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Environmental and Safety Aspects of Integrated BioRefineries (IBR) in Italy

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Among the major new technologies that have appeared since the 1970s, biotechnology has perhaps attracted the most attention. Biotechnology has proved capable of generating enormous wealth and of influencing every significant sector of the economy. Biotechnology has already substantially affected healthcare, production and processing of food, environmental protection and production of materials and chemicals. The achievements and future prospects are in sustainable production of goods and services, especially those that are derived at present mostly from the traditional chemical industry. In fact, the international scientific community, under the pressing demand for a green chemistry, is launching the input about the creation of a new industrial concept based on innovative industrial biotechnological approaches.
To this aim, the concept of Integrated BioRefinery (IBR), defined as a scientific and technical platform through which the biomass, designed as waste products, are turned into fuels, energy and chemicals, such as basic chemicals, fine chemicals and specialties of biopolymers and bioplastics, through technologies and processes that produce minimal waste and have limited impact on the environment are becoming increasingly popular also in the Italian territory.
An IBR is a structure (or a network of systems) that integrates both biomass conversion processes and equipment to produce biofuels, energy and/or chemicals. In this perspective it is desirable the creation of an industrial concept "bio-cluster", in which the exchange of material (flows) between different companies are promoted to transform a residue downstream of a plant in an up-stream of raw material for another industry.
Although the environmental and health risks posed by these new realities are expected to be lower than with traditional chemical and petrochemical plants, there is still a lack of information about safety aspects of these new generation plants. Existing lessons suggest that the development of effective, responsive and responsible safety standard can improve the trust of the public and affected industries in biotechnologies. The fist step should be replacing the current retrospective risk-based paradigm for governing biotechnology with a proactive safety paradigm. Safety principles, applied early in the design process, can benefit multiple stakeholders concerned with safety.
The aim of the present work is providing a tool for transparent development of proactive safety standards and it is a part of the project funded by the National Centre for Disease Prevention and Control (CCM) of the Italian Ministry of Health.
This paper presents an analysis of the unit operations and equipment of the main industrial biorefineries and some of process and occupational hazards are preliminarly discussed. Basing on a preliminary analysis of IBR installations, a substantial reduction of the environmental impact and an increase of both occupational and process safety is expected with respect to the most common chemical plants.
The use of biological agents has been identified as the main hazardous aspect involved in those processes.

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1. The concept of Integrated BioRefineries

The biorefinery concept was introduced in the 80's, when there was a real perception, supported by scientific data, of the depletion of non-renewable resources (Wise, 1987). The production of biogas from waste biomass anaerobic treatment, has contributed to the development of the biorefinery concept within the scientific community that gradually evolved now including the production of biofuels from vegetable extracts. A crucial step, affirming the concept of biorefineries, was definitely achieved when the potential of microorganisms was understood.

Biological systems can convert renewable resources, including lignocellulosic biomass, starch crops, and carbon dioxide, into fuels, chemicals, and other materials: e.g. ethanol and other products are now commonly derived from starch crops, such as corn, while enzyme-based technologies are used for the conversion of lignocellulosic biomass (e.g., wood, grasses, and agricultural and municipal wastes) into fuel ethanol.

In order to support and facilitate the implementation of the European strategy for climate change mitigation and development of renewable energy, including bioenergy, the European Commission has recently decided to undertake a coordinated approach to promote the use of biomass, through initiatives such as the adoption of the "Biomass action plan" and the "EU Strategy for Biofuels" (Communication from the Commission of the European Communities, 2006), thus assigning a high priority for funding research and development in this area. To this aim, the establishment of the working group "Biofuels Research Advisory Council "(BIOFRAC) for the definition of strategic guidelines and the creation of the "European Technology Platform for Biofuels" have been also favored.

Currently, biorefineries have evolved into integrated biorefineries (IBR). Actually the integrated biorefinery concept embraces a wide range of technologies able to separate biomass resources (wood, grasses, corn...) into their building blocks (carbohydrates, proteins, triglycerides…) which can be converted to added value products, such as biofuels and chemicals.

There is not a “scientific” or a commonly agreed definition of biorefinery. A biorefinery is rather a facility (or network of facilities) that integrates biomass conversion processes and equipment to produce transportation biofuels, power, and chemicals from biomass. This concept is analogous to the current petroleum refinery, which produces multiple fuels and products from petroleum (Cherubini, 2010).

A biorefinery, similarly to what occurs in a conventional oil refinery, should be based on feedstock upgrading processes, where raw materials are continuously up-graded and refined. This means that a biorefinery should separate all the biomass feedstock components, and produce, through a chain of several processes, a variety of pure chemical species (e.g. ethanol) or molecules having similar, well identified characteristics. As a consequence, since the main aim of a biorefinery is to increase the value of the different biomass components as material and energy source, the most desirable option is to send to combustion, for heat and electricity production, only the residues and leftovers of previous technological treatments and conversion processes (Ohara 2003).

A biorefinery plant should also aim at running in a sustainable way: all the energy requirements of the several biomass conversion processes should be internally supplied by the production of heat and electricity from combustion of residues (within a properly sized set of processes/technologies).

The biorefinery applies many hybrid technologies from different fields, such as bioengineering, polymer chemistry, food science and agriculture.

The most fundamental core of an IBR is the re-use of biomass, it is based on biological processes such as fermentation and biochemical conversion of products or by-products, which are related to environmental and safety aspects different from those commonly found in oil refineries.

Usually, these industrial processes lead to less severe operating conditions, and therefore with reduced hazard, regarding to temperature and pressure.

2. Unit Processes

Every industrial chemical process deals with a series of unit operations to produce a desired product from specific raw materials. The various processes that take place in an IBR are closely related to the nature of the biomass used: generally the first step is a physical treatment to make it suitable for chemical reaction.

From a conceptual point of view, the processes that take place in an IBR have a non-hierarchical representation, but a reticular one (Figure 1). The figure shows that several process alternatives are available to achieve the production of high added value molecules, unlike petroleum refineries where the raw material undergoes specific lines of treatment. The same final product can be obtained through different pathways. Although the biorefinery’s processes are quite different, the basics of process safety management (PSM) are virtually identical. The goal of a PSM program is to ensure that process facilities are operated safely. Designing safety criteria requires systematic analysis of possible harm, which involves the rigorous identification of hazards, the assessment of risk and planning to reduce and control risk.

2.1 Biomass

The raw material in a biorefinery is biomass: including food crops, crops for energy (e.g., switchgrass or prairie perennials), crop residues (e.g., corn stover), wood waste and byproducts (both mill residues and traditionally noncommercial biomass in the woods), and animal manure. Over the last few years, the concept of biomass has grown to include such diverse sources as algae, construction debris, municipal solid waste, yard waste, and food waste (Laser et al., 2008).

However, since biomass is an extremely heterogeneous material, a careful characterization is strictly required to address the different components to specific process pathways (Hackl and Harvey, 2010).

It is necessary to consider that the heterogeneous composition of biomass involves both a positive and a negative aspect: it allows extending the range of end products used by industry, compared to petroleum refineries, but the varying chemical composition often determines variable performances.

In addition some biomass could present specific occupational hazards. For example at biofuel plants, large quantities of straw or wood waste are handled and exposure to microorganisms, endotoxins and dust occurs, which may cause respiratory disorders (Madsen, 2006).

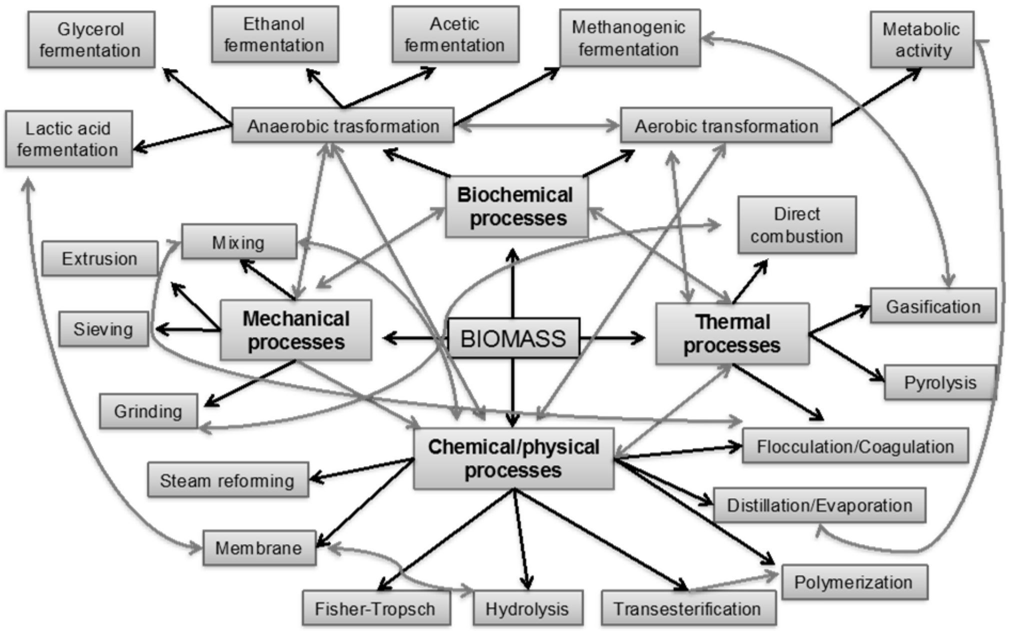

Figure 1: Conceptual representation of the possible processes within an IBR

2.2 Mechanical processes

Mechanical processes do not change the state or the composition of biomass, but only perform a size reduction or a separation of feedstock components. In a biorefinery, mechanical processes are not necessarily used as preliminary operations: sieving operations, e.g., is often an intermediate step. A significant change in particles size, shape and bulk density of biomass is caused by cutting or commuting processes: the possible formation of powders requires particular attention to safety and environmental protection, due to the risk of formation of explosive mixtures and air pollution.

Raw materials in integrated biorefineries are generally stored in silos, tanks and bags according to their nature. For liquids tanks are used, while, solid materials are stored in bags or containers. Silos are used for powders. Raw materials are loaded into the reactors through the use of dosing equipment. A potential danger may be represented by the use of raw materials in powder form (U.S. Department of Labor, 1996).

Combustible dusts may cause violent explosions, but require much higher ignition energies with respect to gases. In the presence of mixtures (called "hybrids") of combustible dust, air and gas, the risk of explosion strongly increases. Three conditions have to occur at the same time to cause an explosion:

a) the presence of combustible dust in suspension within the explosive range;

b) the presence of air or oxygen;

c) the presence of an ignition source of sufficient energy.

The dangers resulting from the use and processing of natural organic dust (starch, sugar, potato starch) can be contrasted with:

a) measures to prevent the formation of dangerous and explosive atmospheres and their propagation to different areas (vacuum, purging, inerting);

b) measures to prevent ignition of an explosive atmosphere (e.g. avoidance/prohibition of hot surfaces, open flames electrostatic accumulation and so on);

c) measures to minimize the consequences of the explosion (outputs to burst test).

Frequently, the greatest risk of explosion is associated to transfer operations of these powders (e.g. from road tankers to storage silos, in manually batch-operated equipment, etc.). To minimize the risks, pneumatic conveying of organic dusts from vacuum-seal systems is usually adopted.

The extracted dust from the aspirations of the hoppers is conveyed to suitable abatement systems before releasing into atmosphere through centralized systems of aspirations, equipped with column backwashing.

2.3 Thermal processes

There are different thermal processes for converting biomass into energy and chemical products: gasification, pyrolysis and direct combustion. Besides the usual hazards connected with the use of fuels the greatest risks for safety and environmental protection results from the high temperatures and possible atmospheric emissions of pollutants generated by incorrect combustion. In addition, due to incorrect combustion, dangerous waste combustion products can be generated.

IRBs do not use high-temperature processes, though the risk of producing explosive, toxic, or corrosive chemicals, due to incorrect thermal process cannot be excluded.

Some gases are poisonous and can be dangerous to life at very low concentrations. In addition, some toxic gases have strong smells like the distinctive ‘rotten eggs’ smell of H_2S, while others like CO and CO_2 are odorless. Explosions can also be caused by the ignition of flammable gas. A large group of gases are both combustible and toxic, so that even detectors of toxic gases sometimes require hazardous area approval. The main reason for treating flammable and toxic gases separately is that the hazards and regulations involved and the types of sensors required are different. With toxic substances, (apart from the obvious environmental problems) the main concern is the effect on workers of exposures to even very low concentrations, which could be inhaled, ingested, or absorbed through the skin. Since adverse effects can often result from additive, long-term exposure, it is important not only to measure the concentration of gas, but also the total time of exposure. There are even some known cases of synergism, where substances can interact and produce by far worse effects than when acting separately.

2.4 Chemical/physical processes

Chemical processes induce strong modifications in the chemical structure of the molecules by reacting with other substances or interacting with physical agents. These processes can lead to the formation of by-products with high added value. In these industrial plants unlike traditional chemical plants where organic solvents are used very extensively to extract and purify other synthetic molecules from manmade sources, the amount of hazardous reagents or solvents is significantly lower.

To what has been said up to now, traditionally, hazardous chemical agents include:

a) substances brought into the workplace and handled, stored and used for processing (e.g. raw materials, solvents, cleaning agents, glues, resins, paints);

b) substances generated by a process or work activity (e.g. fumes from welding/soldering, dust from machining of wood, solvent vapours, dust from quarrying);

c) substances or mixtures produced by the work process including by-products, residues or waste.

Chemical agents can be hazardous not only because of their intrinsic characteristics, i.e. as a constituent or chemical ingredient, but also because of their form or state and their conditions in the process (e.g. water at high temperature or even as steam can cause severe burns, so that proper control measures need to be specified and implemented to prevent harm).

Another risk factor is the use of a catalyst to increase the rate of reaction without impacting thermodynamic equilibrium. Factors, such as diffusion limitations, poison sensitivity and poor mechanism understanding, can increase the risk when implementing processes employing catalysts. As a consequence, environmental legislation is driving the fine and chemicals industries to consider alternative processes that avoid the use of hazardous reagents and chemicals (Azapagic et al, 2003).

Since the introduction of the green chemistry concept, a rapid development of new catalytic systems has occurred and a review of the state of the art will prove to be a great resource for researchers and graduate students working in the field.

Of course, in chemical/physical processes additional elements of environmental risk and safety aspects related to gaseous waste products and temperatures should be considered.

One of the most important issues in IBR is the production of bioplastics that involves polymerization of bio-synthesized monomers (Palmeri et al., 2012). This processes is often preceded by other chemical processes, such as esterification or other purification steps. These processes do not generally require severe operating conditions: temperatures never exceed 473 K and atmospheric pressure is usually adopted; as a consequence, the risk of major accidents with respect to the traditional chemical plants is significantly lower.
In order to obtain a suitable degree of crosslinking of the polymer, plasticizers such as glycerol are added (Liu et al., 2005; Raquez et al., 2010; Wurzel, 2005). The considerable increase in biodiesel production worldwide in the last 5 years resulted in a stoichiometric increased coproduction of crude glycerol. As an excess of crude glycerol has been produced, its value on market was reduced and it is becoming a "waste-stream" instead of a valuable "coproduct". The development of biorefineries, i.e. production of chemicals and power integrated with conversion processes of biomass into biofuels, has been singled out as a way to achieve economically viable production chains, valorize residues and coproducts, and reduce industrial waste disposal (Almeida et al 2012).
The health and safety impact of bio-based plastics has been recently investigated in a comparative analysis based on the production sustainability (Álvarez-Chávez, et al., 2011): although there are some occupational risks in their production (mainly related to exposure to pesticides, GMOs, exposure to elevated temperature and pressure), the bioplastics production is considered less hazardous than the traditional plastics and the other bio-based materials production (Figure 2) also considering the possibility of recovery, reuse and recycling.

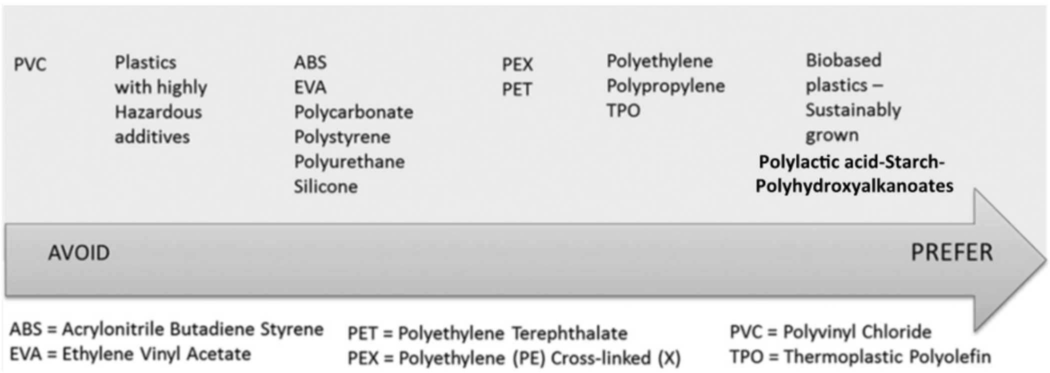

Figure 2 Biopolymers classification on the basis of environmental protection and occupational risks (adapted from Rossi and Lent, 2006).

2.5 Biochemical processes

Biotechnological transformations include a broad range of processes, ordered according to the number of biologically performed process steps and the complexity of the substrates. Biocatalysis has become an important tool for industrial chemical synthesis and is on the verge of significant growth. In the past several decades, many biocatalytic processes have been implemented to produce a wide variety of products in various industries. Most of them use natural enzymes or microorganisms as catalysts.
The use of enzymes, that are active at mild, near ambient conditions of temperature and pH and preferentially in aqueous media, represents an example of risk mitigation instead of using chemical catalysts.
Contained biotechnology application are performed in such a way that contact with humans and the environment is restricted or prevented by physical containment and by a combination of technical and organisational measures. The use of contained conditions serves two purposes: it ensures 1) process and product safety (quality assurance) and 2) human and environmental safety. A technical safety assessment is a basic tool for providing both product and environmental safety. In the case of product safety it helps to identify critical control steps that may be crucial for quality assurance.

3. Conclusions

Biorefineries represent both a new concept and a new generation of industrial plants, which is becoming increasingly common also in Italy. Thanks to the application and mutual integration of a number of

promising technologies they represent an interesting alternative to a number of traditional processes, which can allow a marked reduction of the production of waste materials and an increase in productivity.
Furthermore, as preliminarily seen in the present paper, based on the general characteristics of these process installations, they also have the potential to markedly reduce the environmental impact of the production process and to increase the safety both for workers inside the plant and for the possibly exposed external population.
However, just because of the introduction of new process technologies, like the use of biological agents, a thorough and detailed risk assessment should be applied to quantitatively check these generic assumptions.
In this paper the main operations involved in most of biorefineries active in Italy are summarized and analyzed in term of environmental impact and occupational safety. The critical operations have been individualized and the main risks are outlined, in the view of providing a tool for transparent development of proactive safety standards.

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