

UPDATE ON THE ENFIRO PROJECT: SEARCH FOR ALTERNATIVE FLAME RETARDANTS

Leonards, Pim EG¹

¹Institute for Environmental Studies, VU University, de Boelelaan 1085, 1081 HV Amsterdam, The Netherlands

Introduction

Flame retardants are applied in a wide range of commercial products, such as electronics and plastics, to inhibit or resist the spread of fire. Due to their persistent nature and their toxicity some brominated flame retardants (BFRs), such as pentabromo-, octabromo-, and decabromodiphenyl ether, need to be substituted by non-toxic substitutes, and will or are phased out because of their environmental hazards. Less toxic alternative flame retardants appear to be available already but comprehensive information on their possible toxicological effects, exposure and performance are often lacking.

The European funded ENFIRO project is a research project that evaluates viable substitution options for a number of BFRs for better, safer alternatives. A practical approach is followed, based on the chemical substitution cycle in which the alternative flame retardants are evaluated regarding their environmental and toxicological properties, their flame retardant properties, and their influence on the function of products once incorporated (Fig. 1). The main objectives of ENFIRO are:

- To deliver a comprehensive dataset on viability of production and application, environmental safety, and a life cycle assessment of the alternative flame retardants (FRs)
- Recommend certain flame retardant/product combinations for future study based on LCA, LCC and risk assessment studies

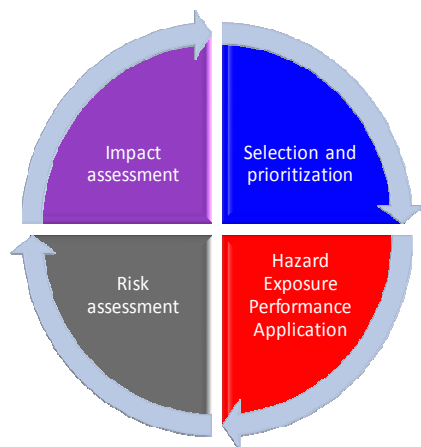


Figure 1: ENFIRO chemical substitution cycle

Approach

This paper provides an update on the findings of the ENFIRO project. ENFIRO follows a tiered approach (Fig. 2), starting in the first tier with a prioritization and selection of alternative FRs taking into account the viability of production, application, flammability, hazard, and exposure of the FRs. This will generate a list of viable alternatives and identify knowledge gaps. To fill some of the data gaps screening studies of the selected FRs were performed. The screening studies focus on relative rapid hazard characterization, exposure assessment modeling and fire performance tests.

Based on the evaluation of the screening results and literature information a further selection of viable FRs is narrowed down to be able to carry out in-depth studies on a selection (Tier 2). These studies cover chronic toxicity tests, neurotoxicity, battery of *in vitro* tests, persistency, and monitoring of the alternative FRs in the

field. In parallel, elaborated fire performance (realistic fire smoldering and flaming incidents) tests and technical assessments of the FRs in various applications are compared with traditional BFR systems.

The hazard and exposure results are integrated in a risk assessment to investigate the possible risk of alternative FRs for humans and the environment and compare these with the risk of existing BFRs. The outcome of that assessment, together with socio-economic information, will be used in life cycle assessments to quantify the analysis of the environmental, economical and social impacts and compare the impacts of the different substitution options with each other. Finally, a list of viable FR/product combinations will be provided.

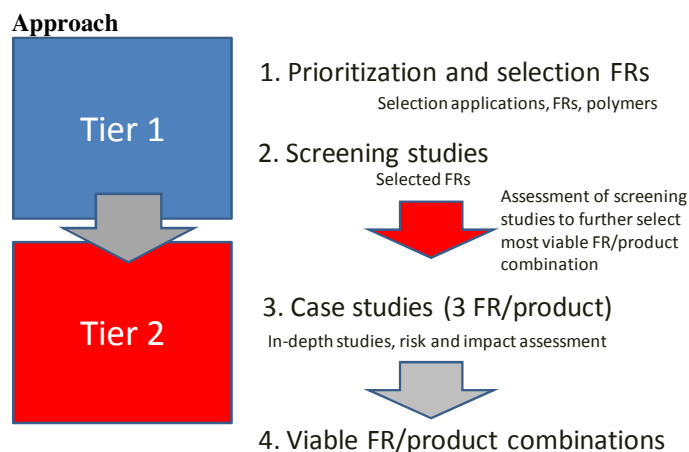


Figure 2: ENFIRO approach.

Results and discussion:

Selection and prioritization

A scientific literature search as well as in industrial reports on halogen-free FRs (HFFRs) was carried out. Information was collected on the availability of these FRs, their characteristics in relation to fire safety regulations, and in relation to their environmental behavior and possible toxic effects.

The selection criteria were: i) the FR should be commercially available on the market, ii) it should be a halogen-free FR (HFFR), and iii) information available on compatibility behaviour in marketable polymers. Five main applications of BFRs (printed circuit boards (PCBs), electronic components, injection moulded products, textile coatings, and intumescent systems) were selected. An overview of the BFRs used in these applications (decaBDE, TBBP-A, brominated polystyrene) and viable HFFRs in a range of commercial applications was made.

In total 15 HFFRs were selected as most promising FRs, including metal-, phosphorous-, and nanoclay-based FRs. The toxicological and ecotoxicological review of the selected HFFRs showed a lack of data or contradictory data for these compounds, and the need for reliable experimental data. The literature was mined for information relevant to the sources, physical-chemical properties, degradation rates, environmental occurrence and behaviour of selected HFFRs. For some FRs wide ranges in physical-chemical properties were found. A FR market synopsis suggested that the FR industry is highly influenced by recent trends, and formed the stepping stone of the economic impact assessments of ENFIRO. Finally, a schematic presentation of the applications, polymer materials, fire requirement(s), BFR, HFFR, and commercial load was prepared that formed the basis for the screening studies.

Screening studies

The hazard characterisation focused on a health and ecotoxicological hazard of the selected HFFRs on a molecular and cellular level, with emphasis on aquatic, geno, endocrine- and neuro-toxicity using *in vitro* studies and a limited number of *ex vivo* validation studies. In the screening phase rapid toxicity tests were performed

(cytotoxicity tests and acute Daphnia immobilisation test), and pilot studies with primary producer (algae) were carried out. Cytotoxicity tests showed that at concentrations up to 10 µM no evident effects for the HFFRs on cell viability were observed. Some FRs showed effects for Daphnia at the mg/l range.

The initial phase of the exposure assessment studies focused on the modelling of the organic compounds using multimedia fate modelling tools to predict the distribution of HFFRs in four environmental compartments (air, soil, sediment, water) under different emission scenarios. These studies also assisted to identify the key environmental compartments to be sampled for the field monitoring campaign: sewage sludge, STP effluents, landfill leachates, house dust, indoor and outdoor air, sediments, water, and biota. The models were also used to identify the most important knowledge deficits to further develop the modelling and exposure assessment. To provide information on the environmental emission, leaching studies of HFFRs from polymers were performed to the water phase. Different leaching protocols were tested using HFFRs and BFRs (see presentation Dioxin 2011).

The major focus of the FR capability studies was to quantify the severity of the toxicity of the product, smoke and heat flux of the alternative HFFRs against BFRs in fire (smoldering and flaming) incidents. A compilation of previous data on the flammability and toxicity of brominated and alternative FRs was made. First formulations of polymers with HFFRs have been investigated for flammability and toxicity, and showed that the polymer/HFFR formulations were viable alternatives for a BFR (e.g. good characteristic fire spread growth and smoke yield).

In conclusion, ENFIRO follows a novel, three level assessment approach, based on the flame retardant, material, and product, by the comparison of the alternative FRs with the BFRs:

- i) **Flame retardant:** hazard characterization and exposure assessment
- ii) **Material:** fire performance and application studies
- iii) **Product:** impact assessment (life cycle assessment (LCA), life cycle costing (LCC), social life cycle assessment)

Acknowledgements:

This project was funded by ENFIRO(226563) a European research project funded by FP7. The ENFIRO team consisting of VU University Amsterdam, University of Ulster, Clariant Produkte (D) GmbH, IRIS Vernici s.r.l., Procoat, IVAM, Stockholm University, IRAS Utrecht, Swerea IVF AB, University of Amsterdam, Callisto, and ITRI Innovation Ltd. are acknowledged for the work on HFFRs and BFRs.