CHEMICAL ENGINEERING TRANSACTIONS
VOL. 31, 2013
Guest Editors: Eddy De Rademaeker, Bruno Fabiano, Simberto Senni Buratti

ISBN 978-88-95608-22-8; **ISSN** 1974-9791
A publication of
AIDIC
The Italian Association
of Chemical Engineering
Online at: www.aidic.it/cet
DOI: 10.3303/CET1331144

Developing Dedicated Methods and Tools for Safe Use and Processing of Key Chemicals in Biorefining

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The emergence of biorefining, as the key concept of the future biobased economy is announced as the ultimate concept in many concerned industrial R&D roadmaps. Therefore, this paper proposes an insight of some safety related issues, as often underscored part of sustainability evaluation. From recent and still on-going research performed by the authors focusing on the appraisal of materials and process hazards in the context of biorefining, a brief review of recent achievements obtained by the authors in terms of the development of appropriate methods and tools aiming at promoting safety management in the related facilities are given. Both material and process driven safety issues are dealt with in the examples reported. Perspective on future related work in relation with the topic is brought in conclusion.

1. Introduction

As soon as in 2006 and soon after the emergence of the biofuel industry of first generation (bioethanol, biodiesel), the importance of biorefining as a versatile concept was revealed wordwide.
Signs of such a major evolution of the agro-industries are the publication in 2006 of the first edition of a book dedicated to biorefineries edited by B. Kamm (2006) and published by Wiley, or the establishment of the task force 42 inside the International Energy Agency. Since that time significant EU-funded as well as private R&D activities have been performed, as the collaboration initiative on biorefineries called Star-Colibry that ended to two major deliverables clearing visions and R&D roadmap for a fully mature model in 2030 (Lugel, 2011).
Whereas lack of sustainability has often been recognized, for various reasons like competition with food and feed, land use change issue, lack of energy efficiency, or poor carbon footprint, the relationship with sustainability and industrial safety remains unclear and in many cases, safety criteria being often considered as implicitly met through simple fulfilment of legal requirements from existing regulations or by recording level of incidents or worker injuries years after years. Such a practice does not allow anticipating the identification of emerging safety issues at early stages of development of more and more complex biorefineries (see Fig. 1) nor facilitate better introduction of inherently safer principles. In reality, errors in safety management may compromise the three pillars of sustainable development as major incidents would clearly impact the environment, may lead to business disruption and temporary and permanent unemployment. In addition, the integration of green chemistry is showing great expectancy in the biorefineries of the future (Clark et al, 2008), also to serve better sustainability. When remembering that at least four of the 12 green chemistry principles claim for safety targets, one cannot ignore the importance of safety goals and thus must be proactive in promoting safety management.
These are reasons why authors of this paper are working on the development of dedicated tools and risk assessment methods that aim at promoting sustainable development of biorefining towards better consideration of safe handling and use of chemicals and safer innovating processes. The paper focuses on some of the initiatives recently taken by the authors in that direction, consolidating the idea that biorefinery-dedicated tools are indeed highly desirable to promote a biobased economy (Hass et al, 2012).

Please cite this article as: Marlair G., Diallo A.O., Benaissa W., Vignes A., Blanc L. and Len C., 2013, Developing dedicated methods and tools for safe use and processing of key chemicals in biorefineries, Chemical Engineering Transactions, 31, 859-864 DOI: 10.3303/CET1331144

2. Qualifying new biofuels components and related value chain safety

Marlair et al (2009) and some other rare contributors have illustrated the reality of hazards in the entire value chain of biofuel production of first generation. There is now doubt that the development of biofuel driven advanced biorefineries will require a detailed look of safety issues for multiple reasons. These may come from the development of new biofuel components or as a result of the promotion of more efficient processing of biofuels integrated in biorefineries for terrestrial applications. The climate change issue is also leading to fast development of potential other use of biosourced fuels, such as in the aviation industry. With regard to this latter aspect, INERIS recently contributed to 1st order evaluation of bio-jet fuel component candidates moking up just agreed jet A1 alternatives in the framework of the Alfa-bird.
EU-funded project, either processed after biomass gasification by Fisher-Tropsch conversion and post processing, or though hydro-treatment of vegetable oils or fats. Whereas no highly challenging issue was found regarding safety on the supply chain of those new fuels, process safety was not actually examined (see Figure 1) due to competitiveness aspects, however collaboration with one late partner of the project underlined some unexplained results deserving more in depth analysis (Le Nevé et al, 2012).

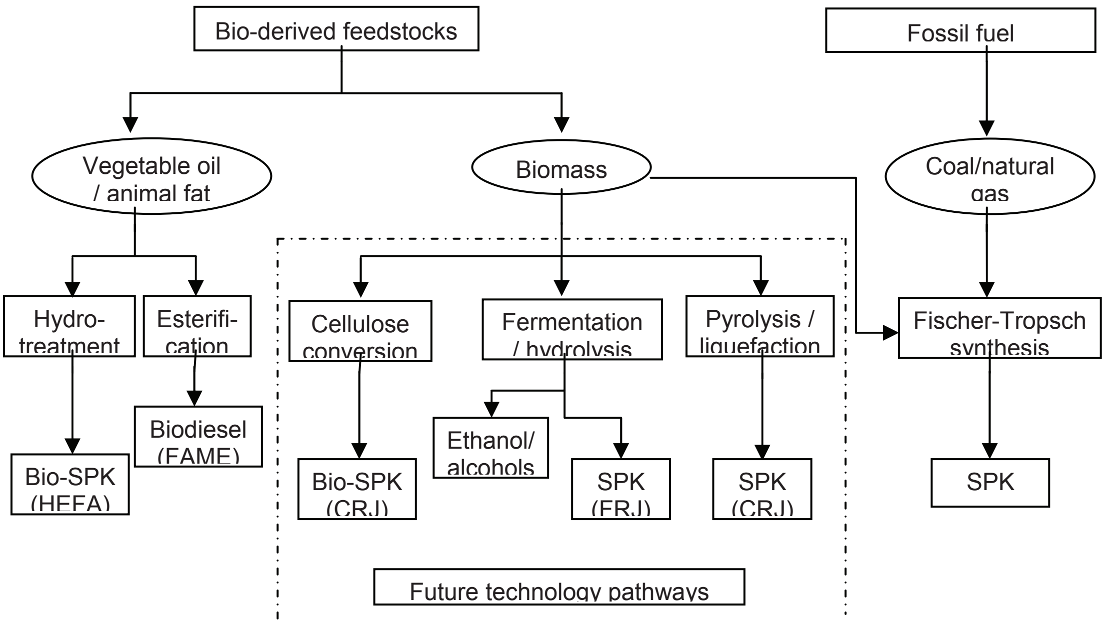

Figure 1: Current and future production pathways in jet A1 alternative fuel driven biorefineries (adapted from Miller et al (2012))

Figure 2a: Fire calorimetry testing of 2,5 DMF as a potential bio-sourced fuel component making use of the FPA (ISO 12136:2011)

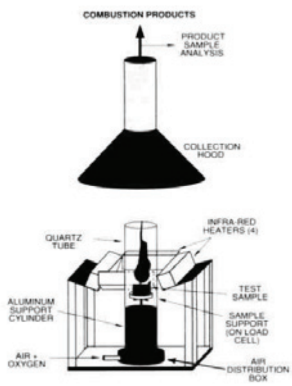

Figure 2b: Schematic view of the FPA

Some advanced fuels potential was also examined briefly during early phase of this project, like the one of 2.5 DMF (see Figure 2). As also confirmed by Salzano et al (2010) previously, recent joint research effort by INERIS (F) and CERL (Canada) also recently confirmed that emerging risks may still emerge from the conventional production of 1G biofuels by catalytic transesterification of oils (Janès et al, 2012). Recent move in the regulation regarding the use of maritime fuels might also trigger new perspective of use of biofuels in this other sector, and that would also deserve some focus on safety issues.

3. Collecting and organising appropriate safety data on key biorefinery products in a user-friendly mode

Considering the full value chains relying on biorefining, chemicals and feedstock materials in modern biorefineries are quite diverse and numerous. They encompass various agro-resources like algae, green biomass materials like switchgrass, many oil containing plants, lignocellulosic rich crops like miscanthus, not to forget all types of biobased residues. In addition, other chemicals of interest are solvents, reactants, catalysts, including biocatalysts, fertilising and crop curing agents, cleaning agents, as well as numerous processed materials like commodities, building block chemicals and high value added chemicals and biomaterials, not neglecting feed and food ingredients. Significant efforts have been done in the past by public agencies like ADEME (F), DOE (USA) and IEA task force 42 (Intl) (Ed Dejong, 2012) to screen potential of commodity platforms and high value added molecules of the future that are likely to drive the market development. Top 50 to top ten lists of those chemicals have been established comprising many organic acids, precursors of biopolymers, furanic derivatives like furfural or 2.5 DMF, chlorinated intermediates, and so on. We currently anticipate according to our current review on conventional and emerging safety issues to consider that no less than 200-300 chemicals would deserve scientific-sound collection and organisation of safety data to serve basic hazard identification in the context of modern biorefining, although many of those chemical and materials are not brand new ones. The need to develop additional more specific databases may also arise from the need of predictive tools like QSPR models, that require consistent database for their pertinent development, see next section of this paper. This is for instance the case at least for two families of chemicals that are considered with increasing interest, namely furanic compounds (as precursors for biopolymers capable of replacing PET or as biofuel components or ionic liquids (ILs), that are experimented as solvent serving biomass fragmentation or biofuel recovery. Experimental work recently performed to check basic information like flash points of less than 10 chemicals show us that direct use of safety data sheet may in some cases be misleading, due to errors, or generalisation of existing data in the literature that does not correspond to technical grades of the chemicals in actual use.

For those reasons, INERIS is currently promoting an interactive and user-friendly database, entirely dedicated to collecting, storing and documenting safety related data on key materials in modern biorefineries, with the main objective of supporting the health and safety engineer with adequate information, brought in the appropriate context. The current version of the database include safety related data about 150 materials distributing among the following categories: a) agro-resources, b) building block chemicals or commodities, c) high value added chemicals or materials issuing secondary biorefining operations, d) biofuel components, e) solvents and catalysts. Some 30 properties are focused in the database including physical properties, thermodynamic data, data regarding flammability, explosivity, reaction to fire data, reactivity/thermal stability. In addition, the link with the included materials within the existing biorefinery value chain is documented as far as possible (e.g. designation of the process making use of the material as a solvent...). Level of reliability is also addressed, distinguishing home measured data from 4 codified levels of reported information: 1) data picked up in usual handbooks, 2) MSDS, 3) non evaluated web sources, 4) predicted values obtained by use of commercial softwares (e.g. Component Plus). Instruction for use in the database for its use and further development is also implemented.

Table 1: Illustration of measured and literature safety data values for well known key chemicals in biorefining

Test Compound	Reported flash point	Measured flash point	Comments
HMF	79°C	168°C	Reported flashpoint as indicated in the MSDS from supplier
Levulic acid	98°C	152°C	Reported flashpoint as indicated in the MSDS from supplier
Sorbitol	292°C	150°C	Reported data in non peer-reviewed web source

During the process of the database implementation, some testing has shown the usefulness of double checking important information regarding key safety parameters. Table 1 illustrates this comparison measured flash points versus reported data in the literature (in some cases given in the relevant MSDS) for same chemicals.

4. Developing adequate predictive tools of properties and selecting the right testing

The pertinent development of high added value chemicals often requires screening processes to consider optimised choice of processed materials. This must be done considering regulatory needs, functional objectives of target chemicals (this is true for e.g. derivatives of furan, ionic liquids (ILs), oil crop derived fatty acids...). In such a case, accessing safety data for the whole family considered is unrealistic, either because to being too much time-consuming or even because this is simply not feasible due to unavailability of test samples.

Based on early pre-examination of existing correlation aiming at assessing complete heats of combustion of combustible materials like the Boie formula (Marlair, 1999) and pioneering experience developed for a while by INERIS to develop QSPR models for predicting phys-chem hazard related data (Fayet et al, 2010), INERIS has started to address the phys-chem safety issues pertaining to ILs, substances that have the remarkable property to be intrinsic ionic media in the liquid phase below 100°C (like imidazolium, phosphonium based ones). Phys-chem hazards for ILs have been a long time denied (Diallo et al, 2011, Marlair 2011) or underscored. The first output of this specific research effort is the qualification of 5 out of the 18 identified empirical correlations allowing quite reasonable predictions of theoretical heats of combustion of ILs, working as a first order indicator of combustibility issues that may pertain to those chemicals depending on the context of use. Thanks to the on-purpose development of a database of some 50 ILs belonging to 5 main subcategories (Diallo et al, 2012), a specific QSPR model developed according to OECD principles for the prediction of the complete heat of combustion has also been set, anticipating the potential need to adjust the model versus time according to the promotion of new subcategories of ILs in the context of biorefineries.

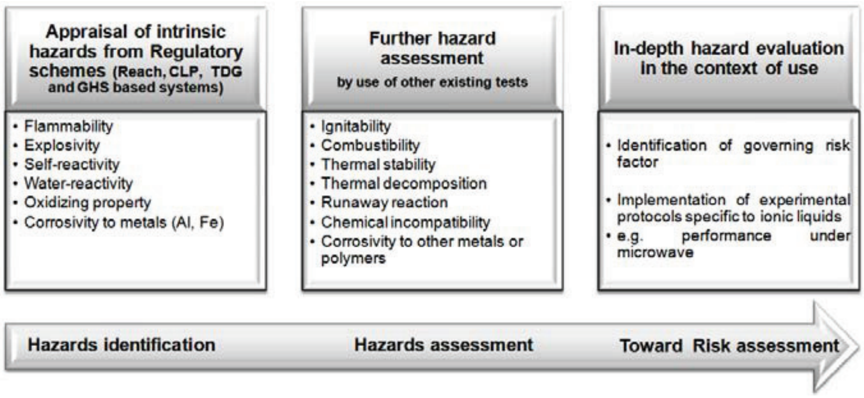

Figure 3: Methodology targeting the appraisal of the full spectrum of physico-chemical hazards of ILs

The design of this tool is part of the development of a more comprehensive and fully dedicated methodology targeting the appraisal of the full spectrum of phys-chem hazards of ILs, encompassing not only combustibility and flammability issues, but also thermal stability, incompatibility issues, corrosivity to metals or polymers, see Figure 3. This work is largely justified, not only because this family of chemicals is nearly infinite (Binnemans, 2011) but chiefly by the fact that the behaviour of ILs reveal in many cases to depart significantly to conventional liquid solvents in the manner they may trigger a hazard of phys-chem nature. Inadequate testing is also sometimes observed and also need to be identified. As an example, by no case close or open cup flash point apparatus is the appropriate testing equipment for appraising flammability of ILs since they, although liquid by nature during use mostly behave like solid polymers under the action of heat, leading to the release of condensable and non condensable potentially flammable degradation products. Moreover, the use of Manilla paper test to compare flammability of ILs or other hardy combustible materials as compared to flammable solvents (classified as such due to flash point values) is also greatly misleading (see e.g. Yonxin An et al, 2011), as this only reflect behaviour difference issuing a very small thermal stress initiating event that may be far from the actual context of potential incidents during use (as additive in a lithium based battery of as a catalyst in a biorefinery). Much more pertinent combustibility and flammability testing may be achieved by use of the so-called Fire Propagation Apparatus (ISO 12136:2011) as illustrated in Figures 3a and 3b.

5. Assessing emerging and often intensified processes without too restricted viewpoint

There also the development of a dedicated database was considered as the best way to capitalize appropriate information serving process safety concept integration and risk assessment at early stage of development, in consistency with the development of the database of materials and chemicals (see section 3), facing the reality of modern biorefining, leading in particular to a variety and fast moving technical process options.

5.1 The importance of intensified processes

For few years now, process intensification has opened new perspectives to chemical industry to reinvent itself: technological innovations and methods have been developed in order to produce more and better in using less and to sustainably produce molecules responding to environmental and economic challenges The modern Biorefineries have benefited of these new opportunities and some applications have already demonstrated their efficiency in the field of biomass transformation or/and biodiesel production: static mixers, microwave reactors, reactive distillation, membrane reactors, nanosized catalysts, pulse electric fields, ultrasound assisted extraction. Process intensification is perceived in that sector as the best option to render those systems cost-effective (Sanders et al, 2012). Regarding safety, another important point is that process Intensification is considered as a concept that allows to prevent or reduce risks related to major accidents: it is even commonly admitted that an intensified process is, by default, inherently safer. However emerging studies have demonstrated that the link between process intensification and the concept of ISD (Inherently Safer Design) was not always obvious. As shown by Ebrahimi (2012), the general claim that safety is always improved by process intensification is clearly questioned.

5.2 Developing the BIOSAFE_PROCESS toolkit

Process safety relies on early detection of potential hazards and their elimination so far as possible to achieve inherent safety, completed by the implementation of modern protective measures as far as needed. An essential starting point for managing process risks in the context of biorefining is the collection of essential data on all types of processes that may be used, that detail operating conditions, materials used in the facility and the hazards related to the use of (bio)chemicals and (bio)materials used or processed. To make the consultancy of such data user-friendly, a tool designated as the BIOSAFE_PROCESS toolkit as been developed in the form of an Excel folder The user will be able to search for information regarding the production of any bio-based chemical that has a promising future in the bio-based economy, no matter what level of knowledge he has of the process. This tool has been built based on most recent inventories (eg.: de Jong, 2012), reports from development laboratories and literature citing similar processes or provided by the industry.

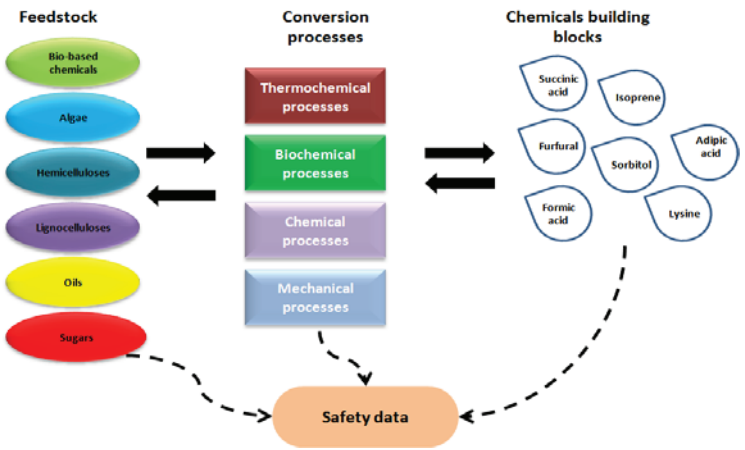

Figure 5: Current structure of the BIOSAFE PROCESS toolkit being developed by INERIS for addressing process safety at early stage of biorefining design

This database is a first step in a more straightforward and comprehensive methodology dedicated for appraising process risks in the context of highly innovating and fast moving biorefinery taking account of main characteristics of such facilities, like high demand in flexibility in material feedstock and portfolio of processed materials, high level of energy integration, no residue target and so on. Configuration of the tool under construction is shown in Figure 5.

6. Conclusions

The paper has recalled that industrial safety is a prerequisite for the sustainable development of biobased value chains in the context of modern biorefining. Modern biorefining is fast moving, leading to integration of more and more innovating concepts, confirming the fast development of biotechnologies and intensified processes, as well as the emergence of lots of key new chemicals of interest. This in turn needs a special outlook in terms of risk assessment and sometimes justifies fully dedicated new tools, as advocated by Marlair (2011) at the occasion of the first summer school on biorefining principles that took place in Paris end of August 2011. Examples of new tools and methodologies under development by the authors have been given. No doubt that a specific R&D safety roadmap is desirable to take account of technical or organizational bottlenecks for adequate safety management. As innovation sometimes drive emerging risks in addition to conventional risks, the authors maintain their research efforts to accompany safe development of biorefineries of the future.

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