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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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KEYWORDS. Humins, thermal and fire hazard analysis, biorefinery, byproducts valorization, calorimetry

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ABSTRACT. The concept of circular economy is aiming at promoting innovative use of wastes, residues or by-products into marketable chemicals and intermediates, while enhancing process economics and environmental sustainability. Within biorefineries, the focus has now shifted towards "humins", polymeric condensation by-products far less investigated than lignins. Humins are produced in many bio-based value chains that start from polysaccharides pre-treatment, targeting access to C6 and C5 sugars and further conversion to furanics or levulinics based platform chemicals. They are complex and versatile substrates, and combustible since of organic nature. A first insight on safety issues of humins is therefore proposed in this paper, considering the growing interest on humins as new bio-based feedstocks for various applications. The current study provides characterization details necessary to establish safety information on a global context. This first attempt has brought in preliminary safety data mainly focusing on thermal and fire hazards of humins, to ensure safe storage, handling, transportation and processing. The obtained results show that, overall fire risk of humins so far is similar to the conventional cellulosic fuels such as woody materials. Further consolidation of safety information shall be done with scenario-based risk assessment approach for conditioning safe use of humins in further innovative applications.

INTRODUCTION.

Humins are heterogeneous condensation by-products produced by random polymerization processes during the acid catalysed dehydration (ACD) of sugars (Figure 1). [1,2] Humins formation is known to the scientific community since almost a century through the caramelization process of sugars. Their formation, so far unpreventable, is the principle drawback of ACD process resulting in loss of feed, reactor fouling and other engineering challenges.[3,4] From a technical viewpoint, three strategies are possible to cope with these challenges linked to production of humins: (a) optimizing the ACD process targeting the minimization of humins production; (b) converting humins into energy to satisfy a substantial part of the energy demand of the biorefinery; (c) integrating humins as a potential valuable carbon source and additional feedstock for new bio-based chemicals, biomaterials or additives of interest. No major breakthroughs were achieved with option (c) [5] therefore, for a long time, option (b) was the unique industrially applied strategy, while nowadays, despite remaining technical challenges, economic considerations and promising recent research advances [6,7] justify a move to option (c).

Considering the real industrial scale ACD of hexoses, humins should be considered more like a mixture. The genuine chemical structure of humins is still under investigation, but seems to be constituted mainly by a furan-rich skeleton containing furfural in an extended conjugated C=C network decorated of several functional moieties. [8–10] Hydroxymethylfurfural (HMF) and derivatives, along with levulinic acid (LA) and other by-products of the ACD process can be present as impurities in the mixture and influence the viscosity.[18] Humins might possess various reactive functional groups such as aldehyde, ketone, hydroxyl and/or carboxylic. However, other functional groups such as alkoxy and ester can be instigated due to side reactions.[4,6,12] The

degree of branching and molecular mass of humins oligomers vary depending on the process and feedstock conditions, with sub-units and structures repeated and connected in a random way. This challenging context has essentially limited industrial uses of humins to energy and/or power conversion through gasification or combustion, however clearly identifying their energy content and combustible nature.[13,52,54]

Some studies have highlighted the potential of humins in catalysis, water purification, energy storage, CO_2 sequestration,[14–16] but also as new bio-based thermosets materials, matrix for impregnations and in producing co-cured composite materials.[6,17] The last case explores the flame retardancy properties of humins (semi-protective char) that reduces the rate of thermal degradation compared to the normal unsaturated polyesters.[18] Furthermore, when crude humins are heated to temperature > 180 °C, they can foam into reticulated, rigid macroporous carbon based material.[19] These foamed humins with versatile potential applications are emerging as a promising alternative in terms of reducing the available quantity of crude humins.

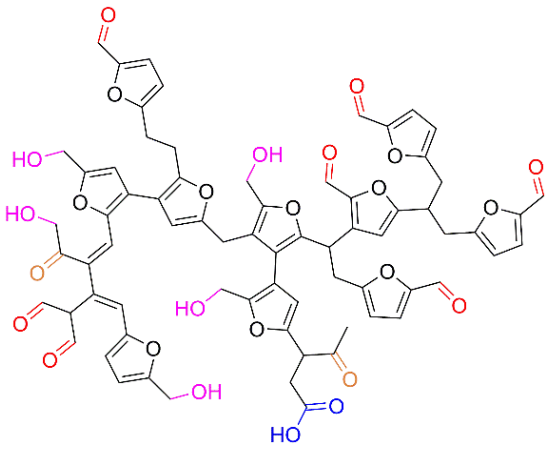

Figure 1. Humins molecular structure model proposed by Van Zandvoort et al. (2013).

Owing to the complex and versatile chemical structure of humins and subsequent wide variety of physico-chemical properties, the safety profiles, and accordingly the nature and intensity of risks may significantly vary during existing and/or innovative uses.

So far, as a residue used in the production site, Humins' conventional hazards are not recognized by any official hazardous material classification systems quoted in the following references. [20–22] Neither there is a definite description of their physico-chemical properties (apart from tentative efforts of some production stakeholders), nor consensual information made available regarding precautions requested for their safe handling, use, storage or conversion. One of the main reasons behind this is the lack of complete characterization of humins.

Therefore, as a feedstock of growing interest, both crude and foamed humins (obtained by thermal curing) [18,23] must be appraised beyond legal requirements more globally in terms of physico-chemical hazards for their safe utilization. Anyway, accessing full characterization of physico-chemical , health and environmental hazards of these products would be a prerequisite for obtaining "end of waste status" according to the EU's waste framework directive.[24]

In addition, due to intrinsic limitations of conventional hazard rating making use of threshold values to fix regulated boundaries, substances or mixtures that are not identified as "dangerous" from hazardous materials classification systems may still induce fire or explosion risks, corrosive or oxidative environments, or trigger some toxic and eco-toxic risks depending on their context of use.[25] Product and process safety performances must be assessed all along the value chain of humins, not only to take all types of risks (physico-chemical, health and environment) under control, but also to seek competitive advantages.

Besides addressing the conventional risks, key safety concerns shall also be appraised in humins valorisation routes, [4,6,19,26] which may otherwise lead to an explosive atmosphere (ATEX) under unforeseen circumstance. Examples such as transformation requiring thermal curing of crude humins, handling or transforming foamed humins leading to dust production, pumping crude humins under pressure, impregnation of humins for developing composites, would justify a detailed characterization of fire and explosion hazards (ease of ignition, flammability limits, dust explosion hazard profile, self-heating characteristics and reaction to fire performance of end products).

In addition, thermal stability, hot spot ignition hazard,[27] speed of combustion, type of surrounding environment, conventional methods of storage and disposal, safety training to the employees, , are some of the governing factors that must also be considered in further evaluation of associated risks during the use and applications of humins.

This is a dedicated research for filling the existing data gaps and developing insights on physico-chemical characteristics of humins and related safety parameters (such as ignitability, flammability or combustible behaviour), that will condition inherently safer and eco-friendly processes for their sustainable valorisation.

MATERIALS AND METHODS

Humins samples. Crude humins were produced in 2016 in the intermediate step of the FDCA production process in the processing plant of Synvina C.V.,[27] operating in Geleen. They are a high-viscous dark colored material (Figure 2a). The molecular weight of Synvina humins has been reported in another study ranging between 270-650 g mol $^{-1}$. [53]Foamed humins (Figure 2b) were prepared in a Nabertherm K430/75 dTRON oven under air ventilated conditions, by placing 1 kg of crude humins in a disposable aluminium pan was heating up to 250 °C with 5 °C·min^{-1}

ramp, kept to 250 °C for 1 h, then cooled down to room temperature at 10 °C·min^{-1}. Mass loss of ~ 20 % was recorded after treatment of crude humins in such conditions. Elemental composition of both crude and foamed humins was obtained by Inductively Coupled Plasma (ICP) by Mikroanalytisches Labor Pascher, Remagen, Germany.

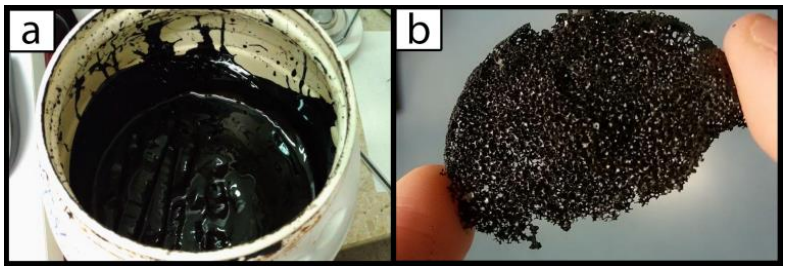

Figure 2. Visual aspect of a) crude and b) foamed humins used in the experiment.

Chromatographic analysis of raw humins.

GC analyses were performed with a TRACE GC instrument from Interscience, equipped with a FID detector and a column VF WAXms, 0.25 mm id film thickness 0.25 µm, 30 m. 1 µl of a solution obtained by dissolving humins into a mixture acetonitrile/H2O 50/50 w/w was injected and analysed, while dioxane was used as standard in both calibration and samples.

UPLC analyses were performed with a column from Waters, model Acquity UPLC HSS C18, 2.1x100 mm, 1.8 µm, equipped with UV and ELSD detector and maintained at 50 °C. Sample mass of 3.5 µl was injected and analysed using 0.2 % TFA in H_2O and ACN/MeOH 50/50 (0.4 mL·min^{-1}) as eluents. Saccharine was used as internal standard (measured at 250 nm)

Differential Scanning Calorimetry (DSC).

Thermal analysis was performed using the DSC apparatus from SETARAM, model 131 evo, computer controlled by the software Calisto. Temperature and enthalpy calibrations were performed by using indium, tin, lead and zinc standards.

Humins sample of 3.1 mg was prepared upstream and introduced into a high pressure stainless steel crucible of 30 μL volume. The crucible was then sealed under air, and introduced into the furnace of the calorimeter along with an empty crucible of the same nature serving as a reference. DSC scans were performed in the temperature range 25 °C - 500 °C with a heating ramp of 5 $°C \cdot min^{-1}$. A straight baseline has been used for thermograms.

In the result section T_{start} corresponds to the first integration bond, $T_{reaction}$ corresponds to the first and last integration bounds and T_{onset} corresponds to the slope for the first part of the peak.

C80 (Calvet) Calorimeter.

C80 CS evo from SETARAM, computer controlled by the software Calisto was used as confirmation test due to its higher sensitivity than standard, first generation DSC.Temperature and enthalpy calibrations were performed by using indium, tin and potassium nitrate. 960 mg of crude humins and 161.8 mg of foamed humins samples were prepared upstream and introduced into a high pressure stainless steel cell, integrating an internal glass crucible. These quantities corresponded to the physical nature of samples with respect to the maximum available volume in the sample holder. Once closed, the crucible was introduced into the furnace of the calorimeter along with an empty crucible of the same nature that is serving as a reference. C80 scans were performed in the temperature range starting from 25 °C up to 300 °C using a heating ramp of 1 $°C \cdot min^{-1}$.

Thermo-gravimetric analysis (TGA).

TGA results were obtained using a Mettler Toledo TGA/SDTD 851e instrument. The microbalance has a precision of ± 0.1 μg and is kept at constant temperature (~22 °C) during analyses in order to avoid its weight variation with temperature 12 mg of crude humins were placed in 70 μL alumina pans. The samples were heated at 10 °C·min^{-1} rate in the range 25 °C-1000 °C under air and nitrogen gas flow of 80 mL· min^{-1} to determine the thermal behavior of humins.

Foamed humins samples were subjected to TGA-DTA (differential thermal analysis) under oxidative environment. This is a purpose-built instrument designed by INERIS (allowing application of test method ASTM E2550)[29] for further assessing the thermal hazard characteristics of solid samples (Figure 3). An interesting feature of this equipment [30] is the use of sample mass in the order of 1 g or more, largely over the classical milligram sample mass used in conventional laboratory scale TGA-DTA commercial instruments. Besides providing both mass loss and thermal decomposition, sample size also allows its use as a screening test for self-heating issues.

Test sample is placed in a small container made from wire mesh; an inert reference substance alumina is placed in an identical container. Both containers are introduced at ambient temperature into an oven and heated at a fixed rate (5 °C·min^{-1}).

Figure 3. Large scale simultaneous TGA-DTA instrument built at INERIS.

The variation of the mass of the sample is recorded as a function of time with an electronic balance. The temperatures of the sample and of the reference are also recorded as a function of time. An air flow of 440 $Nl \cdot h^{-1}$ preheated to the oven temperature is maintained. Under these conditions, comparison of sample and reference temperatures shows whether endothermic or exothermic phenomena occurring during the heating in a semi-quantitative way.

Fire Propagation Apparatus (FPA).

The fire behavior of humins was tested using FPA (Figure 4), commissioned at INERIS in 1997.[31–33] This apparatus is used as a polyvalent equipment to characterize the fire behavior of various compounds under fire scenarios and associated thermal and chemical risks (e.g. fire-induced toxicity). FPA is covered under various national and international standards, namely FM 4910, NFPA 287,[34] ASTM E2058,[35] ISO 12136,[36] and TR 16312. [37] The apparatus is also known as Tewarson Calorimeter from name of early designer. It is capable of measuring ignitability, fire propagation potential, thermal and chemical characteristics of materials in fire conditions. This is

a bench-scale multipurpose testing apparatus belonging to the family of fire calorimeters that has proven repeatability and reproducibility performances.[38]

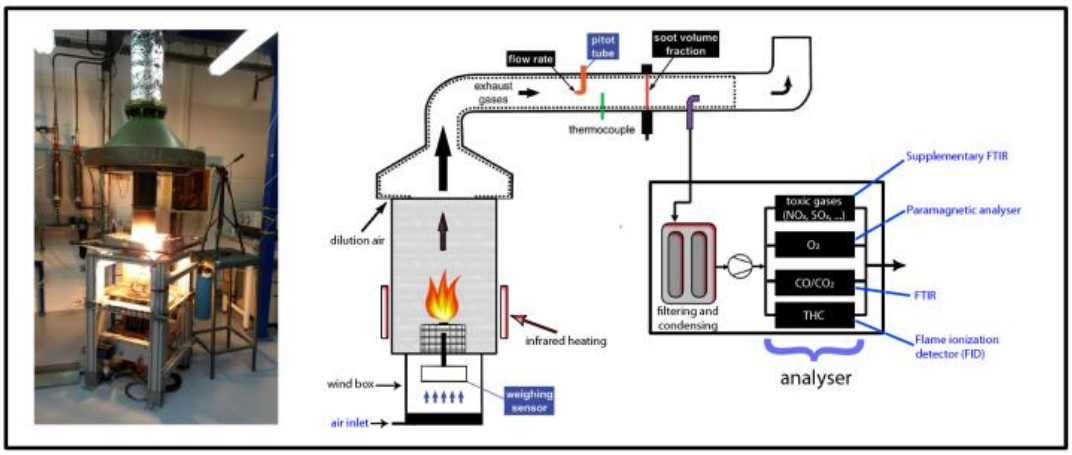

Figure 4. In operation and schematic view of INERIS Fire Propagation Apparatus.

The INERIS FPA is fitted with a Thermo-Fisher Fourier transformer Infra-red (FT-IR) allowing the measurement of many gas species responding in the infrared spectrum. Sample mass of about 20 g to 40 g is usually considered for testing chemicals under controlled gas flow in which characterization of test sample (liquids or dense or divided solids) can be made in fuel rich or fuel lean environment to cover the full spectrum of fire conditions (well-ventilated to under-ventilated). Measurements such as mass loss rate, heat release rate, ease of combustion and yields of combustion products for evaluating fire induced toxicity are made by modern fire calorimetry relying of the assessment of Oxygen consumption (OC) or Carbon Dioxide Generation (CDG).[39] Such measurements give a broader view of the material's response to fire that facilitates a sound scientific diagnosis. Exploration of the full spectrum of ventilation conditions can be done through adjustment of inlet air flow and control of actual ventilation

conditions through determination of real time equivalence ratio (phi factor) [31] which reflects actual fuel versus oxygen ratio normalized by same ratio at stoichiometric conditions.

In the present study, preliminary tests were performed to choose the most suitable operating conditions for ignitability and fire propagation in well-ventilated fire conditions. Humins samples of about 20-21 g were placed in a glass sample holder. An external heat flux of 25 $kW \cdot m^{-2}$ was set in operation by four infrared heaters housed in air and water cooled jackets, allowing piloted ignition of the sample under calibrated heat stress by use of an electric spark or a pilot flame. Combustion gas analysis was performed by the online FT-IR Spectrometer calibrated over 20 gases for derivation of CO_2, CO, SO_2, NOx, HCN, and other species concentrations and relating release rates versus time. In addition, using sample mass loss data, and overall exhaust flow rate measurement, yields of relating emissions may be derived.

RESULTS AND DISCUSSIONS

Crude and foamed humins underwent thermal stability tests determined by DSC, C80, and TGA, while self-heating tests using TGA/DTA. Qualitative and quantitative reaction-to-fire behaviour (e.g. heat and mass release rates, yields of combustion products, duration of combustion) was examined by Tewarson Calorimeter.

Characterization of humins samples.

Several batches of industrial humins [10] were produced via ACD process. Among these, 2 humins samples reflecting the largest variation of observed chemical composition were selected for testing. Along with humins oligomers, an amount of HMF and its alkyl derivatives in these 2 samples have been found between 9 % and 13 %. LA was found between 1.2 %and 1.6 %.

The results discussed further are focusing on these 2 samples of crude humins (humins a and humins b) and another first sample of available foamed humins. Therefore, the results obtained should be considered as early information in the field of study that will require statistical consolidations in line with further process optimization.

It is worth mentioning that foamed humins (obtained by subjecting crude humins to a foaming treatment at 250 °C) differ significantly both physically and chemically from crude humins as reflected by elemental analysis results (Table 3) with values that are consistent with other humins compositions reported in the literature. [12] The efficiency of foaming process in terms of carbon mass intensification (17 % increase in carbon mass fraction compared to crude humins) is obtained at the expense of 25 % of hydrogen and 24 % oxygen mass fractions respectively. Thermal curing of crude humins to obtain foamed humins also affects the material's energy content. By using Bioe correlation [40] to reasonably predict energy values for biomass materials, [41] the heat of complete combustion increased from 20.2 $kJ \cdot g^{-1}$ for crude humins to 23.8 $kJ \cdot g^{-1}$ for foamed humins.

Thermal hazard analysis: DSC and C80 calorimetry.

Crude and foamed humins were subjected to both DSC and C80 analysis and corresponding results were compared (Figure 5a and 5b). For crude humins a wide exothermic thermal event composed of at least two peaks is observed in DSC and C80 starting at around 100 °C - 125 °C. It ends at around 300 °C in DSC and at a lower temperature in C80 which can be explained by the lower heating rate used in this case. This event could correspond to residual crosslinks, self-condensation or vaporization of monomers and is observed for both DSC and C80. The first event close to 150 °C is in good agreement with the first mass loss observed in TGA at around 150 °C. Another exothermic thermal event is observed between 300 °C - 400 °C in DSC. It

occurs at higher temperature for Humins b (300 °C - 400 °C) as compare with Humins a (300 °C - 350 °C). This event is in agreement with the inflexion of the TGA curve observed between 300 and 400 °C. At a temperature higher than 400 °C, the DSC curve shows the starting of increase of the baseline that correspond to the thermal degradation and which is confirmed by the mass loss observed in TGA at this temperature.

Foamed humins showed much less reactivity. The first baseline deviation could correspond to the glass transition, which was confirmed after careful check of calibration tests. An exothermic thermal event is observed at around 150 °C for both DSC and C80, but ends at much higher temperature for C80. This could be explained by a higher amount of residual volatilization of organic compounds in C80 because of the higher sample mass and higher free volume in the pan. Thus, the thermal event observed in C80 could be the sum of the two thermal events observed in DSC between 140 °C and 270 °C, i.e. the first event starting at around 150 °C and the second one, much lower starting at around 200 °C. Finally, an with a single exothermic peak between 263 °C and 337 °C with a T_{onset} value of 273 °C (Figure 5b) is observed in DSC that could correspond to the beginning of the thermal degradation of the sample.

Table 1. Start and onset temperatures and heats of decomposition of crude and foamed humins determined by DSC experiments.

Substrate	**T_{start} (°C)**	**$T_{reaction}$ (°C)**	**T_{onset} (°C)**	**ΔH_d ($J \cdot g^{-1}$)**
Crude humins a	143	143-352	173	-505
Crude humins b	132	132-318	165	-402

Foamed humins	263	263-337	273	-70

For crude humins, in both test methods, i) the decomposition reaction starts earlier due to the volatilization of lower molecular weight compounds and ii) the complexity of reaction mechanisms developing is reflected by the double peaks appearing in the thermogram.

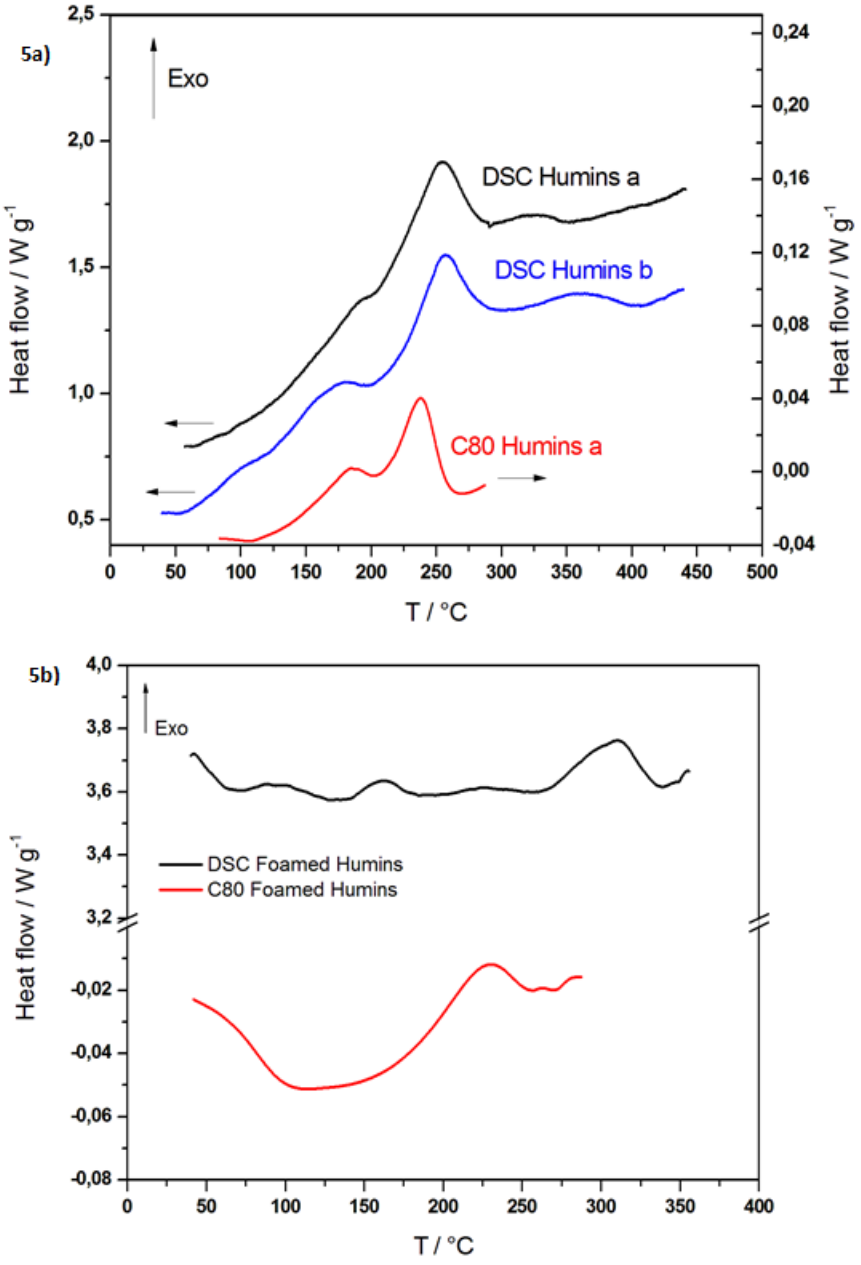

Figure 5. Comparison of DSC and C80 results for a) crude humins and b) foamed humins.

Despite their common origins, the energy levels observed from exothermic decomposition of foamed humins are significantly lower than crude humins.[42] Foamed humins were initially subjected to thermal curing during their preparation, where they underwent partial

oxidation/transformation.[18] This initial thermal curing has contributed to self-crosslinking of humins macromolecules through the functional groups present in humins' structure. These chemical reactions contributed to a better thermal resistance and in turn better thermal stability in foams than crude humins.

For foamed humins, the range of temperature in which thermal decomposition occurs in DSC experiments significantly exceeds the maximum operating temperature explored in C80 (300 °C). This does not render a detailed comparison between the DSC and C80 results.

C80 also operates with a larger sample mass and a smaller heat ramp than DSC. It has been observed that, when solid mixtures are studied, sample size has potentially a great influence on results and the question to be addressed is about the homogeneity of samples used from similar batches of available representative samples.[43] Heterogeneity of samples subjected to different operating conditions might slightly shift the results which are depicted by the slight variation in the range of exothermic peaks in C80 and DSC. Differences in the way pressure may build up in the closed vessels used in the experiment may also be part of the explanation of the observed differences as pressure may affect reaction kinetics. Nevertheless, these variations are not significant and the same was also confirmed during the sample selection.

Thermal stability is not an intrinsic property of any material since apparatus and criteria dependent. As a first statement relating to this aspect, our work allows to conclude that humins thermosets do not entail critical self-heating behaviour. This is an early clearance for storage and transportation of such materials. End use of humins and humins based materials deserve a more detailed evaluation of thermal stability properties depending on the context of use. Similarly, process conditions during the production of crude humins must be considered in further evaluation of thermal stability characteristics.

TGA and TGA/DTA.

The profile of thermal stability of crude humins can be observed by the TGA (Figure 6). Three steps of mass loss could be observed under air and only two under N_2.

A first mass loss of ~ 36 % is observed between 120 and 270 °C in both the conditions, probably due to volatilization of low mass molecules and products of self-condensation. Another mass loss of around 20 % occurs under air in the interval 290 °C - 400 °C, while is barely present under N_2 (~ 7 %). A last mass loss of around 45 % leads to the complete thermo-oxidative degradation of humins under air between 400 °C and 600 °C. Under N_2 the mass loss recorded between 400 °C - 1000 °C is only around ~ 22 %, giving a final residual product of ~ 26.3 %.

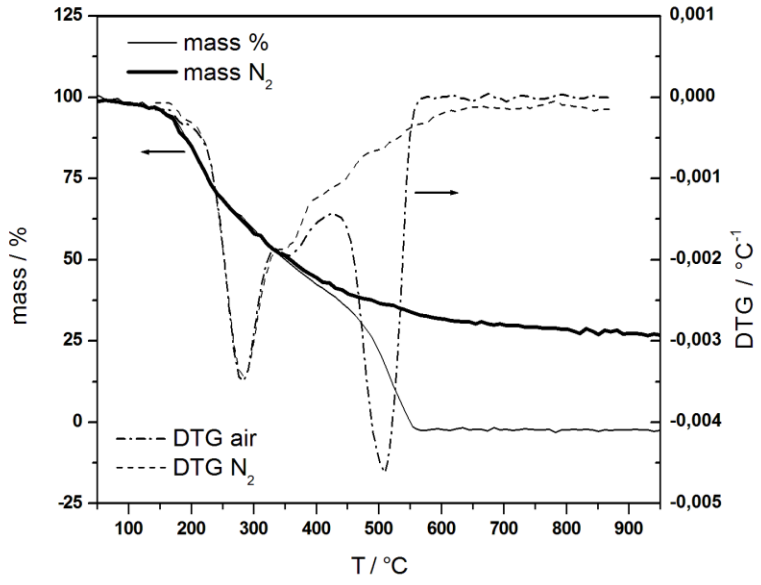

Figure 6. TGA and DTG results for humins in dynamic conditions between 25 and 1000 °C with a ramp of 10 °C·min^{-1}. Gas flow: 80 mL·min^{-1}.

On the other hand, once formed by thermal curing, foamed humins gain thermal stability in function of the temperature used during their preparation. Foams prepared at 250 °C, for instance, gives a mass loss phenomenon only above 150 °C, with only 10 % of mass loss at 290 °C, while thermo-oxidative degradation occurs above 450 °C, possibly leading to ignition We can suppose that if foamed humins are prepared at temperatures higher than 250 °C, all the effects herein observed will result in further delay due to the natural increase in carbon amount.

These results were compared with TGA/DTA measurements of foamed humins samples (Figure 7). Less than 20 % mass loss was observed in the beginning of the reaction up to around 250 °C, followed by the second step of mass loss (50 % – 60 %) between 250 °C and 400 °C, and further down foamed humins is almost completely degraded.

In this case, thermal reactivity of the sample is reflected by the measured ΔT (the temperature difference between the sample and reference). A critical value of ΔT = 50 °C serves as a first order estimation of a potential self-heating hazard based on former experiences.

According to the test protocol, the material is liable to endure high risk of self-heating if a ΔT = 50 °C is observed at a witness temperature (WT) ≤ 250 °C. Moderate self-heating risks is considerate to ΔT = 50 °C between 250 °C - 400 °C WT, while self-heating risk is absent if ΔT =50 °C for WT > 400 °C (or in case ΔT = 50 °C is never achieved).

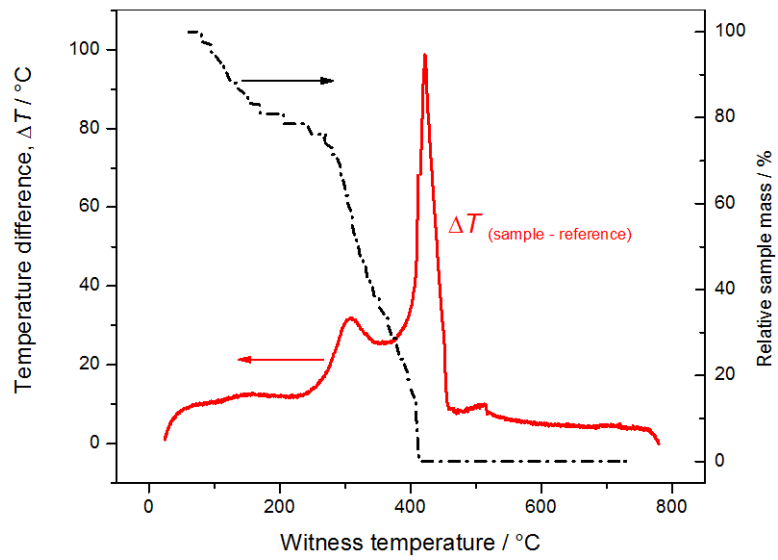

Figure 7. Large scale TGA/DTA results for foamed humins (grey dotted line corresponds to the mass loss profile with its associated scale to the right).

For the foamed humins under investigation, ΔT = 50 °C was observed for WT = 421 °C, indicating that humins used in the current study doesn't pose any significant risk of self-heating. However, slight variation in the characteristics of humins depending on the process conditions[3,4] shall be kept in mind. Indeed, the thermal curing required to obtain foamed humins brings better thermal stability in the final material by further diminishing the effect of differences in composition compared to the pristine crude humins.

Fire Risk Analysis.

Being combustible feedstock by nature - both crude and foamed humins, investigation of their behaviour in fire conditions was performed. The summary of results obtained from FPA test runs and relating overall analysis of mass and thermal balances are presented in Table 2.

Table 2. Burning behaviour of crude humins and foamed humins in the FPA under well-ventilated fire conditions.

Measured Parameters	Crude humins a	Crude humins b	Foamed humins
Sample mass (g)	20.4	20.8	12.6
Mass loss (%)	66.2	65.9	75.4
Ignition time (s)	88	75	22
Duration of combustion (s)	236	275	610
Average mass loss rate (g $m^{-2}\cdot s^{-1}$)	24.6	21.5	5.8
Max mass loss rate (g. $m^{-2}s^{-1}$)	35	40.8	11.9
Phi factor max [44]	0.19	0.22	0.16
NHV (from Boie formula in $kJ\cdot g^{-1}$)	20.2	20.1	23.4
Total energy release [from CDG] ($kJ\cdot g^{-1}$)	14.4	14.7	17
Energy efficiency conversion % (Boie Correlation)	73.5	70	54.5
Carbon mass balance (%)	95	96.3	89

Heat of Combustion

Theoretical heat of combustion value is a basic, very important measurement in any fire safety study. This is the theoretical maximum amount of heat that can be liberated by a product during fire, resulting from complete combustion. When the scientific validation through its actual measurement is unavailable (e.g. from oxygen bomb calorimetry), fairly accurate values of heat of combustion for solid fuels may be calculated using elemental composition of the solid alone

as unique descriptors of the material, making use of well-known correlations that were initially developed for fossil fuels.[45]

Two different underpinning parameters are generally used to qualify heat of combustion, the Gross or high heating value (HHV) where water vapour condensation latent energy is considered and low or net heating value (NHV) where this change in physical state is not considered. The latter value is generally considered more appropriate in fire studies as a level of the fire location. Water is primarily released as vapour due to fire high temperature.

One such empirical correlation used in this calculation is the Boie equation, which is mentioned below.[39,45]

$\Delta Hc\ (kJ \cdot g^{-1}) = 35.160\ C + 116.225\ H - 11.090\ O + 6.280\ N + 10.465\ S$,

where C, H, O, N and S are the mass fractions of carbon, hydrogen, oxygen, nitrogen and sulphur in the burning fuel and ΔHc corresponds to HHV.

In addition to humins produced by Synvina C.V., several other humins compositions reported in the literature [2,6,46] were also considered for calculating CHC values using Boie formulae. Calculated values are represented in Table 3 together with a few reference materials like heptane, sucrose and ethanol for better understanding of energy intensity of humins and to predict their possible impacts.

Table 3. Compositions and NHV data of humins, ethanol, heptane and sucrose.

	C	H	O	NHV ΔHc
	mass-%	mass-%	mass-%	$(kJ \cdot g^{-1})$
Crude humins a*	53.4	5.9	39.7	20.2

Crude humins b*	53.9	5.7	39.8	20.1
Foamed humins*	63.1	4.5	30.9	23.4
Humins# 5	60	5	32	23
Humins# [48]	64.8	4.1	31.1	24.7
Humins# [2]	66.7	3.7	29.6	23.7
Ethanol	52.2	13	34.8	26.8
Heptane	84	16	-	44.7
Sucrose	42.1	6.4	51.5	15

* Experimental humins samples

\# Literature humins data

From Table 3 we can observe that, irrespective of the varying origins of humins, the NHV does not vary significantly, with a standard deviation evaluated to be only ±1.91. Irrespective of structural modifications that may result from humins' production modes, the observed differences in overall elemental composition of those carbohydrate derived structures are not leading to significant differences in heat content. We may conclude from this simple analysis that humins would contribute to fire nearly in the same proportion as a dry wood (HHV = 19.5kJ g^{-1}),[47] and half the proportion of more conventional hydrocarbon fuels in terms of energy release for same mass converted in a fire event. This conclusion cannot reflect any difference in combustion kinetics which is focused in the following section.

Ignition and Heat Release Rate in Fire Conditions.

Both crude and foamed humins were submitted to piloted ignition in the FPA. Foamed humins presented some resistance to ignition but ignited significantly faster (22 s) than crude humins a and b (88 s and 75 s). The primary reason for this is the higher surface area/volume ratio in foams, where oxygen can more easily react with porous foams on the surface. Crude humins,

with less surface area/volume ratio and non-porous physical state, takes relatively more time for ignition. Thermal inertia of crude humins is also more important than for foamed humins, which is another potential explanation of differences observed in ignition times.

Once ignited, the crude humins show a rapid increase in heat release rate which is attributing the combustion of lower molecular weight hydrocarbons near the humins-fire interface. After the peak HRR, the rate progressively decreases in 3 steps, as humins tend to swell and form residual porous char. This reflects a shift from early diffusive flaming combustion mode taking place in the gas phase progressively to some heterogeneous combustion process involving the carbonaceous residue forming at the late stages of the studied combustion process. These results are found in correlation with TGA results discussed in the previous section.

Since lower molecular weight volatile compounds are partially or completely oxidized in foamed humins due to the initial thermal curing during their preparation, we may assume that the combustion of foamed humins is likely comparable with final stage of combustion of crude humins. This is shown in second part of the FPA combustion test, where crude humins has already turned to charring material.

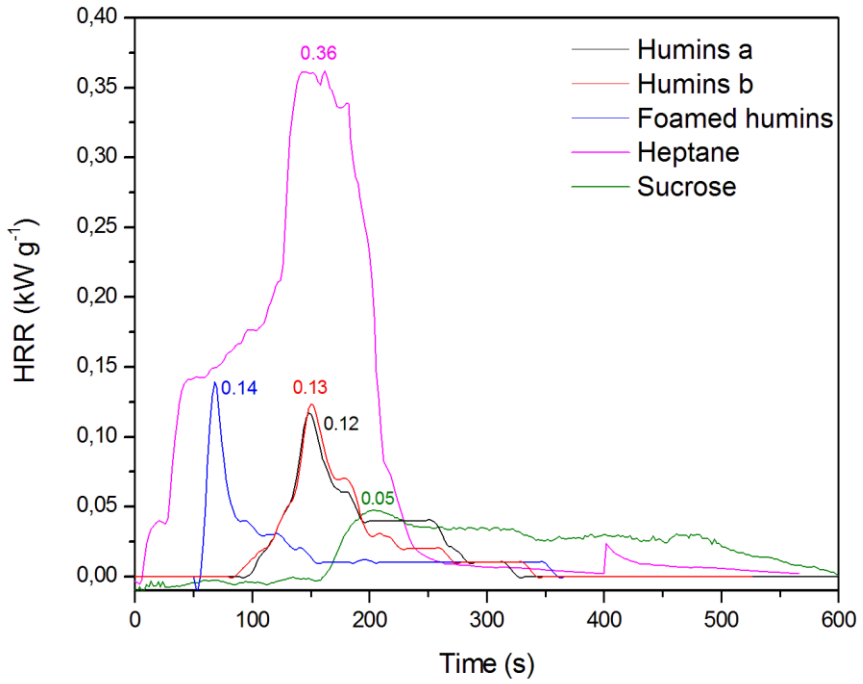

Figure 8. HRR ($kW \cdot g^{-1}$) profiles of crude humins and foamed humins in comparison with heptane and sucrose as reference materials.

The authors have chosen to present HRR data in some unusual way for fire test performed in pool like configuration (e.g. normalized values per gram of sample burnt and not per sample surface area). This is motivated by the fact that test runs (more marked with foamed humins) led to 3D complex burning mode with progressively undefined surface in combustion by contrast to flammable liquid pools burning in fully diffusive flaming mode in the gas phase (Figure 8).

Peak HRR values per gram burnt of crude humins a, b and foamed humins were found to be 0.12, 0.13 and 0.15 $kW \cdot g^{-1}$ respectively, that do not present any significant difference. This is likely to be bound to the fact that flaming combustion process has consumed the major part of

foamed humins sample, while in the case of crude humins a smaller fraction of the sample was consumed in the initial combustion phase. Although the comparison with heptane is not completely adequate (as comparing solid burning to liquid burning process, we have tried to provide a comparison with a former test, where heptane was burned in the Tewarson apparatus making use of the same size of sample holder, containing nearly the same amount of material (~ 22 g) as crude humins. In such conditions the normalized values of HRR (per unit of mass) was found to be ~ 67 % lower than heptane for crude humins, and ~ 59 % lower than heptane for foamed humins, indicating significant lower thermal threats from humins fires compared to heptane fires. However, combustion of humins resulted in significant higher values of HRR (60 % to 70 %) than pure disaccharide sucrose in comparable fire conditions.

Yields of major combustion products.

Considering the elemental composition of humins that is essentially made of C, H, O elements, the major gaseous combustion products expected are carbon oxides (CO and CO_2), water vapour and unburned hydrocarbons that can be accounted in terms of total hydrocarbons (THCs).

Release of combustion products in fire is driving the chemical threat, notably in terms of fire-induced toxicity of the fire gases and soot. This has justified the measurement of these combustion products in the FPA experiments with both crude and foamed humins.

Data available so far is reflecting combustion process in well ventilated fire conditions (phi factor << 1). In these conditions, all carbon available in the crude humins structures would have preferably been converted to CO_2, reflected by the higher carbon conversion efficiency (95 %) than in foamed humins (89 %) (Table 2).

We can further observe from Table 4, a higher CO production in foamed humins than crude humins. This statement simply finds its explanation with an easier mode of oxidation of crude

humins compared to foamed humins in well ventilated fire conditions, also likely to be related to enhance thermal stability of foamed humins by initial thermal curing. Consistently, incomplete combustion of foamed humins in well-ventilated conditions is also reflected by the production of higher quantities of THC (14.9 $mg \cdot g^{-1}$). In same combustion conditions, crude humins a and b release lower amounts of THC (1.9 $mg \cdot g^{-1}$ and 1.6 $mg \cdot g^{-1}$ respectively), as their burning process being more efficient and more favourable in gas phase upon their release in the flame.

CO_2 is clearly the major combustion product like in any combustion process involving hydrocarbons. As there are rather limited amounts of CO and soot produced in the test, we might have expected yields of CO_2 very close to theoretical maximum values. This is not actually the case due to the charring processes taking place and leaving a significant solid residue in both crude and foamed humins. However, due to significant toxicity of CO (known responsible of a majority of fire deaths from building fires from decades), it is important to notice that our tests reveal a significant higher conversion efficiency of carbon into CO in foamed humins under well ventilated fire conditions (~15 % of theoretical maximum yield) compared to crude humins in similar fire configurations (less than 1 %).

Table 4. Yields of combustion products (mg g^{-1}): (a) maximum theoretical yields (b) yields as measured and (c) relating conversion efficiencies (%) of carbon content into CO_2, CO,, hydrocarbon (HC) content into THC, CH_4 and soot from crude and foamed humins.

	Crude Humins a			Crude Humins b			Foamed Humins		
	$mg \cdot g^{-1}$	$mg \cdot g^{-1}$	%	$mg \cdot g^{-1}$	$mg \cdot g^{-1}$	%	$mg \cdot g^{-1}$	$mg \cdot g^{-1}$	%
	a	b	c	a	b	c	a	b	c

CO2	1958	1404	72	1976	1444	73	2314	1572	68
CO	1246	8.2	0.6	1257	6.8	0.5	1473	216.1	14.6
THC	593	1.9	0.3	596	1.6	0.3	676	14.9	2.2
CH4	234	1	0.4	226	0.7	0.3	186	11.3	6
Soot	534*	0.8	0.14	539	3.7	0.6	631*	3.3	0.5

*In theoretical estimations, soot is assumed to be pure carbon

** Carbon from the sample also remained in significant quantities of solid residue

Other products of combustion identified from FPA.

While burning humins in the FPA, production of soot particles was one of the evident observations made both from experiments and visual observations. In a fire, soot is a carbonaceous solid matter produced in a complex way from organic hydrocarbon fragments due to significant incompleteness of combustion process.

Limited quantities of soot (mainly composed of carbon) production was observed in both crude and foamed humins samples (measured yields by optical means were respectively 0.8 $mg \cdot g^{-1}$ and 3.3 $mg \cdot g^{-1}$ respectively), showing not surprisingly values far below maximum theoretical yields (see Table 4). Soot is usually produced after the oxidation of burning material into CO or CO_2, in the fuel rich region of the flame through gas-solid interactions.[45] Indeed, oxygen containing species are rarely leading to significant emission of soot when burning in fire, particularly in well ventilated fire conditions.

Thermal hazard and induced-toxicity from fires involving humins.

In the current study, heat release rates and yields of major combustion products shaping the overall potential toxicity has been determined. These data can be extrapolated to any well-

ventilated fire of interest for fire risk assessment purposes by the use of rather classical fire protection engineering techniques, mostly developed and published by ISO TC92 subcommittees SC3[48] and SC4.[49]

From the peak value of heat release, the point source model (radiant energy fraction is supposed to dissipate isotropically into a sphere of radius R) can be used to determine the distance R from the fire source at which a given amount of humins in fire can critically transfer energy by radiation and provoke burns on living organisms or ignite remote combustible materials.[50]

Fire induced toxicity is far more complex,[51] and still leads in some cases to some controversial views between fire toxicity experts. However, data from two immediate previous sections can be used to build up the 'source term' for fire plume dispersion simulations corresponding to a given fire scenario of interest. Certainly, according to the nature and yields of products measured, fire toxicity will not depart significantly to major cellulosic fires (woody materials) and according to our results may essentially drive an actual concern in confined environment. Nevertheless, some precautions shall be also taken in close proximity to fire events in open environment that would involve foamed humins, according to increased trend to convert humins carbon content into CO.

CONCLUSIONS AND PERSPECTIVES

Until now, industrial humins have been considered as non-hazardous by-product, whilst no rigorous study has been conducted to support this classification. As crude humins are increasingly investigated as new bio-based feedstock for varieties of new applications in advanced biorefineries, no longer restricting its use for in-situ energy conversion, there is a need for clarification on various aspects of humins on a broader perspective. In this direction, this paper is a preliminary attempt to understand the physico-chemical safety concerns such as

thermal stability, ignitability and combustibility pertaining to humins (both in crude and foamed forms).

Compared to crude humins, foamed humins depicted better thermal stability properties, and do not possess critical self-heating behaviour, although presenting as a highly porous structure.

As all organic compounds, humins are to be considered as combustible materials and they are clearly, relatively easily ignitable under presence of an energetic ignition source. The combustion behaviour of both crude and related foamed humins was further studied, both in terms of heat impact (e.g. energy release) and chemical impact (e.g. yields of combustion products liable to drive the potential fire induced toxicity). From experimental data obtained and by comparison of similar data existing for other well studied fuels, we conclude that the overall fire risk associated with humins does not differ significantly from conventional fires that would involve more conventional cellulosic fuels (e.g. woody materials).

To our knowledge, this work is the first published information about humins focusing on safety issues, an often underscored aspect of sustainable use of new bio-based feedstocks and materials.

As a word of caution, the authors also want to draw attention to the readers that further work is still needed to achieve a more comprehensive insight and understanding of safety issues pertaining to use of humins and humins based derivatives. Indeed, industrial humins can vary in composition depending on their origins, as well as the porosity profile of foamed humins can differ depending on their preparation methods. These aspects cannot be fully accounted in our work. Application of humins and relating processing leading to end-products from such bio-based feedstocks might also significantly change the safety side, which was not consider any further in our work .

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ABBREVIATIONS

ACD, Acid Catalysed Dehydration; TGA/DTA, Thermogravimetric Analysis/Differential Thermal Analysis; FPA, Fire Propagation Apparatus; THC, Total Hydro Carbon; HRR, Heat Release Rate; HHV, High Heating Value; NHV, Net Heating Value; FDCA, Furandicarboxylic acid;

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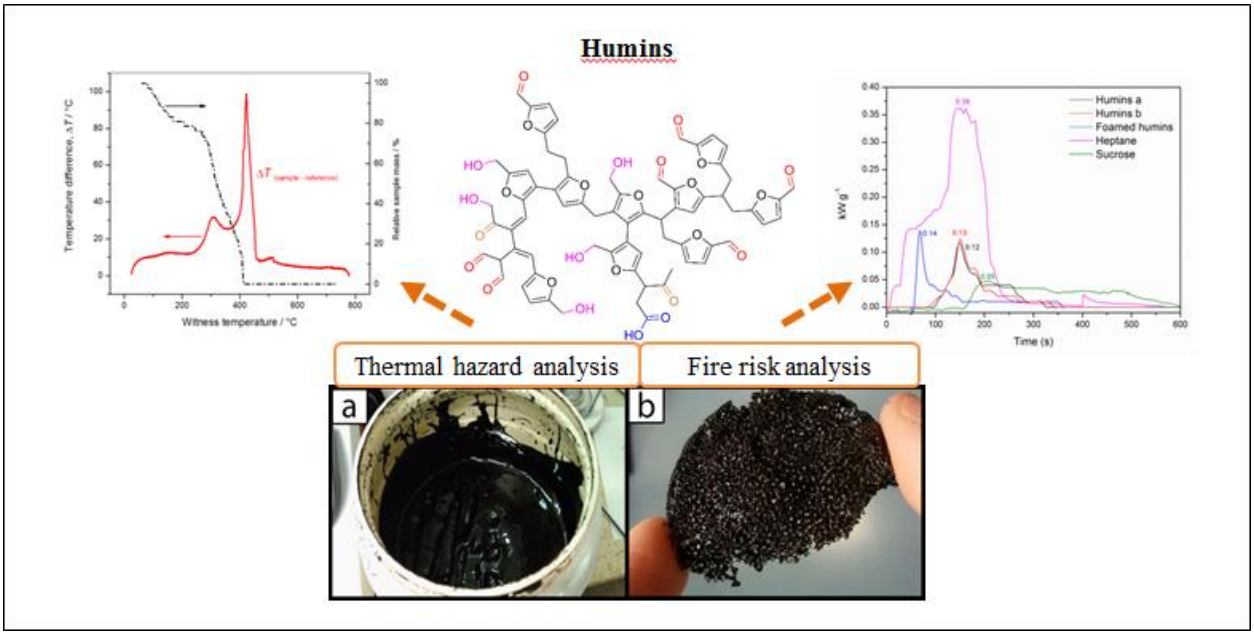
Graphical Abtract



Synopsis:

Physico-chemical safety profiling of humins is a prerequisite to their multi-dimensional (socio-economic and environmental) sustainable development and applications.