First order safety insights on furanic platform chemicals and their side streams

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Furanic platform chemicals have recently gained renewed attention due to their production capability from bio-based sources including lignocellulosic residues, the reuse of which is highly encouraged by the promotion of a circular economy. Apart from lignins, humins, another side-stream residue generated during the acid-catalysed dehydration of C_6 and C_5 sugars to produce furanic monomers, is currently receiving attention as a renewable carbon source. Plenty of efforts are seen towards application development for these furanics-based chemicals and materials. Nevertheless, safety oriented data or information on these materials is scarce and this may hinder the market for new products made out of these chemicals/materials. To compliment this, the current study specifically focuses on the fire risk assessment of humins and many other furanic compounds of commercial interest. The study aims at generating safety-oriented data which may assist the user to understand the anticipated risk profiles for making a fair decision on their selection for the desired application.

1. Introduction

With the ongoing quest for finding an alternative for fossil energy sources to produce fuels, chemicals, materials and energy, the world is now looking at biomass as a viable, economic alternative renewable carbon source. In such an attempt, production of furanic platform chemicals and intermediates from non-edible lignocellulosic biomass has stood out as an effective alternative for improving bio-based economy (Caes et al. 2015).

Despite existing for over a century by now, commercialisation of bio-based furanic derivatives (FD) was not an economically viable option until recently. Now, acid-catalysed dehydration (ACD) process of C_6 and C_5 sugars is used resulting in the production of valuable furanic intermediates such as 5-hydroxymethylfurfural (HMF) and 5-methoxymethylfurfural (MMF), and furfural, respectively. They can either be used as final products themselves or for the production of other furanic monomers and chemicals.

An unavoidable side stream condensation residue of complex and versatile structure is also produced during the intermediate step of the ACD process which is called humins (Schweizer 1938) Humins are carbonaceous, heterogeneous, polymeric residues essentially made of furan rich oligomers, with aliphatic chains containing functional groups such as aldehydes, ketones and alcohols(Figure 1b). Humins are black, tarry and viscous substances whose physical and chemical characteristics depend on the feedstock used, process conditions and degree of thermal treatment the material has been subjected to (Figure 1a). Just like the better known lignins, valorisation of humin residues has gained tremendous importance in recent years as a valuable biomass. Ongoing efforts on characterisation studies of humins by several researchers to understand their structural attributes have been undertaken (Filiciotto et al. 2018; Schweizer 1940; van Zandvoort et al. 2015; Van Zandvoort et al. 2013). As humins are concomitantly generated during the ACD process as an important side stream, valorisation approaches are also being examined to use them in energy and fuel applications (Agarwal et al. 2017; Rasrendra et al. 2013), catalysis (Filiciotto et al. 2018), and innovating co-cured composite materials (Mija et al. 2017).

1.1 Interest in fire safety studies

There are concerns for making the bio-based side streams and chemicals environmentally safe. Yet, not all furanic compounds have received equal attention concerning hazard rating by officially recognized hazardous-material classification systems (GHS (United Nations 2015), CLP (ECHA 2017) and TDG (United Nations 2017)). Despite having a hazard rating, material safety data sheets (MSDS) of many compounds lack information on their thermo-chemical properties such as flash point, lower and upper flammability limits, and auto-ignition temperature, which are necessary for safe processing, storage, as well as handling and transportation of (reactive) chemicals. Most importantly, for some of the existing as well as newly developing furanic compounds, physical hazards classes (Wilrich et al. 2017) shall be checked if they are a) clearly defined b) not prioritized over other classes of hazards, and c) not ignored as another hazard rating has already been assigned. Besides, it is worth realizing that the bio-based origin of FD does not necessarily imply they are (completely) safe. In addition, safety-oriented studies of many important FD such as HMF and its derivatives have been given prime focus on their food industry applications and consecutive impacts and toxicity concerns from FD have so far received heterogeneous remarks and are still a matter of debate (Ventura et al. 2016).

These furanics-derived chemicals and materials, directly or indirectly being used either as a precursor or as a final product, may end up in conventional building and, hospitals; the transportation sector and many other public assemblies where fire risks will arise any point of time (Kandola et al. 2015; Sudholt et al. 2015).Therefore, reaction to fire properties need to be evaluated in their early development, as to satisfy potential applicable regulation to prevent and mitigate thermal and fire induced hazards resulting from their use in critical infrastructures.

Therefore, this study aims at identifying the safety related key elements of concern and provide a first series of adequate safety related input data needed to proceed to scenario-based risk assessment. As an example, estimating heats of combustion data of these materials gives an idea on the fire load – a critical parameter estimated during the fire risk assessment. Also, determining flammability limit by performing reaction to fire tests in a polyvalent fire calorimeter such as the Fire Propagation Apparatus (FPA) to learn on most important fire parameters such as heat and combustion product releases, and thermal stability properties are of key concerns. From literature it was found that studies highlighting the physico-chemical properties of these compounds are so far very scarce and limited in their scope. The current study therefore attempts to understand these chemicals and materials beyond conventional boundaries of hazardous material classification systems that are needed for application focused risk evaluation of their use. Building a safety database of the family of furanics and derivatives also contribute to avoid too generic statements that could hinder appropriate development of relating materials of interest, as well as to prevent right from the beginning, inadequate selection of some of them.

2. Materials and Methods

2.1 Test samples

Humins samples selected for testing were produced during the industrial ACD process at Synvina pilot plant located in Geleen, the Netherlands. Samples reflecting the largest variation of chemical composition were selected for testing in a tentative approach to get an idea on the sensitivity of results to heterogeneity of humins. Among the selected humins samples, HMF and its alkoxymethyl derivatives were present in low percentages (Tosi et al. 2018).

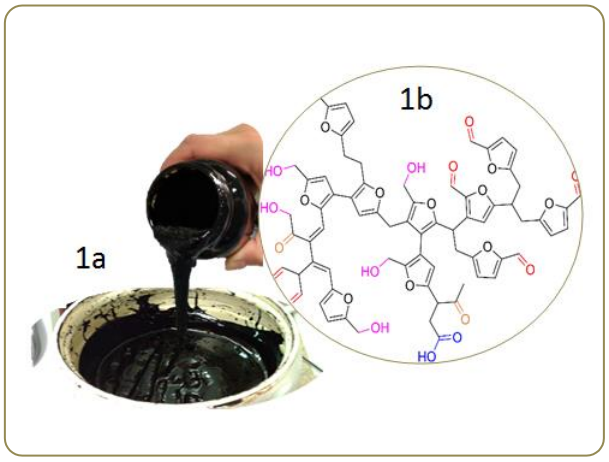
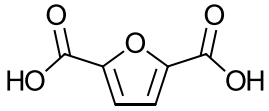
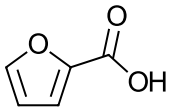
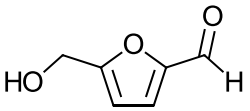
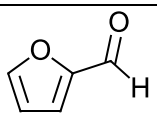
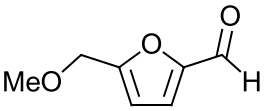
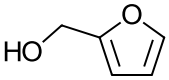
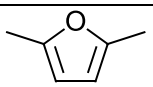


Figure 1. 1a) Visual aspect of industrial humins and 1b) molecular structure (proposed by (Van Zandvoort et al. 2013)*).*

Besides humins, several furanic compounds obtained from various sources illustrating wide varieties in structural and functional attributes (such as variation in alkyl chain lengths, molecular masses, and different functional groups) were also selected for testing (Table 1).

Table 1. List of monomeric furanic compounds selected for testing with the Fire Propagation Apparatus.

Compound Name	Physical State	Molecular formula	Molecular structure	Molecular Mass	NHV (MJ kg^{-1})	Flash point (°C)
FDCA	Powder	$C_6H_4O_5$		156	13.0	207
2-Furoic acid	Liquid	$C_5H_4O_3$		112	17.5	94.2
HMF	Solid	$C_6H_6O_3$		126	20.4	79.4
Furfural	Liquid	$C_5H_4O_2$		96	22.2	60
MMF	Liquid	$C_7H_8O_3$		140	22.7	83
Furfuryl alcohol	Liquid	$C_5H_6O_2$		98	24.3	65
Furan	Liquid	C_4H_4O		68	27.8	-36
2,5-Dimethyl furan	Liquid	C_6H_8O		96	32.4	6

2.2 Method 1- Theoretical estimations of heat of combustion (HoC) values

Estimation of heat of combustion of any given product is one of the first steps in any fire safety study to estimate the maximum amount of heat a product may liberate in the event of fire. Practically, HoC values are calculated using an oxygen bomb calorimeter. When this is not possible, the elemental composition of the compounds can be used to calculate fairly accurate values via a series of empirical correlations developed for fossil fuels (Marlair et al. 2014).
HoC values can be represented either in terms of High / gross heating value (HHV), where the latent heat of water vapour is taken into account or as Net / low heating value (NHV) where this phase change is not considered. NHV is generally more appropriate for fire studies.

One such empirical correlation used in this calculation is the Boie equation (1), which is mentioned below (Marlair et al. 2014)

$$\Delta Hc\ (MJ\ kg^{-1}) = 35.160\ C + 116.225\ H - 11.090\ O + 6.280\ N + 10.465\ S \quad (1)$$

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.

2.3 Development of database

A database containing around 60 FD was developed by compiling physico-chemical properties of FDs from various sources such as MSDS, literature, and via data available on the websites of chemical traders. These were then categorized based on their alkyl chain lengths and the functional groups associated with them.

Table 1 gives a brief idea on the type of exploratory work attempted by the authors. FD with their diverse structural and functional properties were selected as an initial example. By making use of Boie correlation, the NHV data was calculated for the listed furanics. The values reported herein ranging from 13 to 32 MJ kg^{-1} are showing wide range of energy content in FD. In addition to this, flash point data for the same set of compounds are presented in the table ranging from -36 to 207 °C. From this preliminary assessment, a large diversity of values from the same family of compounds is observed. Variations observed in the energy content and flash points indicate that, varying risk profiles may be anticipated during their practical use and that their response to fire conditions shall not be generalized.

The assessments give us an idea on understanding the risk profiles based on the end use applications. Structural and functional attributes of compounds may certainly play a significant role in the overall safety assessment besides some external factors such as type of surrounding environment, hot spot ignition, and chemical incompatibilities.

2.4 Method 2- Experimental work with the use of Fire propagation apparatus (FPA)

The fire risk assessment of FD and humins will be carried out by means of the FPA (Figure 2) (ASTME2058 and NFPA 287), also called the Tewarson apparatus named after the designer, commissioned at INERIS in 1997. The purpose of this FPA is to measure ignition and fire propagation entailing thermal and chemical characteristics of materials or chemicals under fire conditions. Test samples (solids, liquids and powders) ranging from 20 to 40 g can be tested under controlled air flow to achieve fuel rich or fuel lean environments that simulates under-ventilated and well-ventilated fire conditions respectively. Four infrared heaters used to set an external heat flux allowing a piloted ignition of the sample under calibrated heat stress by an electric spark or pilot flame. These heaters do not add any external fuel source required for ignition. Key measurements such as mass loss and heat release rates can be calculated with the application of fire calorimetry laws by assessing the oxygen consumption (OC) and carbon dioxide generation (CDG) (Brohez et al. 2000). Fire effluent concentrations and yields of combustion products can also be measured to understand the fire toxicity issues.

By adjusting the inlet airflow rate, a full spectrum of ventilation conditions can be explored. Ventilation conditions can be controlled through determination of real time equivalence ratio (phi factor) (Brohez et al. 2006) which reflects actual fuel versus oxygen ratio normalised by the same ratio at stoichiometric conditions.

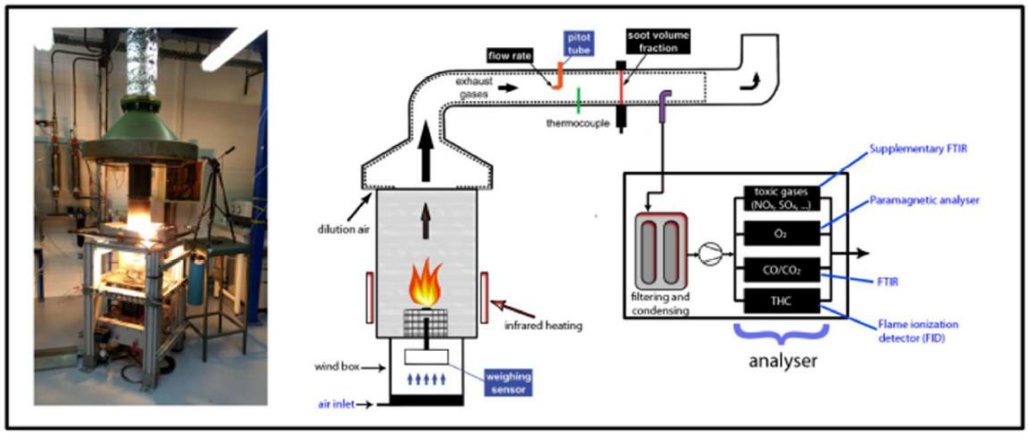


Figure 2. Schematic and practical view of INERIS Fire Propagation Apparatus.

3. Future work (November 2018 to March 2019)

The work focuses on obtaining key safety oriented data on most common furanics compounds as well as their side stream residues that are of commercial interest. The database development and calculation of heat of combustion values gives a first understanding on the heat impact that may be anticipated from the substance even before subjecting them to actual testing. It gives estimation on the suitability of compounds for further testing as well as an anticipation of probable risks. In case of expensive compounds or newly synthesized compounds, heat of combustion values may also help them to estimate their suitability for a particular application.

In addition to this, the experimental work allows us to understand the fire behaviour of the tabulated compounds by testing them with the FPA under different ventilation conditions i.e. fuel rich and fuel lean environments. The results obtained contribute to an understanding on various characteristic features one must consider during the calculation of fire risk assessment such as peak heat release rate and total heat released during the entire duration of combustion, as well as mass loss rate of the compounds. During the assessment, parameters such as ignition delays and duration of combustion will also be considered which are critical factors influencing an event of fire. Furthermore, calculation of the phi factor plays an important role in estimating the shift of combustion process from well-ventilated to under-ventilated conditions. Besides, we can also estimate the yields of combustion products and compare them with the theoretical yields to calculate the combustion efficiency and see how far the process is from reaching complete combustion.

4. Conclusions

Bio-based production of FD is currently of commercial interest due to their diverse suitability in current and prospective applications. Humins generated in the production process of FD, is no longer treated just as a waste, rather as a bio-based residue used as raw material in many downstream processes and applications. Such change also means the material has to be treated outside the waste framework directive, in a separate framework of directives applicable to such side streams. In support of their valorisation routes, they deserve dedicated safety assessment necessary to understand their physico-chemical properties suitable for targeted applications. On the other hand, considering the large diversity observed in the structural, functional and physico-chemical properties observed in FD, understanding them from a safety view point can help in better selectivity of compounds for potential targeted applications. The database developed would serve in bridging the existing data gaps between knowledge and applications, by defining patterns or trends in terms of physico-chemical safety aspects.

Noteworthy, the first order results and may partially or completely change in due course of time depending on the changes in processes conditions, feedstock composition that may change the characteristics of the raw material. Nevertheless, the data collected would give an estimate on the precautions one must take while handling, transportation and storage of such materials/compounds.

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