ZELCOR

Zero Waste Ligno-Cellulosic Bio-Refineries

Targeting safe use of biomass residues in modern biorefinery platform: a focus on lignins

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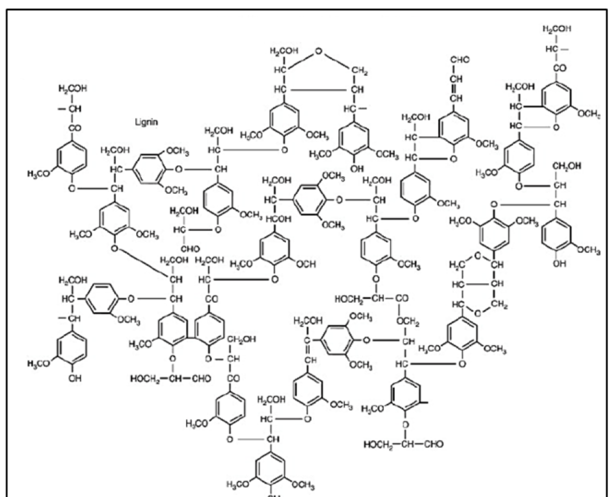
maîtriser le risque pour un développement durable



BIO-BASED INDUSTRIES Public-Private Partnership

Bio-based Industries Consortium

Horizon 2020 European Union Funding for Research & Innovation

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Introduction

- **Biomass residues planned as secondary raw materials of interest in modern biorefineries**
  - **either as main feed**
  - **or towards zero-waste approach in integrated biorefineries:**
    - **Rinaldi (Angew. Chem., 2016) « *To improve the economic feasibility of a biorefinery, biomass must be comprehensively converted into value added products; this includes the lignin stream*"**
- However, durable use of biomass residues need careful consideration of all sustainability aspects, including safety:
  - **Safety issues may concern any step in the value chain in biorefineries**
  - **Accidents do occur in biorefineries**
    - (cf. Rivière et Marlair, Biofpr, 2010, Olivares, J. Loss Prev. (2014, 2015), Moreno Safety Sci.(2019))
- When considered at low TRL of technologies, safety thinking has higher chance to be efficient at most reasonable benefit/cost

Biomass residues overview

- Very large portfolio of such residues, as by-products from current agro-industries, farming activities, wood industries
- Examples:
  - wide variety in:
    - shape (rods, pellets…°
    - source
    - availability
      - ✓ Where ?
      - ✓ How much
      - ✓ When ?
  - not only from crops
    - Shrimp waste;
      fish waste,
      wine exceedings,

Crops	Primary Residues	Secondary Residues	Residue ratio [a]
grains (wheat, corn, rice, barley, millet)	**straw (stover)**		1.0-2.0
	chaff (hulls, husks),	**bran, cobs**	0.2-0.4
sugar cane	**leaves and tops**		0.3-0.6
		bagasse	0.3-0.4
tubers, roots (potato, cassava, beet)	**foliage, tops**		0.2-0.5
		peels	0.1-0.2
oil seeds	**hulls**		0.2-1.2
		press cake	0.1-0.2
sunflower, olive,	***foliage, stems***		0.2-0.5
cocos, palm oil,	***husks, fronts***	***shells***	0.3-0.4
soy, rape, peanut	***foliage***	***seed coat, shells***	0.3-0.5
vegetables	**leaves, stems etc.**		0.2-0.5
		peelings, skin	0.1-0.2
fruits and nuts	**seeds**		
		fruit pulp, peelings	0.2-0.4

Main biomass (residues) characteristics

- CHO carbon source vs CH carbon sources in petrol
  - **More variable compositions than in petrols**

- Energy content lower than in petrol
  - **Due to presence of oxygen (say 10 to 25 Mj/kg, water-free NHV basis**
- Main advantage as Renewable Carbon source:
  - **Pre-existing functionalization**:
    - carbohydrates, hydroxyl groups, furan rings, aromatics
  - **But increased reactivity can be a source of concern**

- Existing data in open literature rarely addressing safety driven purposes
  - **Essentially proximate and elemental analyses and energy content for energy conversion purposes**

Why a focus on lignins in this talk?

- multifold reasons:
  - **much more than academic interest !**
  - **abundancy worldwide, already commercially available**
    - **Ex. : Green Value Protobind lignin**

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Chemicals from lignin: an interplay of lignocellulose fractionation, depolymerisation, and upgrading†

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- One of the 2 key materials considered in ZELCOR
  - **The other one « humins » already regarded in the H2020 HUGS project**

HUGS

GA No. 675325

ACS Sustainable Chemistry & Engineering

Research Article

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Insights on Thermal and Fire Hazards of Humins in Support of Their Sustainable Use in Advanced Biorefineries

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Spotlight

Biofpr Biofuels Bioproducts & Biorefining

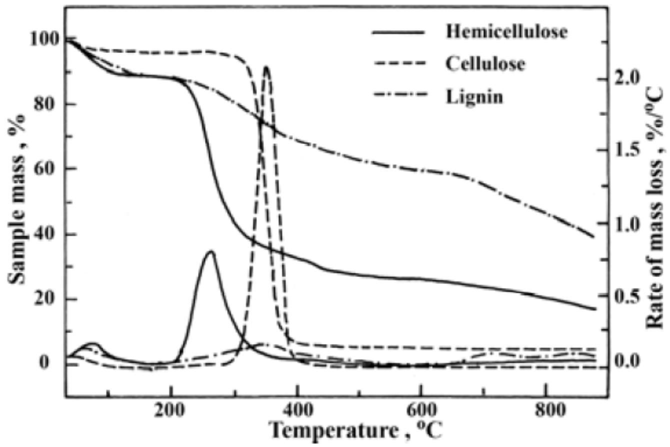
Humins in the environment: early stage insights on ecotoxicological aspects

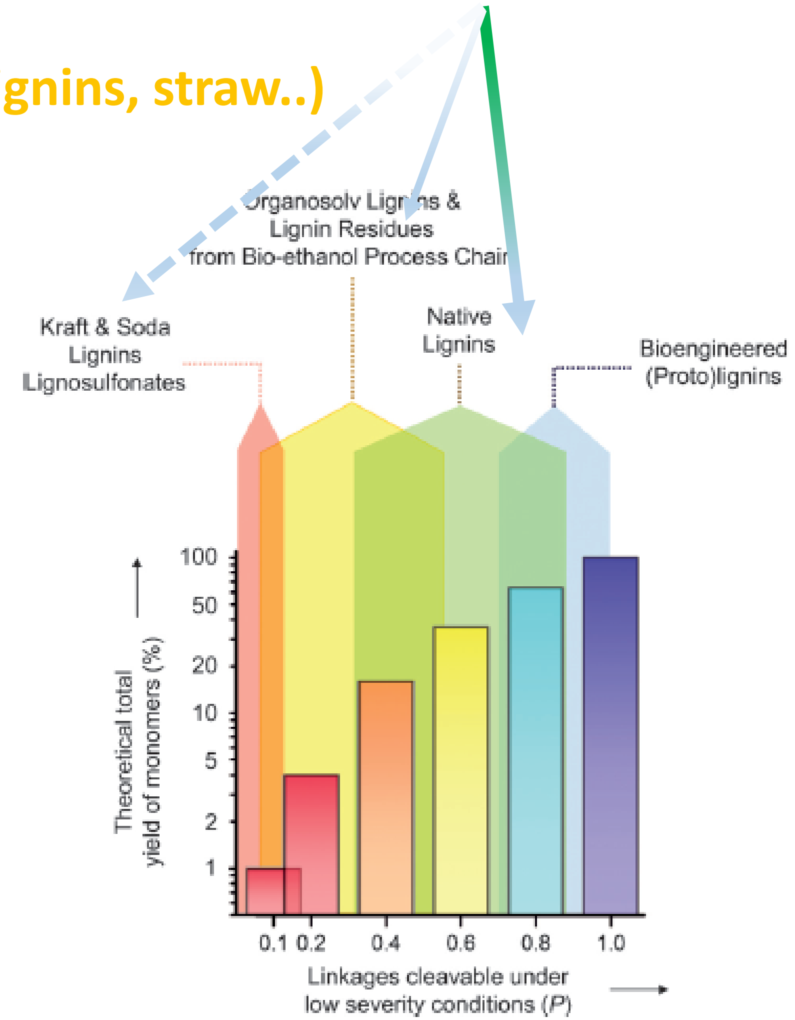
Anitha Muralidhara. Accidental Risk Division. Institut National de l'Environnement Industriel

Lignins specific characteristics

ZELCOR
& EUCALVIA
projects

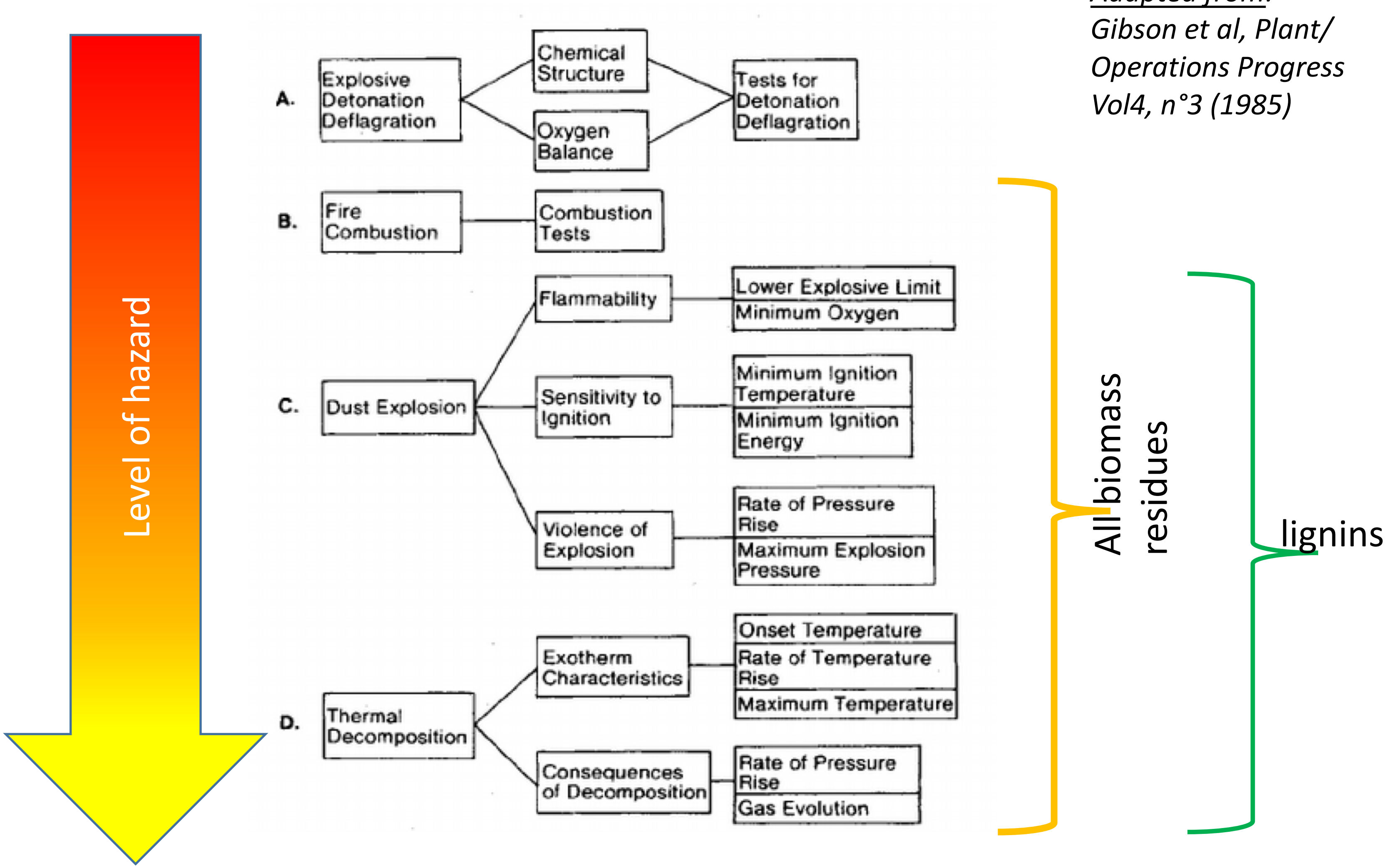
- Important properties depending on:
  - **upstream pretreatment processes**
  - **biomass of origin (soft or hard wood lignins, straw..)**
  - **technical lignins may or not contain S**
  - **structural differences according to various ether and C-C bonding**
- Char forming thermal degradation due to high level of aromatics





Safety thinking with biomass residues

Adapted from:
Gibson et al, Plant/ Operations Progress Vol4, n°3 (1985)



lignin reactivity induced main physical hazards

➢ Thermal and explosion hazards

○ self-heating hazard (thermal stability)

- similar hazard as for some hazardous chemicals
  - ✓ Classified in Division 4.2 for transport and self heating substances in CLP
- Often critical with many biomass in divided form
- Known to lead to spontaneous ignition in large storage facilities

Hazard Statement	Hazard Symbol	Transport Symbol
Self-heating; may catch fire.		
Self-heating in large quantities; may catch fire.		

○ Dust explosion hazard

- Risk pertaining to both organic and mineral matters, when combustible and in powdered form
  - ✓ Some ~5% of all explosions
  - ✓ A major source of concern in USA
- Long history of accidents with grains in silos, also with sulfur, sugar, metal powders, wood saw

lignin reactivity induced other hazards

- Health and environmental hazards
  - **Risks due to micro-organisms like bacteria and fungi**
  - **Process-driven ecotoxicity potential issues**

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Cytotoxicity and biological capacity of sulfur-free lignins obtained in novel biorefining process

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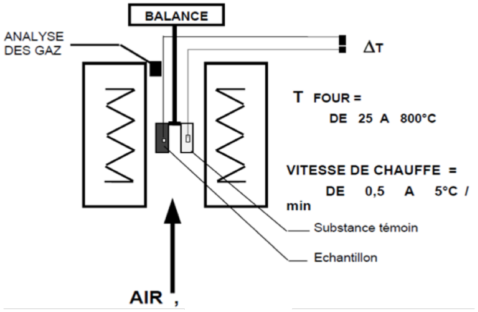
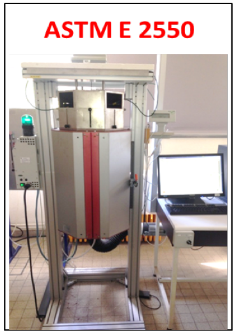
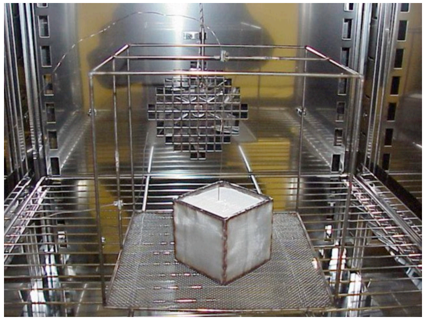
Self-heating experimental assessment

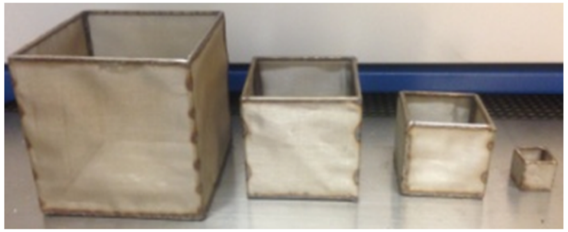
- DSC and DTA/TGA tools for screening purposes can be used
  - Search for an exotherm over 50°C
    - three classes A, B, C of criticity determined
    - Class A (exotherm seen below 250°C requiring detailed analysis)
    - Class C (no exotherm before 400°C°)
      - ✓ Self-heating risk negligeable (most often)

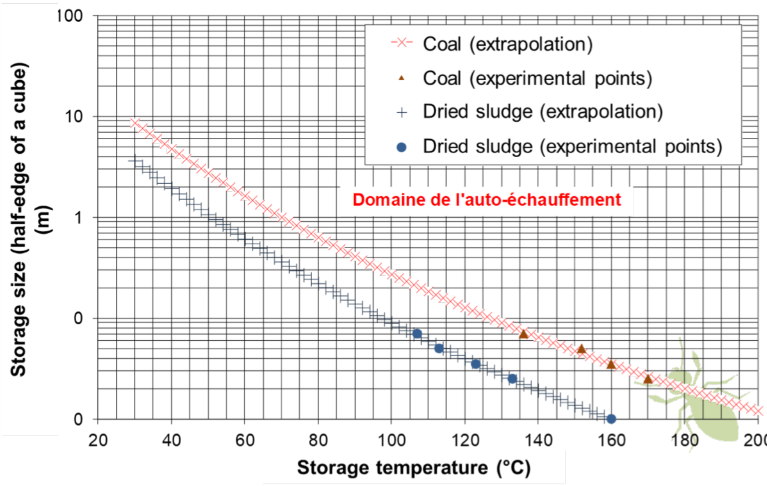




- 'Basket tests' for detailed analysis of self-heating
  - NF EN 15188 isothermal oven tests with various basket sizes

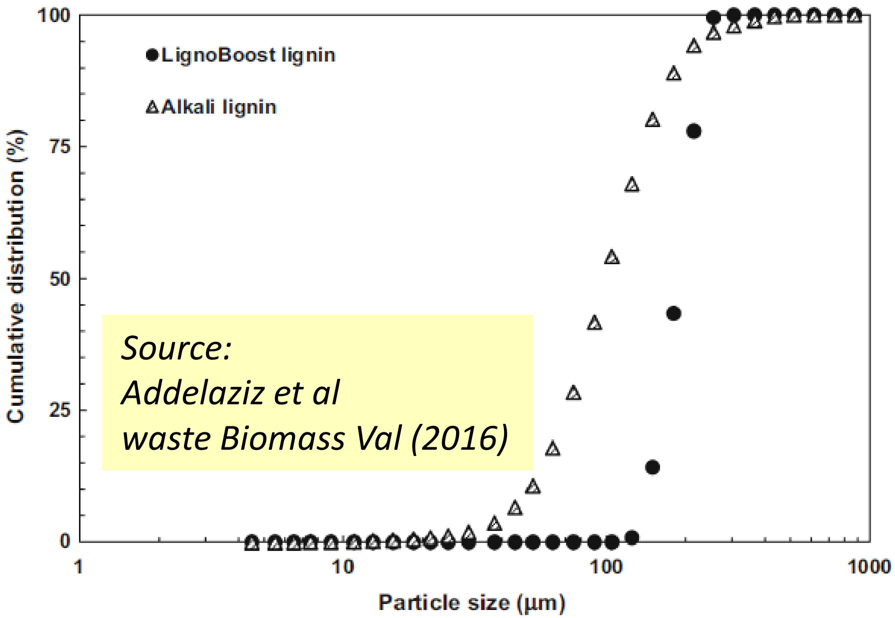






Dusts (powders) suspended in the air: when to consider the explosion hazard ?

➢ Particle size distribution < 0,5 mm



Source:
Addelaziz et al
waste Biomass Val (2016)

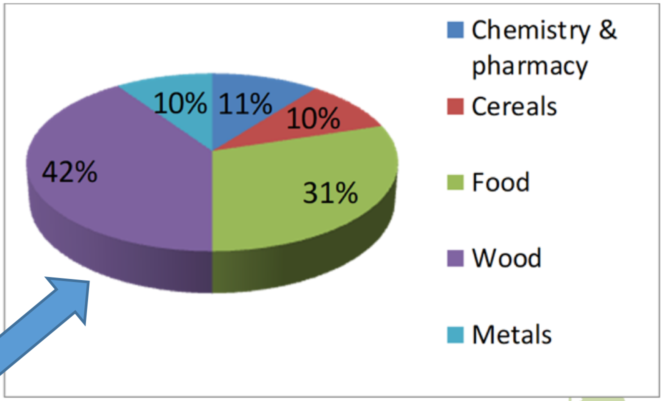
➢ Origin in biorefineries:

- Feed, finished of intermediate products
- Residue/waste processing
- Abrasion of solids (when crushing, milling)

Dust-explosion driven disasters with biomass

3500 dust explosion cases over 28 years in USA (1980-2007), 281 of them rated as disasters, 118 deaths, > 700 injuries

Date	Place	Plant	Consequences
1982	Metz (East region)	Barley storage silo	12 fatalities Significant damage (20 M€)
1997	Blaye (West region)	Grains storage silo	11 fatalities Significant damage
2008	Imperial Sugar, Port Wentworth (GA, USA)	Sugar Plant packaging building	14 fatalities, 38 injured Significant damage



Out of 183 severe cases (1903 – 2007)

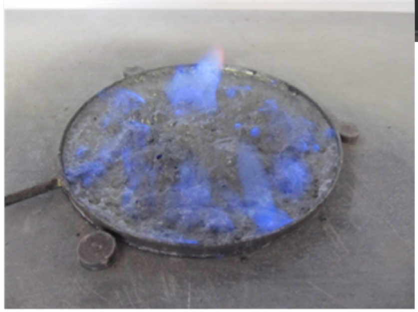
Experimental assessment of fire & explosion hazards of lignins (all BRs)

- The main parameters used to characterize flammability and explosivity of a dust or a powder are:
  - Lower explosion limit (LEL)
  - Minimum ignition temperatures (MIT) in layer /in cloud
  - Minimum ignition energy (MIE)
  - Violence of explosion criteria in a confined environment (Kst, Pmax)
  - Limiting oxygen concentration (LOC)
- Additionnally we may use:
  - Fire propagation German test (BZ classes from BZ1 to BZ6)
    - Abiliy of a strip of material to propagate a fire from local ignition
  - Fire calorimeters
    - Fire behaviour, combustion speed, HRR, emissions…
      - ✓ Cone Calorimeter ISO 5660, FPA (Tewarson) ISO 12136

Dust critical temperatures determination

- **Minimum ignition T in cloud**
  - Godbert-Greenwald oven
- **Minimum ignition T in layer**

EN 50281-2-1



5 mm layer of material deposited on a heated surface at 410 °C, after 30 min

Lower Explosion Limit (LEL)

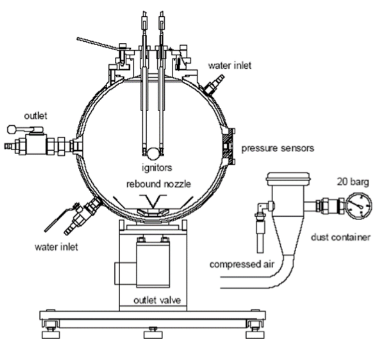
- About 30 to 50 g/m3
- Less than 1mm dust layer deposit
- Measured in 20L sphere
  - or ISO 1m3 vessel
- (also used to severity of explosion)

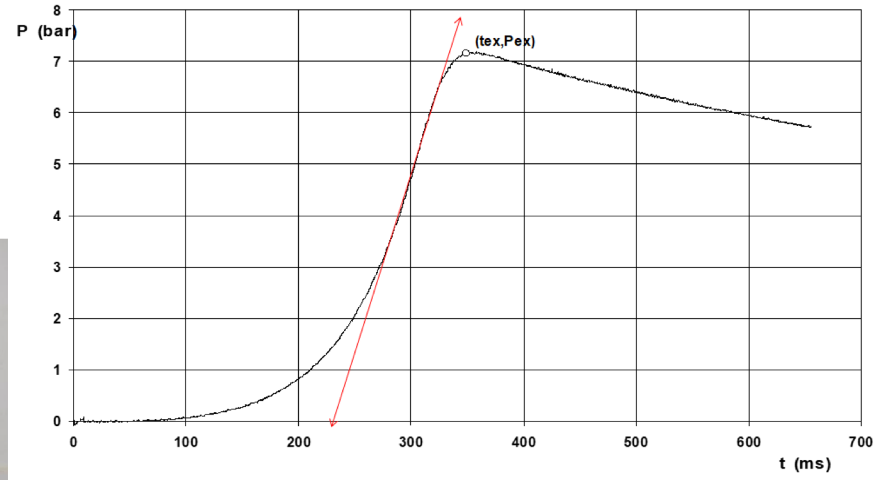
Minimum ignition energy (MIE)

EN 13821
MIKE 3 apparatus

dust explosion severity characterization

- Maximum explosion pressure: P_{max}
- Mamimum rate of explosion pressure rise: $(dP/dt)_{max}$





Cubic law: $(dP/dt)max\ V^{1/3} = K_{st}$

20L sphere apparatus
EN 14034-1/2

Lignins ?

Dust Explosion Classification	Deflagaration index Kst (bar.m/sec)	Qualification	Typical Materials
St-0	0	No explosion	Silicia, Sodium Bicarbonate
St-1	0-200	Weak to moderate explosion	Carbon, Sulphur, sugar and Zinc
St-2	201-300	Strong explosion	Cellulose, wood and polymethyl acrylate
St-3	>300	Very strong explosion	Aluminium and magnesium

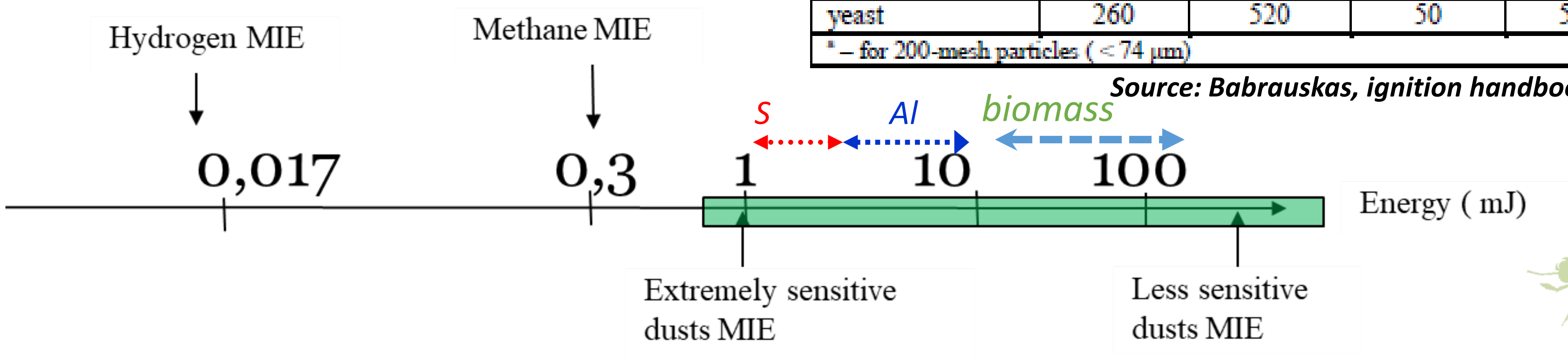
Ignition properties of agricultural dusts

- AIT variation (in layer):
  - 180°C to 440°C
- AIT variation (in cloud):
  - 370°C to 720°C
- MIE (mJ)
  - 25 to > 300
  - Higher than for gases
- LFLs (g/m^3)
  - 20 to 50 (up to >100)

Substance [a]	Ignition temp. (°C) Layer	Ignition temp. (°C) Dust cloud	Dust cloud MIE (mJ)	LFL (g m^{-3})
alfalfa meal	220 - 260	470 - 620	320 - 5100	105
cinnamon	230	440	30	60
cocoa	200 - 390	420 -510	100 - 180	45 - 75
coffee	270	720	160	85 - 150
cork	210 - 280	460 - 490	35 - 100	35 - 50
cornstarch	330 - 380	380 - 430	30 - 60	45 - 55
cotton linters		520	1920	50
flour, cake	230 - 320	450 - 490	25 - 80	55 - 65
grain dust	230	430	30	55
grass seed	180	490 -530	60-260	140-290
lycopodium	310	420	50	70
peat, dried	240	460 - 470		
potato starch		440	25	45
rice	220 - 480	440 - 520	40 - 120	50 - 180
soy flour	190 - 340	540 -550	100 - 460	60 - 140
sugar, powdered	400	370	30	45
wheat starch	360 - 440	380 - 440	25 - 60	45
wood bark	250 - 270	450 - 540	40 - 60	20
wood flour	260 - 300	430 - 470	30 - 40	35 - 50
yeast	260	520	50	50

[a] – for 200-mesh particles (< 74 µm)

Source: Babrauskas, ignition handbook



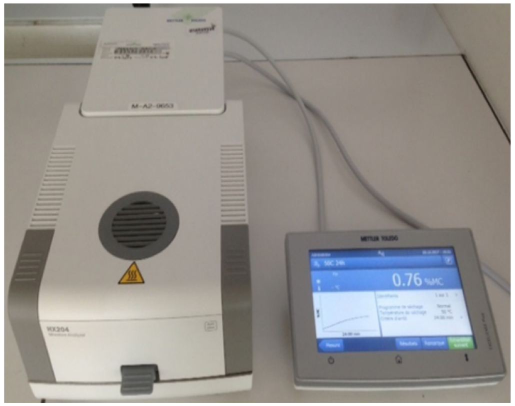
Known influencing parameters of powders/dust fire and explosion hazards

- ***Physico-chemical characteristics***
  - ***Humidity content***
  - ***Particle size distribution***

- ***Other parameters worth being explored:***
  - **Heating Value (HHV)**
  - **Density ?**
  - **Others ?**
    - **Other considered in ZELCOR project**

Particle size distribution
Liquid or dry phase determined by laser diffraction – Malvern 3000E

Moisture content
Moisture Analyzer - METTLER HX 204



Parr instrument 6100
(oxygen bomb calorimeter)

Published data on fire and explosion hazards of lignins

- **From the open source database GESTIS-DUST EX**
  - https://www.dguv.de/ifa/gestis/gestis-staub-ex/index-2.jsp
  - **> 7000 dust samples listed, only… 5 entries for lignins**

search for : **lignin** / number of results : **5**

material	median value [µm]	explosibility	minimum ignition energie [mJ]
Animal feed binder (lignine sulphonate, potato water concentrate)	83	St 1	
Aquatic Fulvic Acid (20%)/ Ammonium Ligninsulfonate (80%)	44,8		
Lignin	<63	St 1	
Lignin	18	St 2	
Sodium lignin sulphonate	<58	St 1	

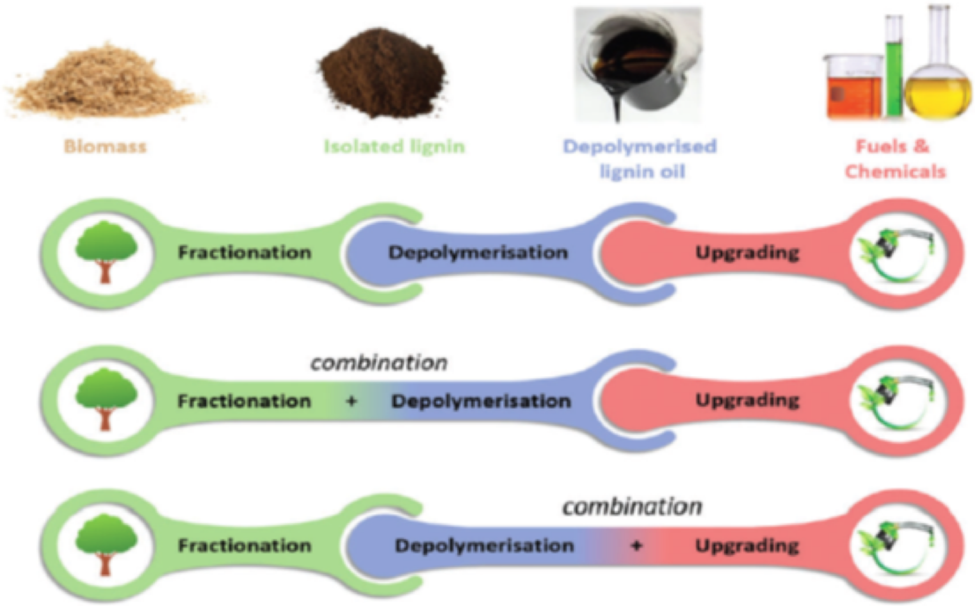
Literature values for lignins

	Hazardous chemical handbook – lignin Carson & Mumford	Safety data sheet – kraft lignin @domtar	Beck et al, BIA report
Average particle size D50	NA	NA	NA
Humidity content (%)	NA	NA	NA
Max explosion pressure (Pmax)	7.3 bar	7.6 bar	8.7 bar
Max. rate of pressure rise : (dP/dt)max	NA	684 bar/s	NA
Product specific constant (Kst)	210 m.bar/s St-2	186 m.bar/s St-1	208 m.bar/s St-2
Minimum Ignition Energy (MIE)	10-100 mJ	500 mJ	NA

- **Further research clearly desirable in support of safe and sustainable lignin biorefining -☺**
  - **Clearly associating the measurement and the archiving all parameters of interest**

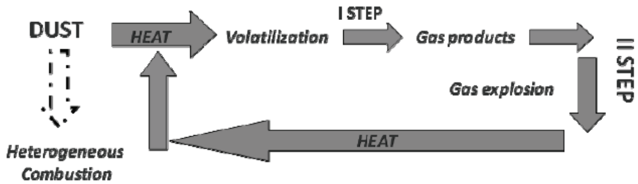
Further considerations towards future sustainable biorefining

- Safe biorefining from lignin as a feed or with biomass residues with zero waste concept much more than simple flammability characterization of biomass residue feed !
  - **Fast innovation may lead to emerging risks…**
  - **Cascading approach requiring testing all intermediates,**
  - **Use on unconventional bioreactors…**



Conclusive comments

- **No unique ‘lignin’, but many lignins ‘ to consider for their safe valorization**
- **Some safety related data on lignins existing, rarely published with appropriate characteristics of interest**
  - We clearly lack enough (reliable) data as compared to lignin diversity
- **Need to continue consistent characterization of technical lignins**
  - with appropriate archiving of all influencing parameters
  - targeting the development of predictive models highly desirable or all important safety data
    - Physical modeling ?
    - (QSPR approach ?)



- **As a residue, little chance lignins to be optimized for whatever reason,**
  - **so careful check versus time of safety related properties needed at regular intervals**

Thank you for your attention !

- Guy.marlair@ineris.fr
  - Technical Advisor at INERIS
  - Senior Research Scientist (HDR)
  - Also chair IEC TC120
    (Electric Energy Storage Systems)

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