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Anitha Muralidhara, Ed de Jong, Hendrikus A. Visser, Gert-Jan Gruter, Christophe Len, et al.. Fire Propagation Behavior of Some Biobased Furanic Compounds with a Focus on the Polymer PEF. ACS Omega, 2022, 7 (11), pp.9181-9195. 10.1021/acsomega.1c05471 . ineris-03823806

HAL Id: ineris-03823806

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Submitted on 21 Oct 2022

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Fire Propagation Behavior of Some Biobased Furanic Compounds with a Focus on the Polymer PEF

Anitha Muralidhara, Ed de Jong,* Hendrikus (Roy) A. Visser, Gert-Jan M. Gruter, Christophe Len, Jean-Pierre Bertrand, and Guy Marlair*



Cite This: *ACS Omega* 2022, 7, 9181–9195



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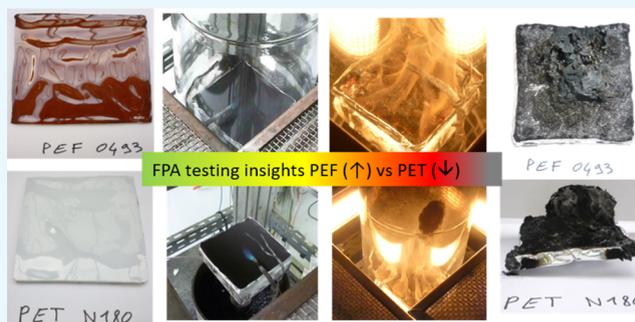
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ABSTRACT: Avantium is in the process of building a flagship plant for the production of furandicarboxylic acid (FDCA) and the derived polyester polyethylene furanoate (PEF) using their YXY process. Because of the status of this development of monomer production, next to storage and shipping, polymer production, application development, and polymer recycling, the understanding of the safety aspects of the YXY process is key for a successful deployment of the technology. In this paper, the focus is on fire propagation-related issues for both monomeric furanic compounds and for the polymer PEF and results are compared with relevant reference materials. The current assessment addresses the fire initiation and propagation behavior of FDCA and PEF for the very first time. From the fire safety viewpoint, it can be concluded that of the furanics tested, FDCA has a better safety margin both in terms of a lower thermal and chemical threat, as fires resulting from FDCA are not easily shifting toward underventilated fire scenarios. The obtained results with the PEF polymer are useful in understanding the nature and behavior of PEF under real fire conditions. PEF seems slightly better in terms of the total energy released from the combustion process than the bulk polyester PET. In addition, PEF fires result in lesser CO and soot yields compared to PET, which is proof for a better completeness of combustion.



1. INTRODUCTION

Avantium has developed a novel catalytic process for the cost-effective conversion of carbohydrates into furanics *via* the YXY process, registered trademark of Avantium. The process uses fructose as feedstock originating from various crops. As indicated in Figure 1, the YXY process mainly targets the production of 2,5-furandicarboxylic acid (FDCA), which is one of the most versatile building blocks for chemicals and polymer applications.^{1–6} FDCA can be obtained by the oxidation of alkoxymethylfurfural (RMF), which in turn can be derived from the acid-catalyzed dehydration of fructose in an alcohol solvent.¹ Last year, Avantium announced that its wholly owned subsidiary, Avantium Renewable Polymers BV (RNP), has selected Chemie Park Delfzijl, the Netherlands, for the location of its flagship plant. The 5-kiloton facility will come on stream by the end of 2023 and will produce plant-based FDCA—a key building block for many chemicals and plastics such as polyethylene furanoate (PEF). Avantium RNP and global specialty polyester supplier Selenis have agreed on the principal terms for a multiyear commercial FDCA to PEF polymerization agreement. Recently, it was disclosed that over 50% of the plant output have been secured by off-take partners. Because of the status of the development of monomer production, next to storage and shipping, and polymer

production, application development, and polymer recycling, an understanding of the safety aspects of the YXY process is key for a successful deployment of the technology. In this paper, we focus on fire propagation-related issues for both monomeric furanic compounds and the polymer PEF and compare them with relevant reference materials.

1.1. Monomeric Furanic Molecules. The original interest on furanic molecules was focused on biofuel.⁷ Spark ignition (SI) engines are one of the most important technologies for the traditional transportation systems. Recently, furanic compounds have emerged as promising alternative biofuels for SI engines as they possess favorable combustion properties that promote their use in SI engines. For instance, 2,5-dimethylfuran (DMF) has superior qualities such as higher energy density (30 MJ/L) and better resistance to undesired ignition with a research octane number (RON) of 119 compared to the most commonly used biofuel in SI engines

Received: October 1, 2021

Accepted: January 27, 2022

Published: March 14, 2022



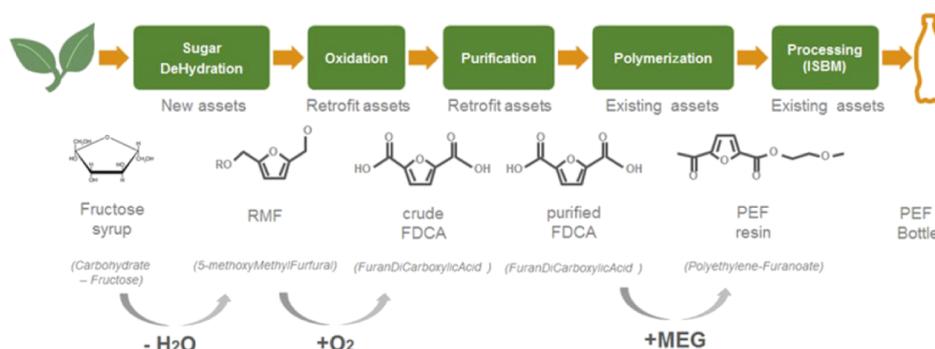


Figure 1. Schematic representation of conversion steps to produce FDCA and polyethylene furanoate (PEF) from fructose using the Avantium YXY process.

Table 1. List of Monomeric Furanic Compounds Selected for Testing with the FPA (Instrument-Enriched Fire Testing Equipment Based on ISO 12136⁴¹)

Compound Name	Physical State	Molecular formula	Molecular structure	Molecular Mass	NHV (MJ/kg)	Flash point (°C)
Furan dicarboxylic acid (FDCA) ^a	Powder	C ₆ H ₄ O ₅		156	13.0	207
2-Furoic acid	Liquid	C ₅ H ₄ O ₃		112	17.5	94.2
Hydroxymethyl furfural (HMF)	Solid	C ₆ H ₆ O ₃		126	20.4	79.4
Furfural	Liquid	C ₅ H ₄ O ₂		96	22.2	60
Methoxymethyl furfural (MMF) ^a	Liquid	C ₇ H ₈ O ₃		140	22.7	83
Furfuryl alcohol	Liquid	C ₅ H ₆ O ₂		98	24.3	65
Furan	Liquid	C ₄ H ₄ O		68	27.8	-36
2,5-Dimethyl furan (DMF)	Liquid	C ₆ H ₈ O		96	32.4	6
Alkoxymethyl furfural (RMF) ^{a,b}	Liquid	Mixture	-	-	-	-

^aTest samples from Avantium renewable polymer pilot plant, other furanic compounds from Sigma-Aldrich. ^bMixture of predominantly MMF and HMF with trace impurities.

ethanol with an RON of 110.⁸ Various engine studies have highlighted the use of furanic compounds in engine applications without significant modifications and resulted in lower NO_x, hydrocarbon, and particulate matter emissions and better knock resistance than conventional gasoline and some well-established biofuels (e.g., bioethanol). However, these applications give a clear message that if not all, some furanic compounds are easily combustible by design,^{7,9–11} and therefore, proper precautions must be taken near any source of heat, flame, or ignitable environments.

Therefore, it is worth investigating and understanding the flammability and combustion behavior of most of the compounds in this chemical family for their potential safe and sustainable use, even if not rated flammable for some of them. Indeed, qualifying a substance as “nonflammable” based on the formal definitions of flammable substances according to the predefined regulatory schemes [e.g., regulation (EC) No 1272/2008] on the classification, labeling, and packaging of substances and mixtures (known as CLP regulation)¹² can be misleading in many instances. Therefore, assigning a

flammability rating to a substance/mixture shall not be limited only to set the flash point limits (e.g., flammable liquid means a liquid having a flash point of not more than 60 °C in the CLP), as the regulation sets these limits by pure convention.^{13,14} Besides, many more or less combustible materials are capable of burning with flames irrespective of their flash points if enough ignition energy is provided in given circumstances, while such materials are not necessarily covered in this definition of flammable substances. Therefore, generalizing these terms for such a large family of chemicals can give wrong messages as witnessed in the case of another large chemical family “ionic liquids”.¹⁵ Several thermochemical parameters such as flash point, lower and upper flammability limits, autoignition temperature, and minimum oxygen concentration for flame propagation are necessary for safe process, operation, handling, storage, and transportation of chemicals. Besides this, estimation of the heat of combustion is another crucial parameter of consideration, giving the maximum energy, which can be released in a fire event, whatever may be the kinetics and completion level of the thermal release.

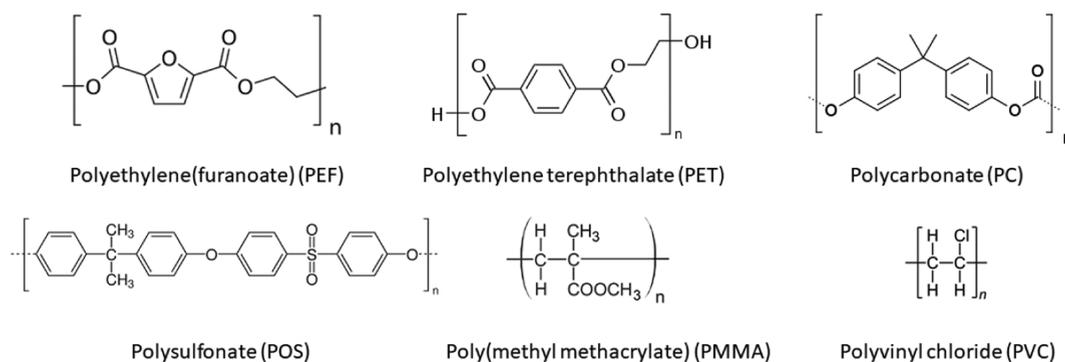


Figure 2. Chemical structures of the various polymers tested with the fire propagation apparatus (FPA) in this study.

From the literature survey, the data on the flammability criteria of furanics were found to be very limited in many of the material safety data sheets (MSDSs), and this may be caused because it is not a mandatory requirement for drafting an MSDS. Referring to the MSDS may not give the best scientific validation of the data presented in them. However, MSDSs were often considered in our study, as it was the chief source of obtaining information about a compound in terms of their physicochemical attributes. To the best of our knowledge, studies focusing on heats of combustion of furanic compounds are rather scarce.^{16,17} Having a larger number of furanic compounds in their family, experimental determination of heat of combustion would be a laborious, time-consuming, and expensive task. Besides, the unavailability of required quantities of compounds for testing may be faced, while the on-purpose synthesis of a new compound just for testing may lead to unreasonable prices and require laborious experimental procedures. Therefore, this study explores the calculation of heat of combustion data for furanic compounds using existing empirical correlations.

Many furanic compounds are relevant chemical building blocks with strong anticipated growth expected over the coming decades, so production, storage, and transport volumes will increase substantially.^{3,18} Based on an extensive search, it was concluded that fortunately no major accidents involving furanic compounds have been reported in the literature. However, fire hazard was one of the common observations in all reported scenarios in accident databases such as the ARIA database.¹⁹ Considering the applications of furanic compounds, it is important to realize the knowhow we have about their physicochemical safety characteristics to better handle these compounds. Indeed, the early access to their volatility, flammability, and combustion properties (from the knowledge of key parameters such as vapor pressure, flash points, autoignition temperature, thermal stability, flammability limits, and potential decomposition products) is an important aspect to mitigate all avoidable risks in the commercialization process of the product.

As safety shall be considered as part of multicriteria sustainability assessment, tackling safety issues right from the beginning may provide competitive advantages. It may help us to select the most appropriate options in terms of processes to establish new furanic platforms or guide the final selection of furanic-based chemicals or products for a given application. Therefore, this study aims at exploring the fire risk assessment of a number of furanic platform chemicals of high commercial interest, listed in Table 1. Key data obtained from this assessment will be further used in a scenario-based safety

assessment of combustion toxicity effects these compounds might cause in a real incident such as pool burning.

1.2. PEF, PET, and Other Polymers. Polymers are organic materials consisting of large macromolecules that are made of smaller subunits (monomers) of the same kind. Polymers can be divided into natural and synthetic polymers. Natural polymers are by definition occurring in nature and can be extracted (e.g., silk, proteins, DNA, and cellulose). Synthetic polymers are manufactured either by modification of natural products or by polymerization of suitable monomers. Synthetic polymers are mainly (99%) derived from petroleum sources (e.g., polyesters, polyolefins, and polyamides), but the market share of biosynthetic polymers such as polylactic acid (PLA) and PEF is growing.

The number and varieties of polymers and copolymers available in the market are very large. These polymers are essentially made of carbon and hydrogen (polyolefins), carbon, hydrogen, and oxygen (polyesters), and carbon, hydrogen, and nitrogen (polyamides, also referred to as nylons). In some specific polymers, chlorine, sulfur, and fluorine atoms are bonded alone or in combination with other atoms in the polymer structure. Polymers can be semicrystalline (very ordered, giving more strength and rigidity) or amorphous (random molecular structure, giving more flexibility and elasticity). The amount of crystallinity in a polymer can also depend on the processing history. Crystallinity can be induced by orientation [like in, e.g., biaxially oriented (stretched) film or drawn fibers].

Synthetic polymers are widespread in today's society and have been an integral part of human life starting from households, commercial environments, and in the transportation sector due to their undeniable benefits. Polyethylene terephthalate (PET) (Figure 2) is one of the most widely used polymer materials in the current market with more than 70 million tons of production per year. Despite its large benefits, the production of PET plastics deals with serious issues in terms of unacceptable CO₂ emissions from plastic waste increasing the carbon footprint and their production primarily relies on fossil resources. The technological progress in the light of producing renewable energy and materials has made the shortage of oil a less significant driver than before.^{20,21}

Plenty of efforts from both academic and industrial sectors have been devoted to producing more sustainable materials from biobased sources entailing superior qualities and cost competitiveness. Among many different efforts to produce bioplastics, their production from furan-based monomers has received considerable attention in recent years.^{2,22} The most

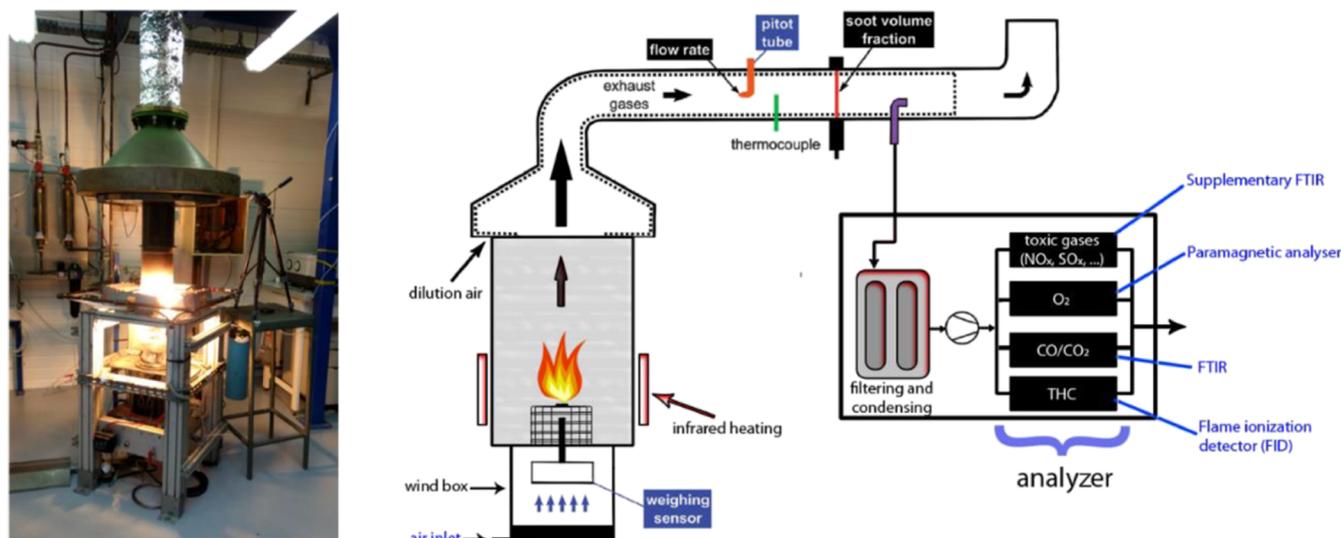


Figure 3. FPA commissioned at INERIS, in operation (left) and schematic view (right).

promising furan-based polyester is PEF, this is the biobased alternative to its fossil-based counterpart PET.

The YXY process uses FDCA and monoethylene glycol (MEG) for the production of PEF. In addition to the YXY process, different production routes for PEF have been addressed by other researchers *via* different process modifications.^{21,23,24} PEF is the most credible biobased alternative for PET at this stage due to its superior physical, mechanical, and barrier properties. PEF can be processed easily and applied to a wide variety of industrial applications including films, fibers (textiles and carpets), food packaging, and bottles for beverages.^{25–28} Compared to PET, PEF has 10 times lower oxygen permeability,²⁹ 19 times lower CO₂ permeability,³⁰ and 3 times lower water diffusion,³¹ in addition to higher strength and stiffness values.^{22,32,33} In addition, it also has higher glass transition temperature (the T_g of PEF is 86 °C compared to the T_g of PET of 74 °C). The melting point of PEF is 235 °C compared to 265 °C for PET.^{25,28} PEF's chain structure and crystallization behavior have been researched extensively.^{34–37} PEF is estimated to reduce around 60% of nonrenewable energy consumption and greenhouse gas emissions compared to PET.^{22,23,38}

The differences in polymer structure and functionalities are also reflected in wide variations of the fire behavior of polymers.³⁹ Synthetic polymers are combustible materials under certain conditions. However, many applications consist of two or more polymers in combination, together with additives such as pigments and fillers. Therefore, the emphasis on fire behavior has gradually shifted from pure polymers to the final compositions in the products.⁴⁰ The majority of such final products (*e.g.*, cables, furniture, and carpet) are ending up in conventional dwellings, public access buildings, and other built-in environments where fire risk is a key concern. As PEF is relatively new and not yet in the market, it is important to start to understand its fire behavior without additives. So far, there are no published studies focusing on exploring the fire behavior of PEF.

The current study explores the reaction-to-fire performance of PEF. The obtained results are compared with other commercially available aliphatic and aromatic polymers (composed of C, H, O, S, and Cl atoms), namely, PET, polysulfonate (POS), polycarbonate (PC), and polyvinyl

chloride (PVC), because of their variations in their generic nature and physical and chemical properties. The study brings an initial understanding on the fire behavior of pure PEF without any fire-retardant additives. This can be useful to understand the necessary modifications to the original material to control/alter its flammability characteristics without actually compromising the unique physical and mechanical properties depending on the target application.

2. MATERIALS AND METHODS

2.1. Monomer Test Samples. A variety of commercially interesting furanics were selected having wide varieties in structural and functional attributes [such as variation in alkyl chain lengths, molecular masses, net heating values (NHVs), and different functional groups] (Table 1) to test their fire behavior with the FPA. Some of these test samples were obtained directly from the Avantium renewable polymer pilot plant in Geleen, the Netherlands, and the rest were ordered from Sigma-Aldrich.

2.2. Polymer Test Samples. The following polymer samples were examined as sheets from the original resins. PEF and PET compression-molded plates were produced and supplied by Avantium. The PEF resin used to produce the plates had a relative, weight-averaged molecular weight of 77 kg/mol as measured in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) using a calibration with a polymethyl methacrylate (PMMA) reference, as determined using gel permeation chromatography. The PET used was of commercial grade produced by Indorama (RamaPET N180), with a reported intrinsic viscosity of 0.80 dL/g and a measured relative weight-average molecular weight of 75 kg/mol. The plates were compression-molded into a cavity of 100 × 100 × 6 mm³ using predried (<50 ppm water content), ground resin granules at a temperature of 245 °C for PEF and 285 °C for PET for a total of six min while ensuring an overflow of material from the mold to minimize the creation of voids. The origin and composition of the other polymers have been described before.⁴²

The fire behavior of PEF, PET, PC, PVC, PMMA, and POS using 10 cm × 10 cm sheets was examined with the FPA in a comparative mode.^{43–47} All experiments were carried out

Table 2. List of Polymers Selected for Testing with the FPA^a

name	type	C (%)	H (%)	O (%)	NHV (MJ/kg)
polyethylene furanoate (PEF)	semiaromatic	52.5	3.4	43.6	17
polyethylene terephthalate (PET)	semiaromatic	61.8	4.2	33.8	22
polyvinylchloride (PVC)*	aliphatic	38.9	4.8	4.3	18
polycarbonate (PC)*	aromatic	75.4	5.5	19.1	30
polysulfonate (POS)*	aromatic	78.9	5.3	15.8	29
polymethyl methacrylate (PMMA)*	aliphatic	61.1	8.6	31.1	25

^aElemental compositions and net heating values (NHV) of test samples (* elemental compositions were adapted from the published work by Marlair and Tewarson³⁷).

under well-ventilated fire conditions under an external heat flux of 35 kW/m². See Chapter 2.3 for an extensive description of the FPA.

2.3. Fire Propagation (Tewarson) Apparatus. The FPA was originally designated by the inventor of the equipment as the 50 kW flammability apparatus in the USA⁴⁸ and used for the study of polymer flammability in application-based contexts.⁴⁹ The customized version based on the ISO12136 standard used in this study by INERIS is illustrated in Figure 3. Details regarding historical development of the FPA apparatus and specific features of INERIS^{15,43,44,50} version are provided as the Supporting Information (see appendix A).

3. RESULTS AND DISCUSSION

3.1. Ignition and Heat Release Characteristics of Monomeric Furanics. The results obtained from the combustion of furanics in the FPA are summarized in Table 3. The table gives an overview of the following data measured or derived from measurements on the FPA in both well-ventilated and underventilated fire conditions.

- Initial sample mass (g)
- Peak HRR (kW/m²).
- Applied external heat flux (kW/m²).
- Total heat release (MJ).
- Duration of combustion.
- Energy efficiency of conversion (%).
- Mass loss rate (%).
- Yield of combustion products (mg/g).
- Time to ignition (Tig).
- Carbon efficiency of conversion (%).

Figure 4a,b shows the representation of the heat release rate (HRR) profiles of all the tested furanics under well-ventilated and underventilated fire conditions, respectively. With the influence of applied (same) external heat flux, variation in ignition time, duration of combustion, peak HRR, and total heat released were observed from all compounds. Such a variation can be considered as obvious due to the diverse structural and functional attributes of the selected furanics. Irrespective of different Tig, all compounds were able to ignite under the influence of external heat stress accompanied by a pilot flame in well-ventilated and electric spark in underventilated tests. From the flash point data presented in Table 1, we can see that many of the tested compounds do not enter the category of flammable liquids according to the CLP regulation (flammable liquids have flash point ≤60 °C). Nevertheless, the first observation clearly indicates that the tested furanics achieved easily or relatively easily self-sustaining flaming combustion under the current test conditions irrespective of the given official CLP classification for the products and their test mixtures. This is, of course, to relate to

the combustible nature of all furanics. Subsequently, all of the tested furanics do entail more or less significant fire hazard, should this hazard be officially recognized by legal flammability classification or not.

Experimental results indicate that when adequate environmental conditions are achieved, these compounds are capable of sustained combustion leading to thermal and chemical threats of varying degrees and hence fire risk from the tested furanics cannot be ignored.

Under well-ventilated conditions, the resistance to ignition (Tig) follows the pattern FDCA (352 s) > 2-furoic acid (160 s) > HMF (122 s) > MMF (88 s) > RMF (78 s) > furfuryl alcohol (63 s) > furfural (31 s) > furan (4 s) > 2,5-DMF (1 s) with FDCA having the highest and 2,5-DMF having the lowest resistance to ignition, respectively. The results were further compared with some common fuels tested with the FPA under the same test conditions as furanics 2,5-DMF (1 s) and furan (4 s) ignited immediately, very similar to other flammable liquids such as heptane, ethanol,⁵¹ or kerosene,⁵² whereas the other furanics having more oxygen atoms presented higher resistance to ignition under the applied heat stress (data not shown).

Under underventilated fire conditions, resistance to ignition of furanic compounds follows the same trend as mentioned above, where the ignition delay was slightly higher (in terms of seconds only) than under well-ventilated fire conditions. All experiments were performed under calibrated external heat flux until all samples were completely consumed.

From our observation, the time for ignition (Tig) pattern for the tested furanics varies as a function of the O/C ratio in the molecular structure. Considering furan as a parent molecule, we can see that the addition of any alkyl groups to furan (without any oxygen-containing species) resulted in a compound (2,5-DMF) having lesser O/C ratio, higher flash point, and lesser Tig than the parent compound. On the other hand, the addition of oxygen-containing species to the parent compound resulted in the increase in Tig, O/C ratio, and flash point. The same scenario is illustrated in Figure 5. However, as the whole family of furanic compounds is much larger than those tested in the present study, this trend observed is valid only for the tested compounds in this study.

Once ignited, clearly flaming combustion was observed in all compounds under both well-ventilated and underventilated conditions and all compounds showed varying trends in terms of HRR profiles. 2,5-DMF and furan resulted in higher total and peak HRR than other furanic compounds tested, which is reasonable due to their higher energy density.⁵³ Upon providing sufficient heat, the furanics can ignite and therefore cannot be qualified as nonflammable. Noteworthy that the selected furanic compounds for this FPA test contain both liquids and solids (FDCA and HMF) at ambient temperature.

Table 3. Burning Behavior of Tested Furanic Compounds in Well-Ventilated and Underventilated Fire Scenarios^a

chemical name formula	FDCA C ₆ H ₄ O ₅		2-furanoic acid C ₅ H ₆ O ₃		HMF C ₆ H ₆ O ₃		MMF C ₇ H ₈ O ₃		RMF (mixture)		furfuryl alcohol C ₅ H ₆ O ₂		furfural C ₅ H ₄ O ₂		furan C ₄ H ₄ O		DMF C ₆ H ₈ O	
	WV	UV	WV	UV	WV	UV	WV	UV	WV	UV	WV	UV	WV	UV	WV	UV	WV	UV
sample mass	20	35	20	35	19.4	35.1	21.1	35	19.9	35.2	21.9	37.6	20.5	35.6	20.2	35.1	22.5	26.1
mass loss	99.5	99.4	100	100	94.8	95.7	100	100	99	99.4	99.5	100	100	99.7	100	100	100	100
time for ignition	362	500	160	152	122	173	88	112	78	102	63	74	31	52	4	6	1	12
duration of combustion	414	406	225	224	348	260	224	200	233	194	236	312	162	252	126	186	156	180
Av. mass loss speed	13.7	14.2	25.3	25.7	15.8	22.2	26.8	28.8	24.3	29.9	26.4	19.9	35.9	23.3	27.8	27.8	32.4	32.4
phi max	0.10	0.56	0.20	1.57	0.22	1.50	0.28	2.11	0.30	2.50	0.33	1.59	0.37	1.86	0.46	2.48	0.56	2.15
net heating value	13.0		17.5		20.4		22.7		22.7		23.7		22.2		27.8		32.4	
cumulative energy release (OC)	11.6	12.7	17.4	12.9	17.2	13.9	20.5	12.4	20.1	14.2	21.7	17.6	20.9	15.6	25.6	18.0	28.7	24.1
cumulative energy release (CDG)	12.2	11.5	16.6	13.7	17.4	14.2	19.8	13.2	19.8	13.7	21.7	18.4	21.0	16.2	25.9	16.1	28.3	20.2
Av. cumulative energy release (OC + CDG/2)	11.9	12.1	17.0	13.3	17.3	14.1	20.1	12.8	20.0	14.0	21.7	18.0	18.0	16.2	25.7	17.1	28.5	22.2
energy efficiency conversion	91.8	93.1	97.2	76.2	84.7	68.9	88.7	56.2	88	61.6	91.3	75.8	94.2	71.5	92.6	61.5	87.9	68.3
CO ₂	1500	1500	1856	1502	1778	1403	1900	1125	1908	1186	2038	1645	2150	1580	2398	1364	2370	1594
CO	7.5	12.4	13	86.8	20.6	107.5	20.9	249.3	18.5	241.5	14.9	145.7	16.6	171.2	17.2	216.4	39	165
Soot	13.3	13	31.1	20.1	41.6	37.6	54.3	45.9	43.4	43.5	38.4	38.9	35.7	36.1	39.7	40.3	71	62.2
THC	0.6	2.4	2.4	35.9	2.7	29.7	2.8	91.5	2.5	81.8	1.8	51.5	1.6	60.8	3.8	170.1	9.8	156
CH ₄	0	0.2	1.1	2.2	0.1	2.6	0.6	10.9	0.2	11.2	0.1	4.9	0.1	3.3	0.2	7.6	0.8	13.5
SO ₂	0	0	1.8	0	5.6	3.4	6.9	0	0.1	0	2.1	0	1.2	0	1	0	0.9	0
carbon balance	101.1	93.8	101.9	93.9	98.4	90.6	97.5	92.3	96.5	92.6	98.8	98.4	101	96.4	100	95.8	99.3	95.6

^aNet heating value (NHV): theoretical maximum heat that can be released by complete combustion; Phi: fuel/air: ratio (normalized by the same ratio as established under stoichiometric conditions); phi < 1: well-ventilated conditions (WV)—phi > 1: underventilated ventilated conditions (UV); cumulative energy release (OC): overall effective energy released during experiments, as calculated from the oxygen consumption (OC) technique; cumulative energy release: same parameter, as obtained using the alternative carbon oxide generation (CDG) calculation technique; and carbon balance: balance between carbon as measured as released carbon-containing species and initial carbon content in the test sample.

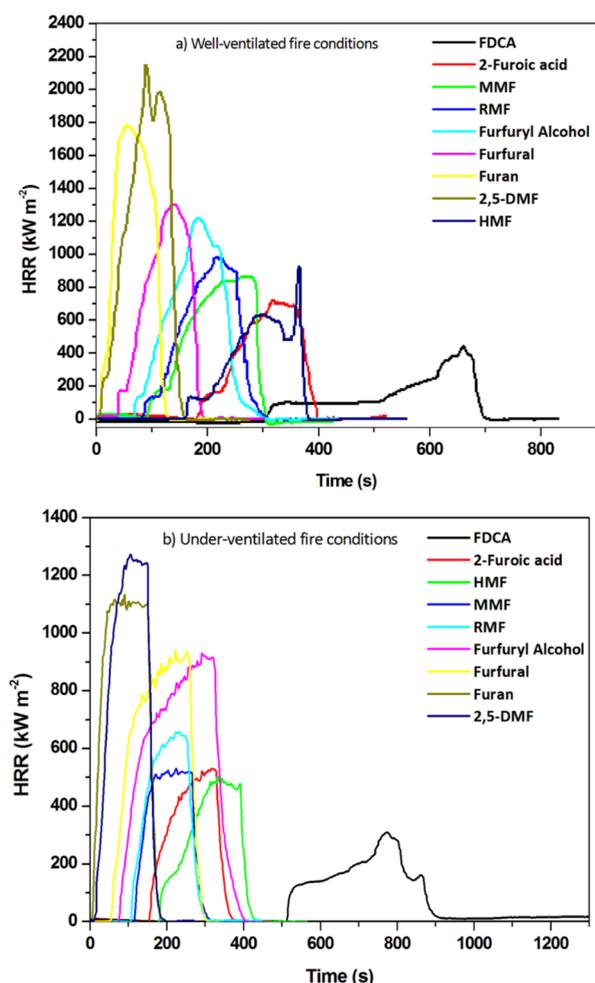


Figure 4. Heat release rate (HRR) profiles of furanic compounds under (a) well-ventilated conditions and (b) underventilated conditions tested *via* the FPA.

The vaporization of liquids is a surface mass transfer phenomenon where the chemical structure of liquids generally

remains the same as the vapor. On the other hand, solids undergo thermochemical degradation or pyrolysis producing combustible mixtures of gases and vapors, leaving behind a carbon-rich residue called char.⁵⁴ Therefore, in the case of liquid furanics, we observe pool fire combustion where the vapor phase of the burning liquid is driving the combustion phenomenon. As the kinetics of solid and liquid burning is entirely different, the different HRR profiles of furanics observed in Figure 4a may only infer the different burning behavior witnessed from different compounds belonging to the same family.

In well-ventilated conditions, all tested furanics show varying combustion rates (Table 3) and both thermal and chemical release vary accordingly. 2,5-DMF and furan depict very fast kinetics with the peak HRR of 2153 and 1787 kW/m², around 60 and 50% lower than heptane, whereas about 42 and 50% more than ethanol. As indicated by many researchers, the higher energy density of these two compounds have reflected their suitability in fuel applications.^{53,54}

When comparing the heat release rate measurements as indicated in Table 4, we can see that the results from both OC

Table 4. Peak HRR Values of Tested Furanics in Well- and Underventilated Fire Conditions

peak HRR	well-ventilated fire (kW/m ²)	underventilated fire (kW/m ²)	difference in peak HRR (%)
2,5-DMF	2153	1272	59
furan	1787	1134	63
furfural	1304	941	72
furfural alcohol	1218	931	76
RMF	984	658	67
MMF	865	531	61
HMF	931	503	54
furoic acid	725	531	73
FDCA	450	309	69

and CDG are in good agreement with each other in both well-ventilated and underventilated tests with a standard deviation of ranging between 0 and ± 2 kJ/g. The peak HRR drastically

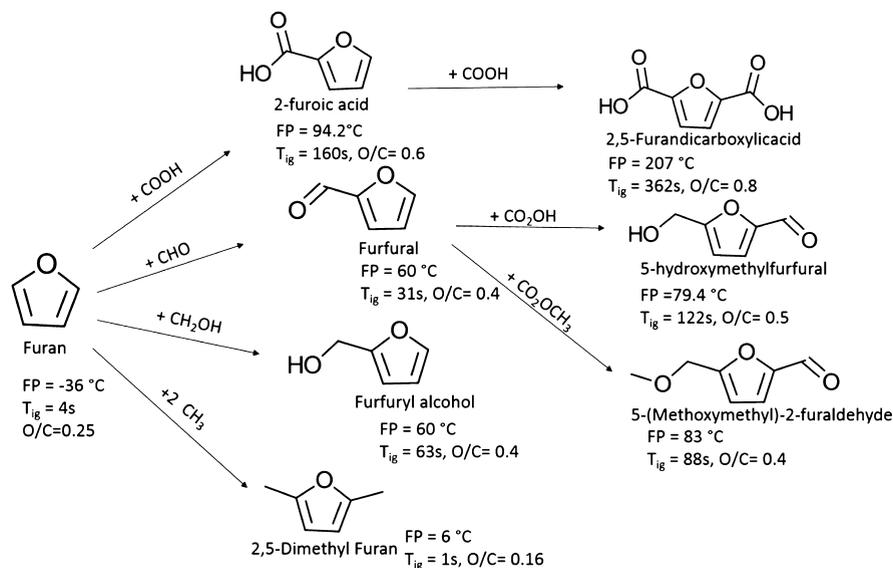


Figure 5. Variation of time to ignition and the O/C ratio of the tested furanics.

reduces under underventilated fire conditions as indicated in Table 4. This is mainly due to the incomplete chemical reaction between the oxygen from the air and the products of incomplete combustion (CO, hydrocarbons, soot and other intermediate products), resulting in the decrease in peak.

3.2. CO Yield as a Function of Equivalence Ratio. The early-stage fire is normally well-ventilated as there is enough oxygen available for the oxidation process. At this stage, it is easy to control the fire and to extinguish. As the fire grows, with limited ventilation and the large surface area, the reduction process becomes dominant with increasing amounts of toxic species (CO, smoke, hydrocarbons and other products) leading to a dangerous situation. In such a case, 2/3rd of the fire death resulting in an enclosed space is due to the presence of CO.⁵⁵ Our bench-scale test results can be considered as a small room fire as the small room fire can have the same scale as the burning specimen in the bench-scale tests. Accordingly, in early-stage room fire, the CO yield depends mainly on the chemistry of the fuel being burned. From the Table 3 we can observe that, in well-ventilated conditions, the tested furanics resulted in $\phi < 1$ in the order FDCA (0.1) < 2-furoic acid (0.2) < HMF (0.2) < MMF (0.3) < furfuryl alcohol (0.3) < furfural (0.4) < furan (0.5) < 2,5-DMF (0.6). As the fire grows, the fuel/air increases and therefore CO yield rises. This is also evident from the variations observed in the average CO yields in different ventilation conditions plotted as a function of the O/C ratio of the fuel molecular structure as shown in Figure 6.

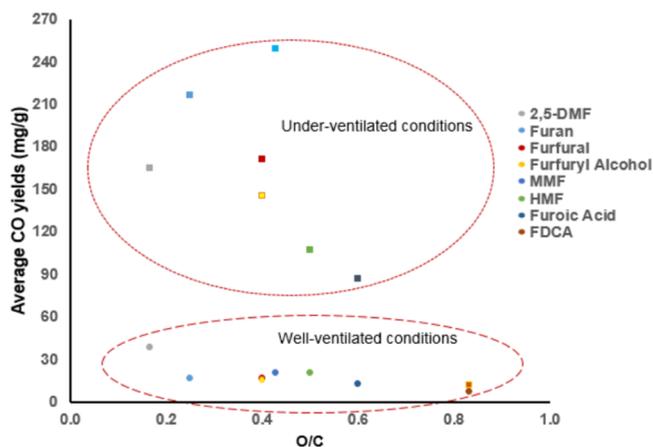


Figure 6. Average CO yields resulting from furanic fires in well-ventilated and underventilated fire conditions plotted against the O/C ratio of the respective tested compounds.

Under underventilated conditions, the furanics resulted in $\phi > 1$ (Table 3). We can also observe that with the increase in equivalence ratio (ϕ), the products of complete combustion such as CO_2 decreased and the products of incomplete combustion that is CO, THC and soot increased⁵⁵ in our test results.

By comparing the CO yield with the global equivalence ratio from our tests, we can see that the number 0.2 holds good for many tested furanics as presented in Figure 7. Nevertheless, amongst the tested furanics under underventilated conditions, ϕ values of FDCA clearly stayed $\ll 1$ (Figure 7), despite providing adequate underventilated environment. FDCA resulted in the longest time to ignition (>8 min) and lower speed of combustion compared to other tested furanics. Higher

O/C ratio in FDCA could be helping the combustion process to stay under well-ventilated conditions. From the fire safety viewpoint, we can say that FDCA has a better safety margin both in terms of a lower thermal and chemical threat as fires resulting from FDCA are not easily shifting toward underventilated fire scenarios.

3.3. Other Combustion Products of Monomeric Furanic Molecules. Besides the generation of CO, ventilation-controlled fires also provide a favourable environment for the increasing yields of soot and other species for various chemical substances.^{50,56,57} Accordingly, soot production was one of the evident observations made both visually and experimentally during the combustion tests performed in the FPA.

Varying quantities of soot production was observed in both well- and underventilated fire conditions from all tested compounds. In a classical hydrocarbon fire, soot and total hydrocarbon production are generally lower under well-ventilated conditions than under underventilated conditions. The same situation was observed in most of the other FPA test results presented in this manuscript in the upcoming chapters. According to Figure 8, we can see that the higher quantities of soot production were observed in well-ventilated conditions in DMF, HMF, MMF and 2-furoic acid than in underventilated fire tests. This pattern does not follow the same trend in total hydrocarbon production.

The presence of oxygen in the structure of furanics could be a reason not facilitating an easy transition to reach underventilated conditions resulting in lower soot quantities. On the other hand, soot is considered to be composed of 100% carbon in our calculations. This could lead to a slight overestimation in well-ventilated conditions as the soot particles may contain other elements than just carbon. Further exploration on this matter is in due consideration to better understand the current situation.

It can be seen that except for FDCA, the yields of unburnt hydrocarbons in other tested compounds seem quite important to be considered under underventilated fire conditions, whereas the values are negligible in well-ventilated scenarios. As no heteroatoms were present in the tested compounds, yields of sulfur or nitrogen oxides were not detected from the combustion experiments.

3.4. Scenario-Based Assessment of Combustion Toxicity Form Fires Involving Monomeric Furanic Compounds. The scale-up of Avantium YXY Technology for industrial applications of furanics could result in the production and storage of large(r) quantities of furanic compounds in the industrial storage premises upon commercialization. Not all furanics are flammable compounds, but our test results clearly indicate that they are capable of ignition and achieving self-sustaining flaming combustion with the influence of a sufficient external heat source. Therefore, a contextual fire-induced toxicity assessment for the tested furanic compounds was performed using the data obtained from the FPA experiments such as time taken for ignition, rate of combustion, heat release rate, and emission of pollutants and can be referred to as “source term” information. This allows us to perform a contextual risk assessment for furanic compounds assuming a real-world scenario.

Table 3 presents the summary of the data obtained from the combustion tests conducted using the FPA. These data are key input information for the study of future industrial scenarios of interest involving furanics where potential fire-induced toxicity

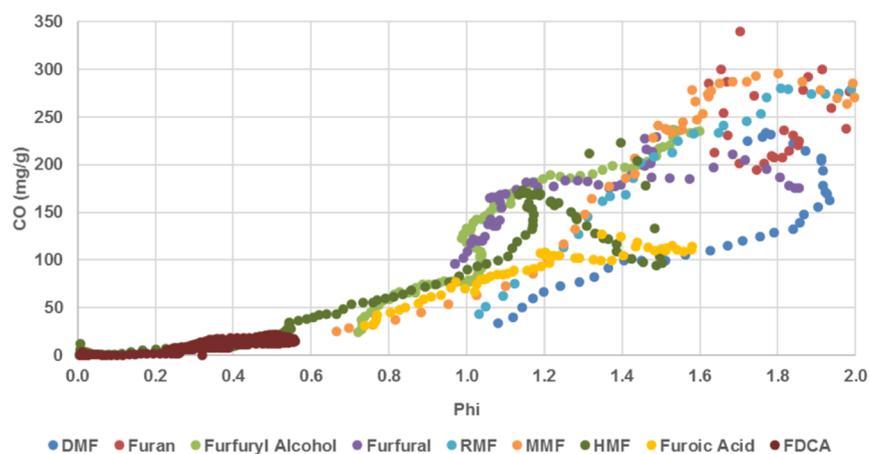


Figure 7. Variation of CO vs phi profile of furanic compounds under underventilated fire conditions.

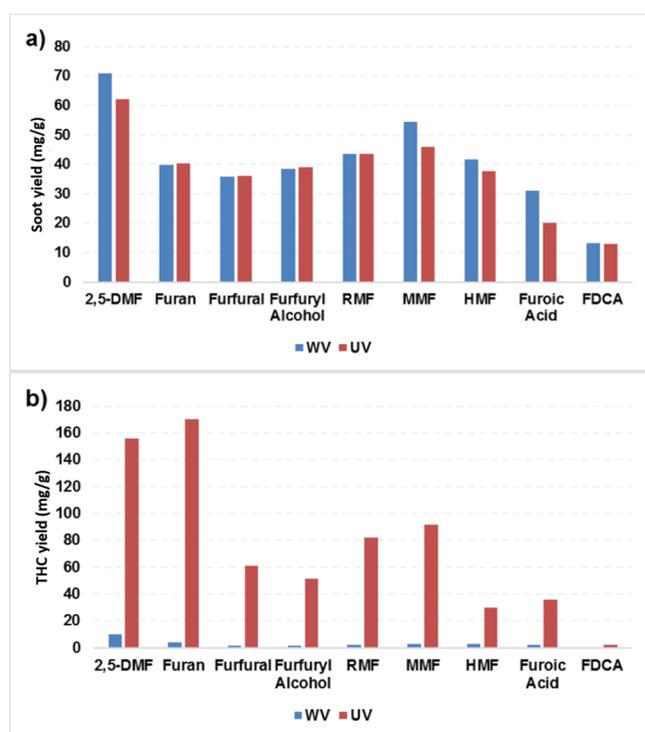


Figure 8. Experimental (a) soot yields and (b) total hydrocarbon (THC) yields (in mg/g) from tested furanic compounds under well-ventilated (WV, blue) and underventilated (UV, red) fire conditions.

effects need to be predicted for the inherently safer design of concerned facilities and definitions of safety prevention and protection measures. Under certain situations, a legal obligation to perform simulation of worse case accidents may result from applicable industrial safety regulation. This attempt is an assessment of one of the possible scenarios that led to the fire outbreak. It is noteworthy that in-depth examination certainly requires specifically defined objectives and access to much more reliable input data and multiple scenarios. Our preliminary study is not in the scope of fulfilling these in-depth toxicity assessments. The main objective of such an estimation is to predict the toxicity effects in the fire environment based on the chemical measurements. In these tests, it is not necessary to expose animals.⁵⁸ The data obtained can be related to the toxic effects in animals with some degree of error

or uncertainty (depending on the chemicals analyzed in the emitted gases).

To exemplify how data from Table 3 may be used for such purposes, we developed a factitive case study. In this case study, we consider the situation where 10 L of a furanic compound is used in a batch reactor in an 80 m³ building. If we assume that through a leak in the reactor, a massive fire scenario occurs, with pool burning of the furanic compound due to an undefined ignition. The pool is assumed to be limited to a surface of 0.06 m², and the building is assumed to behave as a well-stirred reactor. This case study addresses all of the tested compounds as individually present in the reactor. Although the tested furanics resulted in self-sustained combustion during the tests, assuming that the firefighting operation was started rather quickly and also to make a fair assumption based on the FPA results obtained, we assume the 100% combustion of furan and 2,5-DMF, 70% consumption of furfural and furfuryl alcohol, 50% consumption of MMF and RMF, 30% consumption of 2-furoic acid and HMF, and 15% consumption of FDCA of the 10 L of total quantity of available furanics.

Although the scenario developed herein involves some basic assumptions that have limited validity, it is bound to complexity of fire gas toxicity still leading to limited consensus between experts.⁵⁹ However, the underpinning approach based on the use of fractional effective dose (FED) and fractional effective concentration (FEC) concepts as described in ISO 13571, currently constitutes the best available fire safety engineering technique to estimate the criticality of fire scenarios involving chemicals of interest in given configurations. The computations shown here as illustrated here in Figure 9 allow access to the toxicity data, in terms of tenability *versus* time, considering the various toxic gases released as a result of the combustion of furanic compounds and assuming a simple additive effect of contributing gases. Therefore, the user/reader can make use of the experimental data in order to assess the fire toxicity threat to exposed people of given furanic compounds under fire conditions, considering appropriate variables of the fire scenarios that need to be considered (*e.g.*, ventilation conditions and relating dilution factors, expected time for evacuation, or duration time for fire suppression).

Figure 9 represents the various trends of fire-induced toxicity illustrated in the factitive case study involving furanic compounds in an event of a fire. A very first observation is that fire-induced toxicity potential of tested furanics clearly

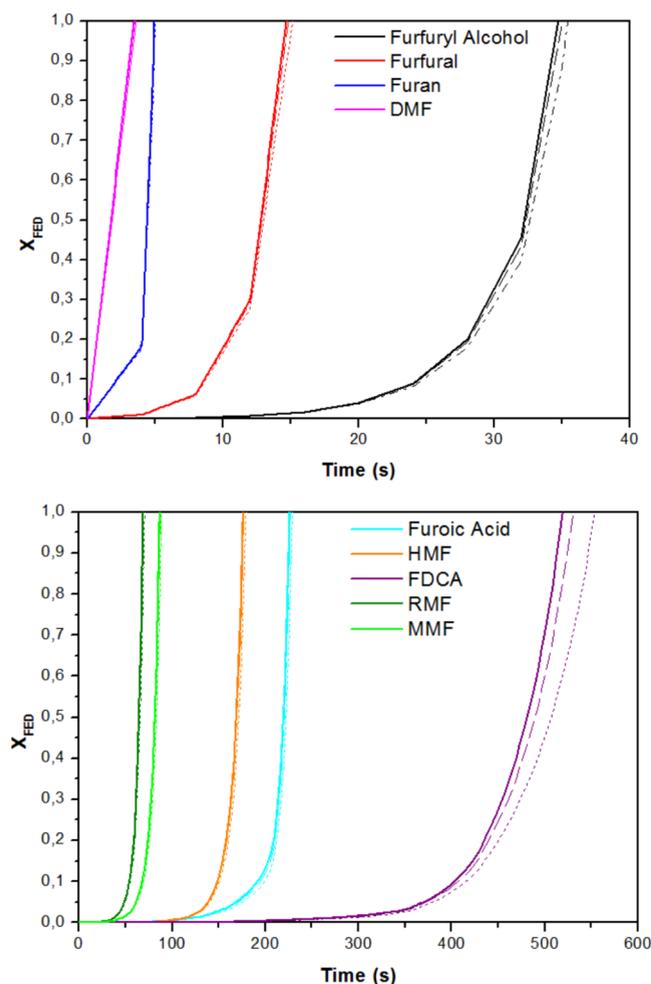


Figure 9. Evolution of fractional effective dose (X_{FED}) of toxic gases in an accidental fire scenario involving furanic compounds as a function of air renewal rate (τ). Straight line represents $\tau = 3$, dashed line represents $\tau = 6$, and dotted line represents $\tau = 12$.

varies from each other because fire dynamics and in particular dynamics of production of toxic species vary from one furanic compound to the other; although for those tested, the emitted toxins are similar in nature. The case study describes a factitive,

worst-case scenario that leads to the production of large quantities of irritant gases to mainly observe if the fractional effective concentrations rise above the critical threshold value in any given air exchange rate. Nevertheless, in our case, as the selected furanics did not contain any heteroatoms, the combustion of furanic compounds did not produce any significant quantity of irritant gases, as shown in Table 3 in the previous section. Therefore, the concentration of irritant gases produced did not surpass/exceed the critical threshold value in the case of any tested furanics (X_{FEC} —fractional effective dose at any time in the modeled scenario far below 0.1 to be compared to 1 as an X_{FEC} value considered as triggering so called “incapacitation”, *i.e.*, critically impeding self-evacuation for ordinary people). On the other hand, in an accidental fire scenario involving the tested furanics, major toxicity concern would be due to the asphyxiant concentrations such as CO (Table 3).

Figure 9 presents a detailed comparison of the evolution of asphyxiant gas (limited to CO and HCN) for all furanic compounds tested in all different air exchange rates considered in the factitive scenario. This comparison indicates that the concentration of toxic species evolved *versus* time in the studied case was not greatly influenced by the number of fresh air renewal rates for the selected volume enclosure. Mostly emergency situations would arise at their respective time interval where the concentration of asphyxiant gas produced would exceed the critical threshold value, in all cases but FDCA where the X_{FED} remains far below 1. If there is a fire involving FDCA, furfuryl alcohol, or furfural, increasing the air change rate of the room [up to 12 volumes (of the room) per hour] could be effective by allowing higher evacuation time before the critical value (X_{FED} strictly below 1) is reached. In other cases, increasing the building ventilation would not help in controlling the postfire hassles. As we have not tested all the members of the furanic family, there could be possibilities where the higher air exchange rate might hinder the escape of victims by recirculating the toxic species back to the premises.

This illustration below indicates that in the case of similar scenarios, the main concern would be the concentration of asphyxiant gases and their change *versus* time. Clearly, irritants did not pose any significant threat. However, if the same scenario occurs in chemical storage or transportation truck carrying various chemicals, the situation could result in a

Table 5. Burning Behavior and Yields of Combustion Products from Polymer Fires under Well-Ventilated Fire Conditions

measured parameters	PEF1	PEF2	PET1	PET2	PVC	PC	POS	PMMA
sample mass distribution (g)	78.1	77.8	70	70.3	133.2	119	128	48.3
mass loss (%)	92	92	89	87	82	78	66	100
time for Ignition (s)	80	73	107	110	63	228	331	87
average mass loss rate ($\text{g}/\text{m}^2\cdot\text{s}$)	33	32	19	17	13	22	15	21
max mass loss rate ($\text{g}/\text{m}^2\cdot\text{s}$)	53	57	46	34	55	41	75	34
peak heat release rate (kW/m^2)	730	823	539	456	171	511	432	781
carbon efficiency of conversion (%)	98	96	89	93	117	92	101	98
residue (g)	6.1	6.0	7.4	12.1	23.8	26.2	43.5	0.0
CO/CO ₂	0.01	0.01	0.02	0.02	0.13	0.03	0.04	0.005
Yields of Combustion Products								
CO ₂ (mg/g)	1582	1558	1528	1574	583	1681	1631	2082
CO (mg/g)	17	19	26	26	78	46	64	10
Soot (mg/g)	33	33	63	67	103	110	114	15
THC (mg/g)	3	3	7	8	36	15	15	2
CH ₄ (mg/g)	0.2	0.3	0.3	0.4	4.9	1.1	1.0	0.1

different outcome. As a word of caution, this factitive scenario only gives the trends on understanding the criticalities related to fire-induced toxicity of furanics and helps the user to be aware of the risks involved with the calculations made using the equations (data not shown). The real fire toxicity assessment in buildings is a rather complex issue that certainly requires different tools to perform compartment fire modeling (integrating hot and cold smoke layers and fire plume) and the use of dedicated zone models such as computational fluid modeling. In such a case, the “source term” indicating the emission characteristics of fire gases would serve as input data, whereas Q_{in} and Q_{out} would be the output resulting from boundary conditions.

3.5. Ignition and Heat Release Characteristics of PEF and Other Polymers. The reaction-to-fire performance of the polymers listed in Table 2 was evaluated with the FPA under well-ventilated fire conditions. The summary of the test results obtained from the FPA test runs and the related analysis of mass and thermal balances and of the yields of various chemical species are presented in Table 5.

All test samples were subjected to piloted ignition in the FPA under the influence of an external heat flux of 35 kW/m². The heat flux >30 kW/m² was previously measured as the ideal value for some of the tested polymers to have sustained combustion with minor variations in previous FPA tests conducted by Marlair and Tewarson (2003). Therefore, 35 kW/m² was chosen as an ideal heat flux in the current experiment.

From the first observation, we can see that all tested polymers presented some initial resistance to ignition. The resistance to ignition follows the pattern PVC (63 s), PEF (77 s), PMMA (87 s), PET (109 s), PC (228 s), and POS (331 s). The presence of higher quantities of oxygen in the PEF structure (see Table 2) is probably facilitating its earlier ignition than PET. Once ignited, the test samples showed varying heat release rate profiles, as shown in Figure 10b. It has to be noted that only PET and PEF samples were tested in duplicates in the current investigation. Therefore, only for PET and PEF, average values are further considered in the discussion. PEF fires led to better completeness of combustion reflecting lower amounts of the residue (8%) remaining at the end of the combustion process compared to the initial sample mass than PET (14%), PVC (18%), PC (22%), and POS (34%). There could be a slight underestimation in the quantity of residue in the case of PET as we observed some mass loss issues in one of the tests. The PET sample grew during the combustion and fell out of the sample holder and was stuck on the quartz tube.

Concerning thermal impact, the peak HRR from PEF (777 kW/m²) is slightly lower than PMMA (781 kW/m²) but higher than all other tested polymers. Nevertheless, the overall energy released in PEF is comparable to PVC and PET relating to limited fire load of PEF (17 MJ/kg) compared to PVC (18 MJ/kg) and PET (22.2 MJ/kg) and is much lower than the other tested polymers (Figure 11).

3.6. Yield of Combustion Products from PEF Fires. Considering the elemental composition of PEF, which is essentially composed of C, H, and O elements, the major gaseous products observed from PEF combustion are carbon oxides (CO₂ and CO), water vapor, soot, and unburnt hydrocarbons that are accounted as total hydrocarbons (THCs). As explained in previous chapters, assessing the yields of combustion products is an important aspect of fire

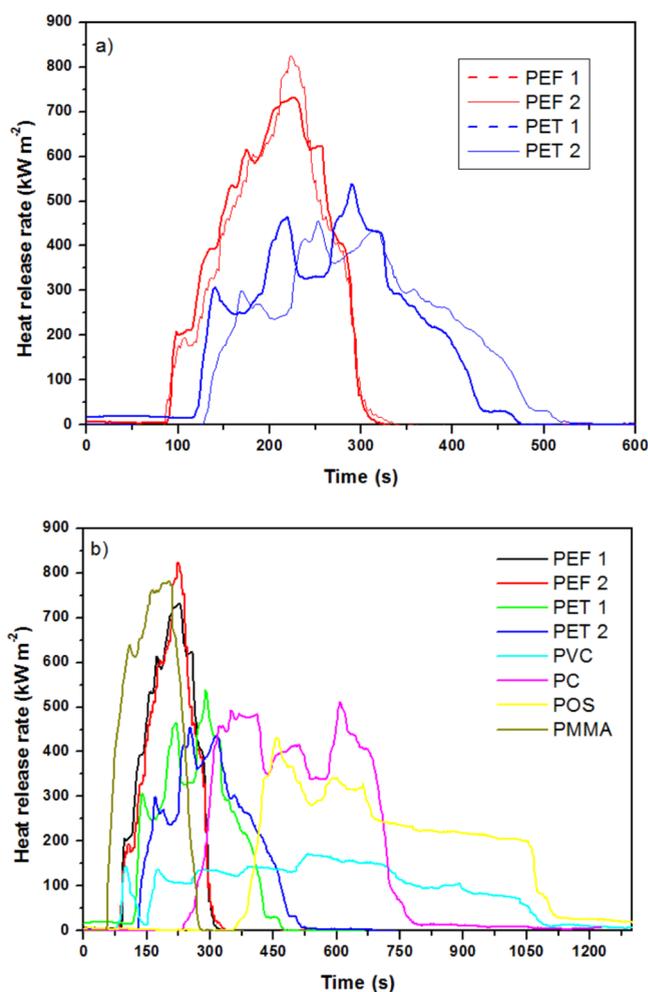


Figure 10. Heat release rate profiles of (a) PEF and PET alone and (b) PEF in comparison with other tested polymers under well-ventilated fire conditions.

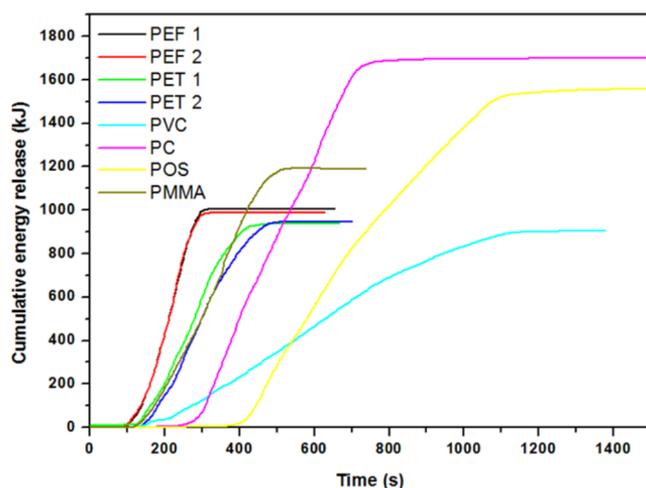


Figure 11. Cumulative energy release profiles of PEF in comparison with other tested polymers.

safety studies as this helps in bringing information on the combustion products resulting from any given fire scenario leading to chemical threats notably in terms of fire gases and soot emissions referred to as fire-induced toxicity.

Table 6. Maximum Theoretical Yields, Yields as Measured^a

	parameter	unit	CO ₂	CO	THC	soot	CH ₄
PEF1	max theoretical yield	mg/g	1925	1225	525	559	137
	experimental yield	mg/g	1582	17	33	3	0
	conversion efficiency	%	82.2	1.4	6.3	0.4	0.1
PEF2	max theoretical yield	mg/g	1925	1225	525	559	137
	experimental yield	mg/g	1558	19	33	3	0
	conversion efficiency	%	80.9	1.5	6.4	0.5	0.2
PET1	max theoretical yield	mg/g	2267	1443	618	660	168
	experimental yield	mg/g	1528	26	63	7	0
	conversion efficiency	%	67.4	1.8	10.2	1.0	0.2
PET2	max theoretical yield	mg/g	2267	1443	618	660	168
	experimental yield	mg/g	1574	26	67	8	0
	conversion efficiency	%	69.4	1.8	10.8	1.2	0.2
POS	max theoretical yield	mg/g	2673	1701	729	777	179
	experimental yield	mg/g	1631	64	114	15	1
	conversion efficiency	%	61.0	3.7	15.6	1.9	0.6
PVC	max theoretical yield	mg/g	1426	908	389	437	177
	experimental yield	mg/g	583	78	103	36	5
	conversion efficiency	%	40.8	8.5	26.4	8.2	2.8
PC	max theoretical yield	mg/g	2204	1402	601	687	291
	experimental yield	mg/g	1681	46	110	15	1
	conversion efficiency	%	76.3	3.3	18.3	2.2	0.4
PMMA	max theoretical yield	mg/g	2204	1402	601	687	291
	experimental yield	mg/g	2082	10	15	2	0
	conversion efficiency	%	94.5	0.7	2.4	0.3	0.0

^aRelated conversion efficiencies (%) of carbon content into CO₂ and CO, hydrocarbon (HC) content into [total hydrocarbons (THCs)], soot and methane (CH₄) from the tested polymers (in theoretical estimations, soot is assumed to be pure carbon).

The CO/CO₂ and phi ($\ll 1$) data available from Table 6 clearly indicated that the combustion tests prevailed under well-ventilated conditions throughout the duration of the test. Under these conditions, essentially all carbon available in the molecular structure would have been converted into CO₂. This is reflected by the higher carbon conversion efficiency in PEF than in other tested polymers. Consequently, the CO yields are reduced as indicated in Table 6.

Lower quantities of CO (18 mg/g) production in PEF compared to PET (26 mg/g), PC (46 mg/g), PVC (78 mg/g), and POS (64 mg/g) and their related conversion efficiencies (Table 6) indicate the easier mode of oxidation in PEF leading toward better completeness of combustion. In addition, a fire originating from PEF seems to be less sooty⁶ compared to PET and other tested polymers. Under classical conditions, the presence of aromatics in the molecular structure generally results in higher quantities of CO, soot, and THCs as we can see from PC and POS. PEF being semiaromatic, the presence of oxygen in the molecular structure seems to play a role in lower CO, soot, and THC emissions from PEF.

However, with the limited amounts of CO observed from the experiments, we would expect the experimental CO₂ yields to be very close to the maximum theoretical CO₂ yields indicated in Table 6. Nevertheless, the charring process leaving some quantities of the residue at the end of the combustion process could be a reason for the observed difference in the experimental and theoretical CO₂ yields.

3.7. Further Exploration of Thermal and Fire-Induced Toxicity Data Resulting from PEF Fires. This study presents the data from heat release characteristics and the resulting yield of combustion products from PEF fires. This information can be very much extrapolated into a scenario-based fire-induced toxicity assessment to any well-ventilated

fire scenario of interest, making use of the classical fire protection engineering techniques as developed and published by the ISO TC 92 subcommittees SC3 and SC4.

A similar scenario has been exemplified in the previous chapter with fires resulting from furanic compounds. Such an assessment can provide a better understanding of the anticipated scenarios in the case of fire originating from this new class of biobased PEF plastics. Indeed, from the experimental results, we may say that the fires originating from PEF do not significantly vary from those from PET in terms of thermal impact under well-ventilated conditions. However, further examinations on the ventilation-controlled fires could result in better predictions in a worst-case scenario.

4. CONCLUSIONS

Industrial applications of furanics could result in the production and storage of large quantities of furanic compounds in the industrial storage premises upon commercialization. Not all furanics are flammable compounds, but our test results clearly indicate that they are capable of ignition and achieving self-sustaining flaming combustion with the influence of a sufficient external heat source. From the fire safety viewpoint, it can be concluded that in this evaluation of furanic monomers, FDCA has a far better safety margin both in terms of lower thermal and chemical threats as fires resulting from FDCA are not easily shifting toward underventilated fire scenarios compared to the other monomeric furanic compounds evaluated in this study. This is very relevant news because FDCA is the principal product of the YXY plant in Delfzijl, so it will be stored on site and subsequently shipped to the polymerization partner(s).

As the world is looking at new renewable carbon alternatives to fossil-based (PET) polymers, PEF sets a new dimension by

being from a biobased origin and having several superior physical properties compared to PET. In addition to these known advantages of PEF, the current assessment addresses the fire risk assessment for the very first time. The obtained results are useful in understanding the nature and behavior of PEF under real fire conditions. PEF seems slightly better in terms of the total energy released from the combustion process than PET. In addition, PEF fires result in lesser CO and soot yields compared to PET approaching better completeness of combustion. Suitable fire retardant additives could be good add-ons for further improving the resistance of PEF to ignition characteristics. However, compatibility issues between PEF and the fire retardant materials must also be thoroughly investigated. In addition, careful selection of fire retardant materials should be done in such a way that they do not bring additional toxic elements into the environment. Nevertheless, any further modifications to the original (PEF) material entirely depends on the target application.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.1c05471>.

Historical development of the FPA based on ISO 12136 used in this study, technical details regarding the equipment and relating capabilities, supported by complementary references, and details regarding the FPA test procedure applied in the present work (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This research was in part funded (A.M.) by the European Union's Horizon 2020 Research and Innovation program within the project HUGS, which has received funding as a Marie Skłodowska-Curie Innovative Training Network under Grant Agreement no 675325. The authors acknowledge all participants of the HUGS project for fruitful collaborations and discussions on this subject.

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