Humins: Still-unknown Antagonists in Polysaccharides Valorisation

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Among the primary objectives of modern biorefineries is the production of furfural, hydroxymethyl furfural, and their derivatives, which are key compounds for the synthesis of widely used fine chemicals, including plastics and other everyday materials. However, the industrial development of these processes is hindered by the formation of unwanted by-products, most notably humins. Humins are highly cross-linked macromolecules of complex nature with limited technological applications. This editorial offers a brief overview of the "humin issue", discussing the challenges posed by these materials from an analytical perspective. Despite considerable efforts towards their characterization, the structure of these materials remains largely unresolved, representing an ongoing challenge for green chemistry and the optimization of biorefinery processes.

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The current socio-economic context, characterized by climate emergency, depletion of fossil resources, pollution, and waste management challenges, calls for a radical transformation of the industrial paradigm. In this scenario, the optimization of lignocellulosic biomass valorization strategies emerges as a key priority. Beyond traditional approaches that rely on well-established pulping and saccharification industries, the biorefinery sector has gained increased attention in Europe and the United States. These industries are introducing green intermediates to the market that can be readily converted into products formerly accessible only *via* traditional petrochemical routes. Among these intermediates, furfural (furan-2-carbaldehyde, FF) and 5-hydroxymethylfurfural (5-(hydroxymethyl)-furan-2-carbaldehyde, HMF) are particularly promising. Indeed, a wide range of valuable chemicals, including furan, levulinic acid, pentane-1,5-diol, γ-valerolactone, hexane-1,6-diol, caprolactam, and caprolactone, can now be obtained from FF and HMF through convenient catalytic processes. The relevance of these green intermediates is underscored by their market value: in 2024, FF was estimated at approximately $610 million, while HMF reached $56.2 million. All of this is made possible by the extraordinary progress achieved in carbohydrate chemistry over the past two centuries.

The basic step in converting lignocellulosic biomass into furans lies in its acid-catalyzed treatment. This process promotes hydrolysis of glycosidic linkages in polysaccharides, yielding simple pentoses (*e.g.*, arabinose and xylose) and hexoses (*e.g.*, glucose and mannose). Subsequent rearrangement reactions, including dehydration and

isomerization, lead to the formation of FF from pentoses and HMF from hexoses. Although this sequence appears straightforward, suggesting ease of industrial scale-up, several drawbacks limit its application. These include product separation issues– given that hydrolytic steps are performed in water, and both FF and HMF are water-soluble– the heterogeneous composition of hydrolysates due to biomass variability, and the formation of dark, insoluble carbonaceous residues commonly referred to as *humins*. While several strategies have been proposed to mitigate separation and processing challenges, what can be called the "*humins issue*" remains largely unresolved. This issue encompasses two major aspects: (a) the origin and (b) the structure of humins. Addressing these aspects with rigor would significantly improve biorefinery process efficiency, increasing yields of FF and HMF, thereby accelerating the transition towards a more sustainable chemical industry.

The in-depth understanding of the mechanistic aspects at the basis of humins origin is strongly sought after but still unachieved, as demonstrated by the still-limited number of efforts available in literature. For sure, from an industrial perspective, the empirical development of technological solutions to minimize humins formation can, in some way, act in opposition to a deeper understanding of the chemistry and reactivity of these materials. Economic and profit-driven considerations often take precedence over theoretical research, especially in a novelty field such as this one. The only undoubted fact is that both FF and HMF play pivotal roles in their formation. In fact, once generated, these intermediates rapidly undergo secondary reactions, resulting in complex pathways that ultimately produce carbonaceous by-products.

Existing literature from the 1940s attempts to formulate mechanistic hypotheses regarding humin formation on the basis of studies involving model compounds. Through examining the reaction products obtained from FF and HMF under acidic conditions, key intermediates have been identified and plausible reaction mechanisms suggested. Acetalisation, aldol condensation between furan derivatives, etherification, and esterification (with *in situ*-formed carboxylic acids) are now recognized as crucial steps. More recently, aromatization processes, such as the conversion of HMF into hydroxylated benzene derivatives, have been postulated, leading to speculative hypotheses about the presence of lignin-like structures within humins. This hypothesis remains controversial. The classical marker of lignin, methoxy groups, has not been correlated with humin formation mechanisms, and no rigorous pathways have yet been proposed to justify their incorporation on hydroxylated structures. The possible presence of lignin-like domains in humins becomes more plausible when considering real biorefinery-derived humins, where the feedstocks contain residual lignin and other polyphenols. In this context, the co-participation of lignin in humin formation is reasonable. During FF and HMF production, lignin is not directly involved. However, the acidic conditions employed may favour lignin condensation processes, potentially involving FF, HMF, or their oligomeric derivatives. Although this interpretation seems logical, compelling evidence and mechanistic justification are still lacking, highlighting a crucial area for further research.

Characterizing Humin Structure

At the current state, there is a clear lack of robust and rigorous analytical methodologies for characterizing humins and their derivatives – including potential condensation products with natural polyphenols like lignin. The major limitation is their insolubility in conventional solvents. Elemental analyses reveal a high carbon content along with oxygen and hydrogen, suggesting a highly crosslinked network generated by

strong intra- and intermolecular interactions. This complexity precludes the use of characterization techniques commonly employed for polymeric matrices such as polysaccharides and polyphenols (*e.g.*, gel permeation chromatography [GPC] and solution-state nuclear magnetic resonance [NMR]). As a result, available data on humin structure is derived from less specific methods, including infrared spectroscopy, thermogravimetric analysis, and pyrolysis. While these approaches provide valuable qualitative insights– such as the presence of functional groups (*e.g.*, carbonyls) and structural motifs (*e.g.*, furans)– they fall short of delivering a comprehensive structural model. Degradation-based techniques, such as alkaline hydrolysis under high-pressure and high-temperature conditions, have been explored to break down humins into smaller oligomeric fragments, which are easier to characterize using traditional tools. However, the reliability of these methods is debatable, as alkaline conditions may induce undesired chemical modifications, potentially altering structural interpretations. Recent studies employing ^{13}C CP-MAS NMR have offered limited, yet promising, insights, as the overall poor spectral resolution remains a challenge. More informative studies will require ^{13}C-labelled humins derived from isotopically marked sugars, which would enhance resolution and signal assignment. Furthermore, the use of cutting-edge solid state NMR techniques, such as dynamic nuclear polarization– where polarization is transferred from unpaired electrons to nuclei– should be considered, given its potential to significantly improve spectral resolution and signal-to-noise ratios.

All in one, although the "*humins issue*" remains a niche area of academic research- partially hindered by instrumental limitations - but also from an evident some-how limited interest - it is not difficult to imagine that, with the global expansion of biorefineries in the upcoming years, interest in this field will grow, positioning humins as an attractive material alongside other natural polymers such as chitin, tannins, and humic acids.

The Future of Humin Utilization

It is now clear that we need to change our paradigm regarding humins: instead of considering them as a problem, we should reconsider them as a potential resource derived from a by-product, like lignin in the pulping and biorefinery industries. This shift could pave the way for a new "humins supply chain. In this regard, beyond their chemical formation and structure, broader questions arise regarding the fate and potential utilization of humins. How should humins be disposed of? Are they biodegradable or should they be incinerated? Are they environmentally hazardous, or could they be regarded as "biochar"-like materials? In terms of potential applications– towards greater process circularity– several opportunities may also be considered. Could humins be employed as fillers in composite materials? Could their aromatic character be exploited for absorption applications, such as water remediation treatments? What is their thermal behaviour: are they flammable, or could they serve as thermal insulators? Might humins be valorised as industrial energy sources, akin to black liquor in the pulping industry? Furthermore, could pyrolytic processes be adapted to humins, enabling their cracking into high-value products?

Overall, unresolved analytical challenges regarding the origin, formation, and structure of humins, combined with the limited studies exploring their valorization, highlight that these materials constitute an underexplored class of biopolymers. As the industrial availability of humins continues to rise, their critical consideration by the global scientific community becomes an essential aspect for transition to a more sustainable chemical industry.