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EXPLORATORY ANALYSIS OF FIRE RISKS PERTAINING TO FURANIC PLATFORM CHEMICALS

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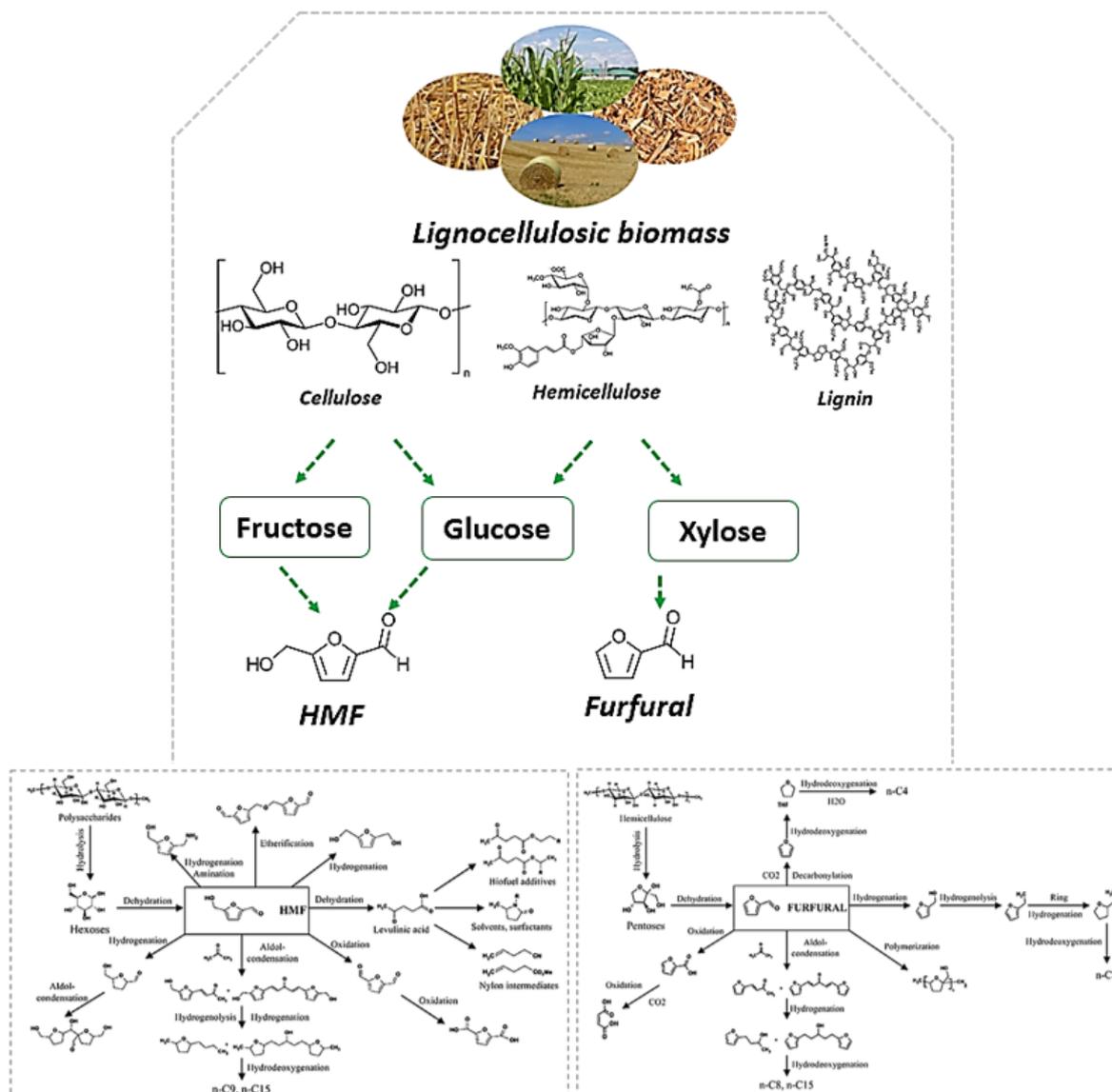
ABSTRACT

Bio-based feedstock are the current interest and used extensively in producing chemical intermediates, platform molecules and final materials. Key furanic compounds such as 5-hydroxymethylfurfural (HMF), methoxymethylfurfural (MMF) and furfural (FF) are produced from the dehydration of hexoses (C₆) and pentose (C₅) sugars present in the lignocellulosic biomass. With their structural and functional diversity, these compounds have found plenty of useful application pathways. However, in support of sustainably assessment of relating value-chains, safety oriented studies concerning furanic compounds are so far scarce while many if not all of these compounds are combustible in nature. The current study therefore targets a complimentary approach generating safety related information on a wide range of furanic compounds with a scenario-based assessment. The results can bring out a preliminary insight on the risk profiles of furanics, helping the users to make suitable choices of compounds for a given application.

INTRODUCTION

Climate change is globally driving humankind towards finding fossil free energy vectors, materials and chemicals alternatives. The demand for energy and materials is growing at an elevated pace. In fulfilling this quest, biomass currently stands as a unique alternative to produce fuels, chemicals and materials due to its abundant availability and economically viable options. In the search of adequate bio-based feedstock in this context, lignocellulosic biomass has gained significant attention in the production of alternative and unrivaled bio-based building blocks.¹ Acid catalyzed Dehydration (ACD) of C₆ and C₅ sugars from lignocellulosic biomass can produce some of the key furanics intermediates such as HMF and furfural further leading to plenty of final molecules with useful applications (Figure 1).² Furanics are a large family of chemicals, with diverse structural and functional attributes,³ leading them into various industrial applications such as solvents, pharmaceuticals, polymers, catalysis etc.⁴

Recently, the US department of energy has recognized some bio-derived furanic compounds as key building block chemicals owing to their wide application capabilities among which furfural is a key product.^{5,6} The first bio-based industrial production of furfural was by Quaker oats in early 19th century. HMF is another key furanic intermediate results in the production of 2,5-furandicarboxylic acid (FDCA) to produce bio-based polyethylene furanoate (PEF) plastic.⁷ Hydrogenation of HMF results in 2,5-dimethylfuran often used as a fuel additive. HMF when reacts with a simple alcohol such as methanol or ethanol that leads to the production of 5- (methoxymethyl)furfural (MMF) and 5- (ethoxymethyl)furfural (EMF) generally named as alkoxymethylfurfurals (AMF or RMF).⁸ The energy density of EMF (8.7 kWh/L) is nearly equal to that of a regular gasoline (8.8 kWh/L) and comparable to diesel fuel (9.7 kWh/L) and much higher than ethanol (6.1 kWh/L).⁹ AMFs derived by HMF are able to produce higher yields, using cheaper raw materials containing lignocellulosic biomass, and are liquids at room temperatures making them effective candidates for fuel additives.⁸



1. Schematic representation of key furanic compounds produced from lignocellulosic biorefinery (adapted from Aristizábal M. et al. 2015)¹⁰

By understanding the importance of these bio-based furanic platform chemicals, significant dedicated efforts were invested in the recent years to commercialize the relating ACD process; with advanced and efficient process technologies to cope with the large diversity of available feedstocks, and target molecules.³ By contrast, and despite their obvious combustibility property, much less efforts were devoted to the generation of the physico-chemical safety data in terms of ignitability, flammability, oxidizing potential, or thermal stability of furanic compounds. Access to safety data is very important at early stages of furanics end-use development to learn on physico-chemical risk trends according to their structures, since a wide variety of risk profiles can be anticipated from a diverse group of chemicals in a single family.

Bio-based origin of furanic compounds do not make them completely risk free. Moreover, not all compounds of the furanic family have received harmonized classification under the official hazardous material classification systems such as CLP,¹¹ GHS,¹² and TDG.¹³ Information on some important thermo-chemical properties such as flash points, upper and lower flammability limits, auto ignition temperature are not easily accessible for many important compounds. These are the key information a

user needs to refer for the safe handling, storage and transportation of reactive chemicals.

Many furanics are flammable in nature and the materials derived from them may end up in various built environments, including public access buildings or collective dwellings where fire risk is a key concern. On a more general way, safe transportation, storage and handling of such chemicals and materials shall be ensured in adequate manner. It is therefore important to evaluate the reaction to fire properties of these chemicals or materials in their early stage of development.

Safety still today is often considered as an underscored aspect of sustainability and has been receiving a low priority in many instances. However tackling safety issues right from the beginning may provide competitive advantage in many ways. Safety studies shall be considered as part of multi-criteria sustainability assessment as they can help selecting the most appropriate options in terms of processes or final materials involving furanics. Although not on focus in our review work, health and environment related issues pertaining to furanics compounds are also a subject for further research. All the more these aspects are still a matter of debate and conflicting views in some cases,^{14,15} our literature review shows that no significant research has been dedicated so far to safety profiling of furanics with regard to their potential of risks of physico-chemical nature (thermal reactivity/flammability, oxidising properties, corrosivity, etc.). Fire hazard may of course be significant since some compounds have been considered due to their high energy density as bio-based alternative fuels components.^{9,16,17}

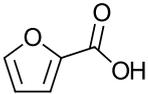
This is a dedicated study focusing on generating physico-chemical safety related information including information on ignition, combustion and fire propagation potential of a few selected furanics of commercial interest. Reaction to fire performances of these compounds will be learned via the experimental investigation using the Fire Propagation Apparatus (FPA). The results would give an idea on the heat impact leading to thermal threats and the chemical impact leading to toxic species release from furanic fires. In addition, the study also focuses on understanding the fire load of several furanic compounds by estimating heat of combustion data. The study clearly exemplifies the varying risk profiles originating from the same family of chemicals with a key message to avoid generalizing the hazard statements of a specific compound to the whole family of chemicals.

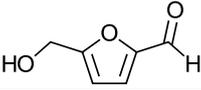
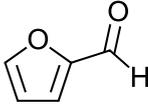
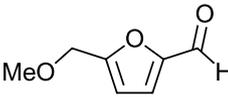
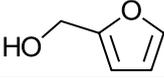
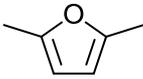
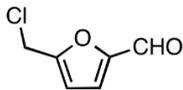
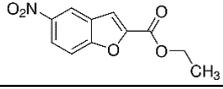
MATERIALS AND METHODS

Test samples

Key furanic compounds of commercial interest were selected from various sources illustrating wide varieties in structural and functional attributes (such as variation in alkyl chain lengths, molecular masses, and different functional groups) as shown in Table 1.

1. A few examples of furanic compounds used in the exploratory work

Compound Name	Physical State	Molecular formula	Molecular structure	Molecular Mass	Heat of combustion (MJ kg ⁻¹)	Flash point (°C)	Melting Point (°C)
FDCA	Powder	C ₆ H ₄ O ₅		156	13	207	>250
2-Furoic acid	Liquid	C ₅ H ₄ O ₃		112	17.5	94.2	128-132

HMF	Solid	C ₆ H ₆ O ₃		126	20.4	79.4	32-36
Furfural	Liquid	C ₅ H ₄ O ₂		96	22.2	60	-37
MMF	Liquid	C ₇ H ₈ O ₃		140	22.7	83	-17
Furfuryl alcohol	Liquid	C ₅ H ₆ O ₂		98	24.3	65	-14.6
Furan	Liquid	C ₄ H ₄ O		68	27.8	-36	-85.6
2,5-Dimethyl furan	Liquid	C ₆ H ₈ O		96	32.4	6	-62
5-chloromethyl-furfural	Liquid	C ₆ H ₅ ClO ₂		144.5	18.4	N.A.	37
Ethyl 5-nitrobenzofuran-2-carboxylate	Liquid	C ₁₁ H ₉ NO ₅		235.2	30.2	N.A.	152-156

Estimation of heat of combustion values

Heat of combustion (HC) of any given product, as relating to fire lead, stands as a basic information in any fire risk assessment. The theoretical heat of combustion is the maximum amount of heat a product might liberate in case of complete combustion in a fire event. HC values can be represented as Low heating value (LHV) when the water vapor produced by complete combustion is released in gas state and high heating value (HHV) when the water is accounted for in the energy balance in the liquid form. The most preferred and observed value in the literature is the LHV, obtained from the oxygen bomb calorimeter. The net heat of combustion values of organics generally fall in the range of 20 MJ kg⁻¹ to 45 MJ kg⁻¹.¹⁸ When direct measurement is not feasible, the HC values can be calculated using the elemental compositions of desired compounds through a series of empirical correlations developed mainly for fossil fuels.

Among many empirical correlations available, the one used in our calculations is the Boie correlation.

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

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

Database establishment

More than 30 furanic compounds depicting wide range of molecular structures containing one or more furan rings were listed and categorized based on the alkyl chain lengths and associated functional

groups. MSDS, websites of various chemical traders, producers and literature review were some of the main sources of the available data.

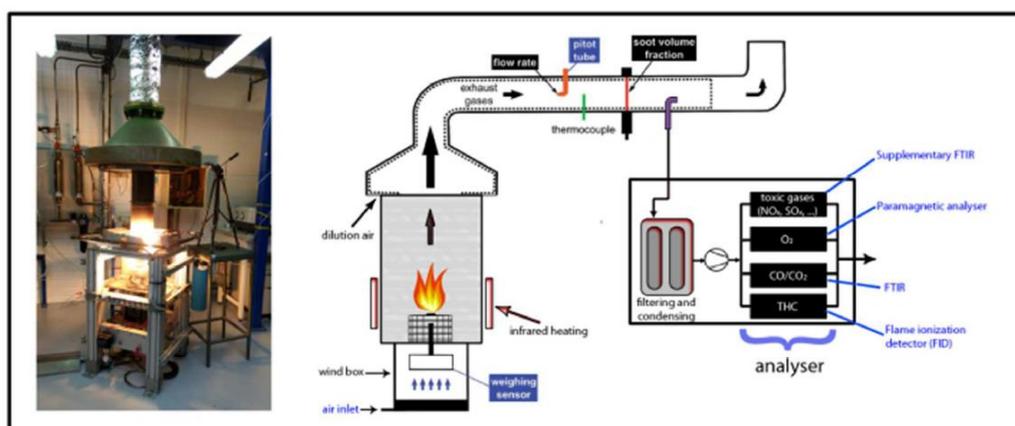
Table 1 is an example of the exploratory work carried out concerning furanics. As we can observe, the selected compounds clearly show diverse structural and functional attributes. Two important factors considered for the assessment is the flash point data and the heat of combustion values of furanics. As we can observe, the flash point data listed in the table ranges from -36 to 207 °C and the heat of combustion values calculated using the empirical Boie correlation ranges from 13 to 45 MJ kg⁻¹. The wide range of values observed from the exploration of those two key indicators of the fire hazard clearly supports the assumption that the fire behaviour and related fire risk of furanics may highly vary in practice and shall be carefully assessed in due course, considering both their synthesis, transformation and final end-use. This gives also a clear message that their reaction to fire performances of furanics shall not be generalized from limited measurements pertaining to one or another furanic compound, as it was erroneously done for ionic liquids for example.¹⁹

Fire calorimetry

A few furanic compounds were selected to test their reaction to fire performance. The tests were carried out using the fire propagation apparatus (FPA) commissioned at INERIS. The FPA is a multipurpose, polyvalent testing apparatus covered by various national and international standards such as ASTM E2058,²⁰ and NFPA 287,²¹ ISO 12136,²² capable of measuring key parameters addressing the full life cycle of a fire event from ignition, combustion, fire propagation and extinguishment data.

In the current investigation, experiments were conducted to understand the reaction to fire behaviour of key furanic intermediates as well as their mixtures. Samples of about 20 g were used and the tests were performed at well-ventilated fire conditions under a controlled environment with an inlet airflow rate of 200 NI h⁻¹. The tests were performed under calibrated external heat flux 25 kW m⁻² provided by the four infrared heaters under piloted ignition conditions (using either an electric spark or a pilot flame).

Key measurements from the FPA such as heat release rates, mass loss rates were calculated by the application of fire calorimetry laws in redundancy, based on the principles of Oxygen Consumption (OC) and Carbon dioxide Generation (CDG).²³ Concentration of the fire effluents were obtained by use of the online Fourier transform infrared spectrophotometer (FTIR) coupled to the FPA. By controlling the inlet airflow rate, it is possible to simulate fuel rich (under-ventilated) or fuel lean (well-ventilated) environments in the tests, thereby allowing the possibility to explore the full spectrum of ventilation conditions that may apply in real fire scenarios. Ventilation conditions set in practice are controlled through the determination of real time equivalence ratio (Phi factor) is the [(fuel/air)/(fuel/air)_{stoichiometric}].²⁴



2. In operation and schematic of the fire propagation apparatus at INERIS adapted from Muralidhara et al., 2018²⁵

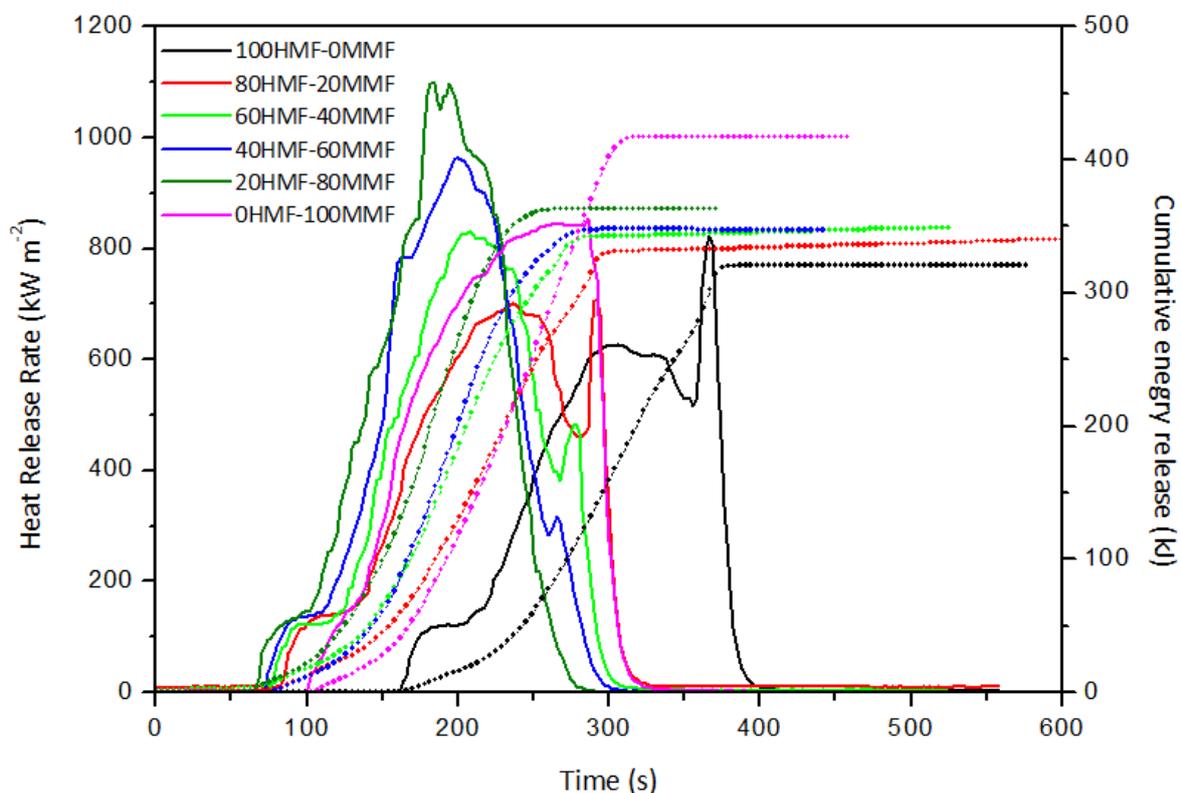
RESULTS

Exploratory testing on flammability and fire behaviour of some furanic compounds mentioned in table 1 have been performed. The current work focuses on presenting the fire behaviour of HMF, MMF and their mixtures (alkoxymethylfurfurals) in various proportions presenting the industrial interest of key furanic building blocks.

Table 2 presents the various products tested and main characteristics resulting from the fire tests in terms of mass loss and mass loss rates, combustion duration, resistance to ignition and carbon mass balance (from carbon in the test samples and all carbonated measured emissions or solid residues).

2. Burning behaviour of HMF, MMF and their mixtures in the FPA under well-ventilated fire conditions

HMF-MMF mixtures (%)	HMF100-0MMF	HMF80-20MMF	HMF60-40MMF	HMF40-60MMF	HMF20-80MMF	HMF0-100MMF
Measured Parameters						
Sample mass (g)	19.4	19.2	19	19.5	19.5	21.1
Mass loss (%)	94.8	96.2	96.7	97.7	98.1	100
Ignition time (s)	157	76	70	69	61	88
Duration of combustion (s)	229	232	233	224	217	224
Average mass loss rate ($\text{g} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$)	24.1	23.5	23.2	24.8	25.6	26.8
Max mass loss rate ($\text{g} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$)	66.1	38	43.3	48.7	53.6	49.9
Phi factor max ²⁶	0.22	0.21	0.24	0.28	0.32	0.28
Peak HRR ($\text{kW} \cdot \text{m}^{-2}$)	931	805	829	970	1167	865
Carbon mass balance (%)	96.2	98.7	98.9	93.3	94.6	97.5



3. Experimental heat release rate and cumulative energy release profiles of HMF, MMF and their mixtures under well-ventilated fire conditions

Figure 3 illustrates the variation of the heat release rate (HRR) profiles as a function of time and according to proportions of the two studied compounds in the mixture. The results from the FPA combustion tests are summarized in table 2. The data obtained and the visual observations made during the combustion tests clearly indicate that the tested compounds offer some initial resistance to ignition. However, the combustible nature and energy content of the test mixture may clearly achieve a self-sustaining flaming combustion process in the current test conditions, irrespective of the given official CLP classification of the products and their test mixtures. The ratio of MMF/HMF seems to play some role in ignition delay characteristics of the mixtures, although differences in flash points of the two neat chemicals do not support this observation. Higher concentration of MMF resulted in shorter ignition delays i.e. – 76s, 70s, 69s, and 61s for 20%, 40%, 60% and 80% MMF respectively.

Both thermal and chemical impact originating from the furanic fires will be further assessed in detail by making use of other measured parameters, including the influence of ventilation conditions that may significantly affect CO driven fire induced toxicity. This work has a similar approach as the exploratory work conducted earlier by the same group on the fire behavior of humins; a biomass side stream residue generated during the ACD process ²⁵.

Future work

The primary focus is on generating and further exploring the safety-oriented data for some of the key furanics of interest. From the database, specific patterns in terms of flash point and heat of combustion data in relation to the structural and functional aspects of furanics will be identified and related trends will be explored trying to identify some safety property-structure relationships. This information gives an initial understanding on the heat impact anticipated from a specific material prior to the actual experiments. Such data can be very useful in case of testing very expensive chemicals or for compounds that are newly being synthesized. The results can be useful in estimating the suitability of compounds in a specific application based on their anticipated risk profiles.

CONCLUSIONS

Bio-based value chains are becoming increasingly important in producing chemicals and materials for the future needs, thereby improving bio-based economy. Plenty of chemical (furanic) intermediates, platform molecules and final materials containing furanic compounds are expected to end up in soon future in varieties of applications, beyond those already on the market. For such a large group of chemicals, with structural and functional diversity, varying risk profiles can be anticipated. Therefore, early appraisal of safety profiles of new compounds of interest of the furanic family may be very important to make the best choice at the right time in innovation processes. This can be achieved by conducting dedicated safety-oriented studies combining testing and modelling approaches. Generating safety oriented patterns and defining some trends from the current work can help in filling the existing data gaps. Such information may lead to better suitability of compounds in desired applications. In addition, a dedicated fire risk assessment can help the users to get better insights on the thermal and chemicals risks associated with furanic fires and thus help in taking necessary precautions while handling, transportation and storage of such chemicals/materials. This can also be beneficial to legal obligations in the field of registration, classification and labeling of new chemicals.

ABBREVIATIONS

CLP- Classification, labelling and packaging of substances and mixtures

GHS- Globally Harmonized System of Classification and Labelling of Chemicals

TDG- UN Recommendations on the Transportation of Dangerous Goods

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