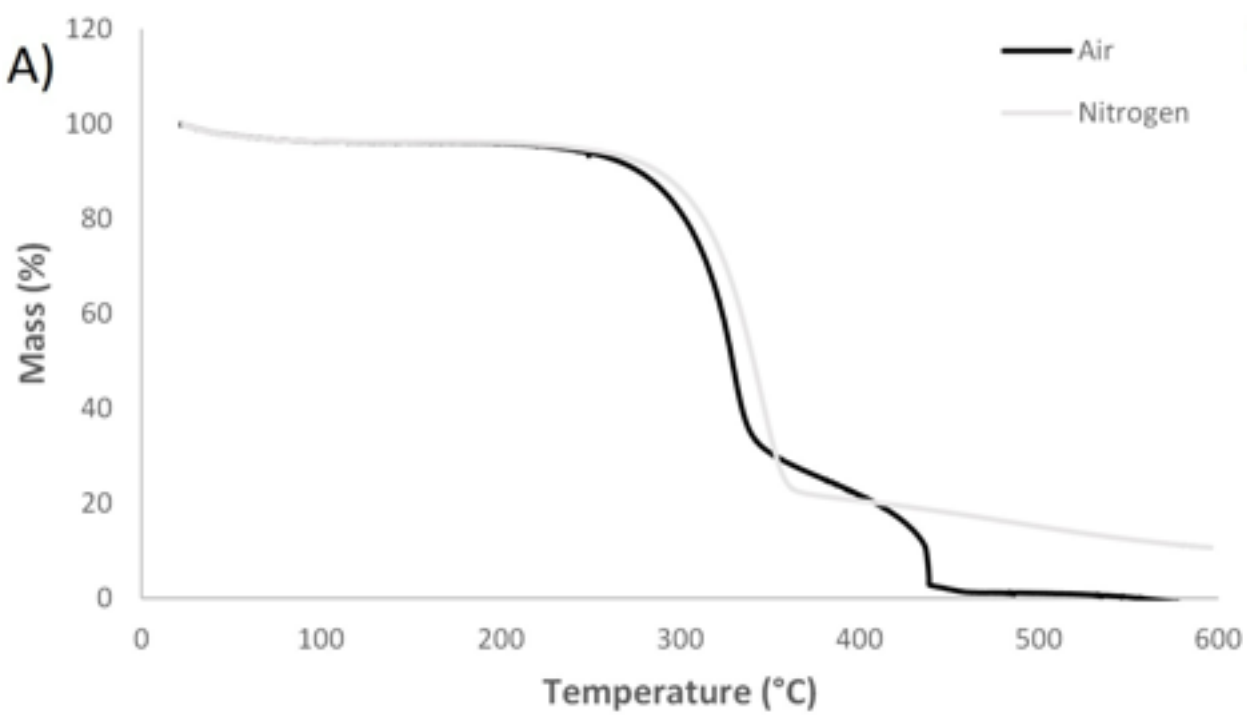
Synthesis 1 -IR



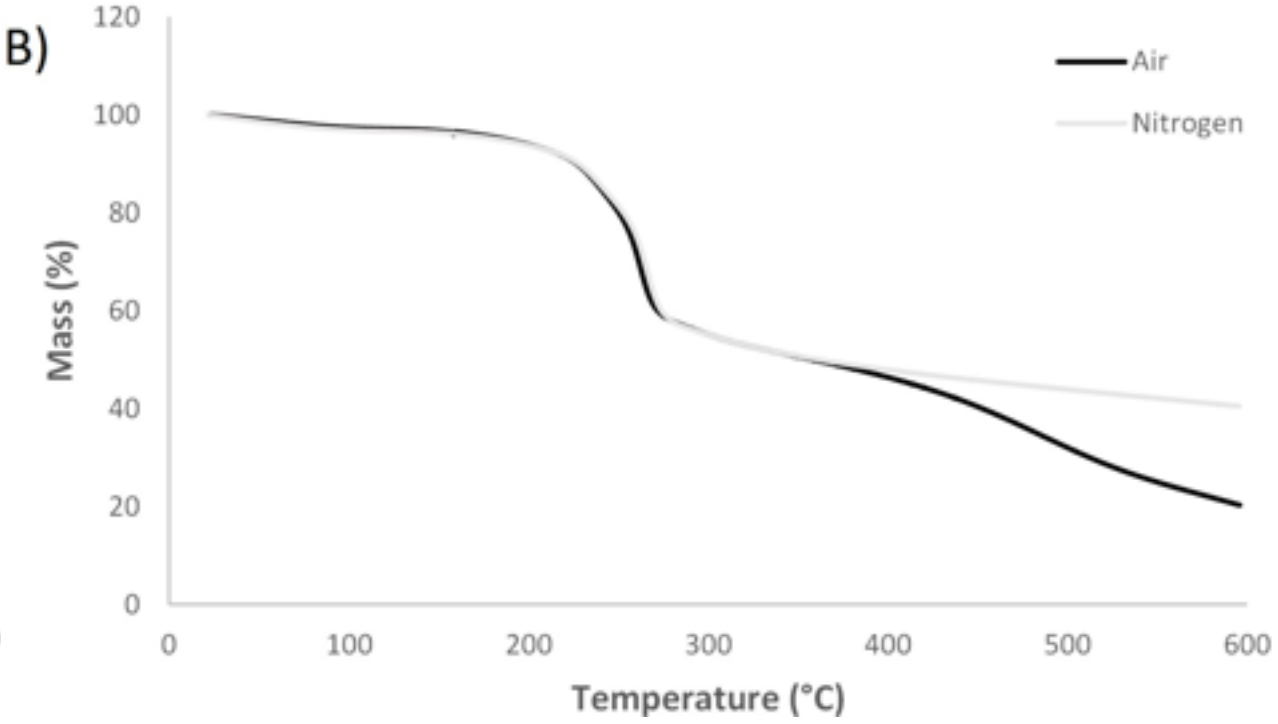
sorbitol

P-sorbitol

Synthesis 1 - TGA



Cotton



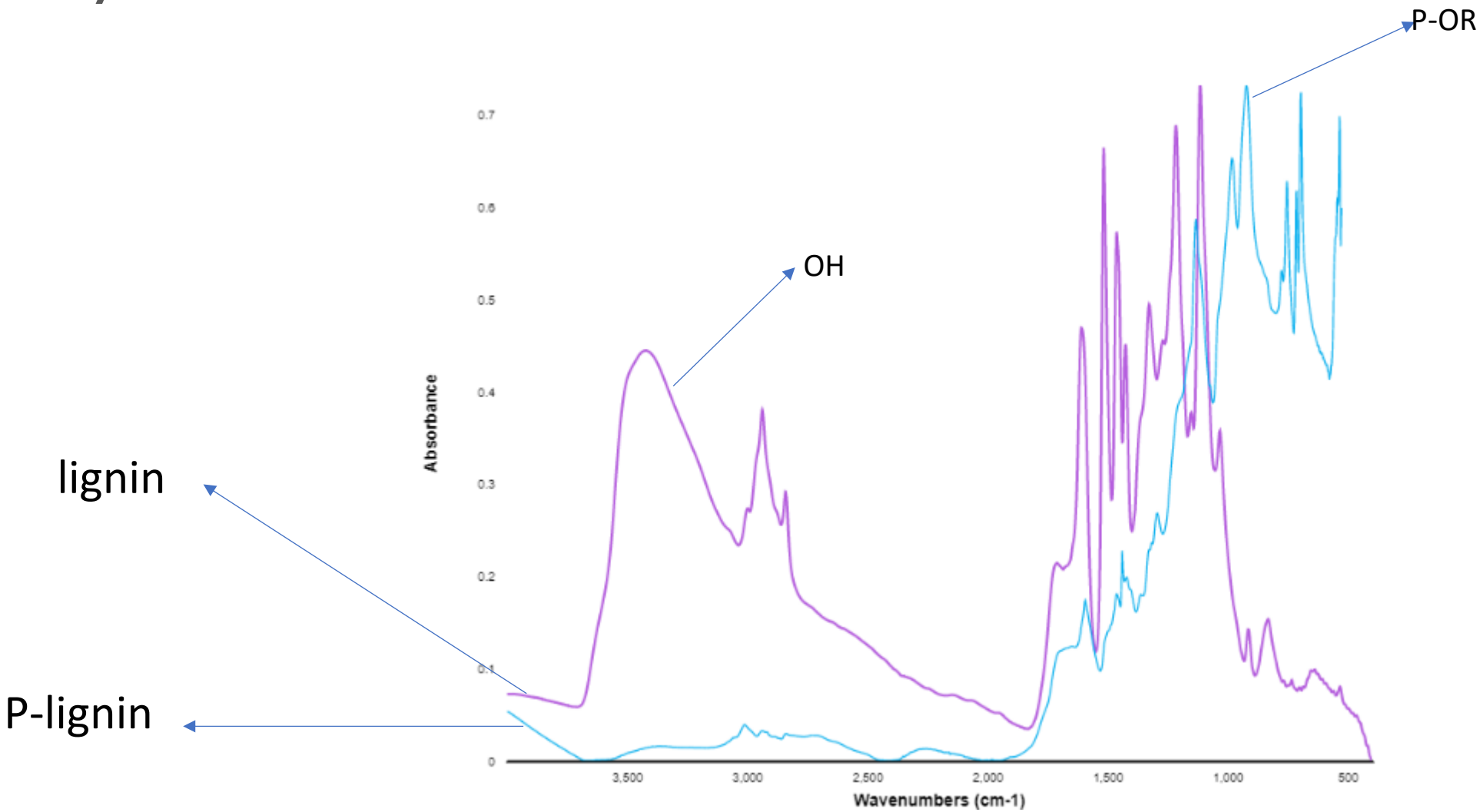
Bio FR finished cotton

Synthesis of FR from lignin/vanillin

Synthesis 2

- Substitution reaction of OH-group to introduce P in backbone
- Green process (free of chloroform and phosphoryl chloride)
- Lignin, vanillin,…

Synthesis 2 - IR



Synthesis 2 – FR test

- Compatible with bio-based 2K PU and PU dispersion
- Applied in PU coating on PET fabric

ISO 15025 surface ***V***

Coming up

- Requests are welcome
- Pigmented system in acrylate + PU
  - Incorporation of struvite
  - Incorporation with exolit terra
  - Incorporation with gelatin
- Combining of the more succesful systems

Conclusions

- Flame retardants are essential for fire protection, reducing the spread of fire, smoke density, and smoke toxicity
- There is a wide variety of flame retardant products and chemicals, each with specific interactions with fire and different properties
- Biobased flame retardants are being explored as alternatives to traditional flame retardants, with various biobased ingredients showing potential
- Proteins and peptides can be used as flame retardants, but they often need to be formulated with phosphorus components and may not withstand processing temperatures
- Organominerals, such as hydroxyapatite and struvite, are relevant for biobased flame retardants
- Polyphenols, such as lignin and vanillin, can be used in flame retardant formulations, but are preferably modified with a phosphate
- The synthesis of flame retardants from polyols and lignin/vanillin involves modifying hydroxyl groups to introduce phosphate and ammonia groups

Thank you for your attention!







