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Pre-treatment and extraction techniques for recovery of added value compounds from wastes throughout the agri-food chain

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The enormous quantity of food wastes discarded annually force to look for alternatives for this interesting feedstock. Thus, food bio-waste valorisation is one of the imperatives of the nowadays society. This review is the most comprehensive overview of currently existing technologies and processes in this field. It tackles classical and innovative physical, physico-chemical and chemical methods of food waste pre-treatment and extraction for recovery of added value compounds and detection by modern technologies and are an outcome of the COST Action EUBIS, TD1203 Food Waste Valorisation for Sustainable Chemicals, Materials and Fuels.

Introduction

The vast amounts of bio-waste produced in the agricultural sector and society creates huge environmental, economic and social problems; the global volume of food wastage is estimated at 1.6 billion tonnes of "primary product equivalents" and total food wastage for the edible part of this amounts to 1.3 billion tonnes.[1] In addition, packaging and non-consumable material associated with the food chain are added burdens to the consumer, the industry and the environment. With global climate change challenges and its various effects on ecosystems and resource depletion, the issue of food waste and its diversion from landfill is becoming an increasingly urgent priority and has captured the attention of governments, environmental and social organisations, businesses and academics. There is now a growing recognition that the problems of waste management and resource depletion can be solved together through a more efficient utilisation of waste as a resource, using green and sustainable technologies.

This potential source of raw materials originates not only from harvest and initial processing but also importantly from the food/feed processing industry and society. Thus, utilisation of such wastes, by-products and co-products (i.e. side-streams) from the agricultural sector and related industry, should find an efficient and increasing use in obtaining value added chemicals and materials.

In principle, the major challenges to face for obtaining value added products from biowaste reflect the nature and source of the biowaste, rather than from the technology available to use. Mature technology, developed for the exploitation of fossil sources of organic matter, is available to be applied to and be optimised for processing biowastes. However, food wastes present unique features. Although high volumes of food wastes are available, from a practical perspective, the density of this material is often very low making practical conversion uneconomic. Hence, the developable processes are most of-

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ten only viable for major cities and/or certain processing centers. For examples, municipal biowaste treatment plants are a most cost effective source of food waste. Municipal solid wastes contains from 18-60 % biowaste.[2] It comprises food wastes and green wastes from private gardening and public park trimming activities in approximate 1.6 ratio, respectively.[3, 4] Food waste is a major contributor to the total waste production. Urban food wastes are often not properly treated and recycled, unlike recyclable materials such as paper. Hence, food waste often ends up in landfills along with regular waste. This has an alarming impact on environment and health through production of hazardous substances such as methane and bacteria which build up from food waste in landfills. In the last decade, public opinion sensitivity to food waste issues has grown concerning wastes created during both processing and product distribution.[5, 6] Urban food waste has two contrasting features. On one hand, it represents an economic and environmental burden. On the other hand, it contains potentially valuable chemicals and energy. Urban food wastes are produced by households, restaurants, food manufacturers, and farms,[3] at the stages of food production, processing, retailing and consumption. As of 2013, approximately half of all food is wasted worldwide.[7, 8] Loss and wastage occurs at all stages of the food supply chain or value chain. In low-income countries, most loss (81-97 % of total food waste) occurs during production, while in developed countries much food waste occurs at the consumption stage (about 100 kg per person per day, amounting to 32-60 % of total food waste). In Europe, of the total 89 million tons food loss and waste created per year 47 % arises from household, 16 % from catering, 6 % from retail and wholesale and 44 % from manufacturing activities.[9]

The above data highlights that in relation to the abundance and easy availability, the organic humid fraction of municipal wastes is potentially the most convenient exploitable source of recyclable renewable organic matter. According to various statistics, American families throw out between 14 and 25 percent of the food and beverages they buy. This can cost the average family between $1,365 to $2,275 annually.[10] The majority of waste from households consists of food wastes, close to 60%,[3] their environmental impact has grown dramatically, due to the increase of population urbanisation and consumption habits. This has generated higher costs for society due to the need to dispose higher amounts of wastes. On the other hand, the population urbanisation has resulted in the creation of a low entropy source of chemical energy by concentrating the bio-wastes in confined spaces. As taxpayers have already paid collection costs, municipal bio-wastes are a negative cost source of chemical energy.[11]

In this review, central established and emerging technologies suitable for the recovery and quality enhancement of value added products from a variety of by-product and waste streams are reviewed. Methods for physical and chemical pre-treatment, extraction and/or chemical conversion, separation, chemical characterisation and purification of added value products are covered with examples given from key areas in the field. Aside from the cost effectiveness of the target bio-wastes to be processed, the technologies reviewed herein should be appreciated for their intrinsic merits. All biowastes contain the same types of proximates, i.e. polysaccharides, fats, proteins and lignin. Thus, the technologies reported in this paper can potentially be applied to all kind of biowastes. Rough estimates on operating costs and the feasibility of implementing the proposed techniques on industrial level are reported in the chapter dedicated to municipal biowastes, as a typical example of most viable feedstock for the production of bio-based speciality chemicals and chemical intermediates.

Physical pre-treatment techniques

In order to increase the storage and handling properties (especially density) of different waste materials and residues, drying, particle size reduction and densification are often required. In many cases, wet or moist biomass will start to biologically and chemically degrade during storage. If the material cannot be stored or further processed in a wet state, drying is necessary. Size reduction by cutting or grinding might be needed if the waste material or residue is very bulky or consists of large particles. If the material to be processed is transported to a conversion facility or stored for year around supply, densification by baling, briquetting or pelletising might be needed to reduce transport and storage costs.

Furthermore, after recovery of added value chemicals, residual materials have to be taken care of. Incineration or use as fertiliser or soil amendments are possible, however in this case, drying and densification might also be needed.

Size reduction

The macroscopic pre-treatment of food waste has previously been described in detail.[12] Size reduction can be divided into crushing and grinding. Size reduction can be done either in a wet or in a dry state. Wet grinding is generally more power consuming. A considerable amount of heat may be generated in a mill, particularly if it operates at a high speed. This temperature can cause the temperature of the feed to rise significantly and a loss in quality might be the result. Cryogenic milling, where solid carbon dioxide or liquid nitrogen is mixed with the feed, is a way to reduce undesirable heating effect and facilitate milling of tough fibrous material.

Drying

Biomass feedstocks often need to be dried prior to the conversion process. A number of different dryer types may be suitable for this purpose, and the final choice should be made after careful consideration of operational and economic factors specific to the application.

Evaporative drying processes require heat exchange, by convection or conduction. Frequently used sources of heat for drying are 1) hot furnace, engine or gas turbine exhaust gases; 2) high-pressure steam from a steam or combined cycle plant; 3) warm air from an air-cooled condenser in a steam or combined cycle plant; and 4) steam from dedicated combustion of surplus biomass, or diverted product gas, char or bio-oil.

Dryers can be classified, according to the drying medium (e.g. flue gas dryers and superheated steam dryers), or to the heat exchange used (conductive/convective or indirect/direct dryers, respectively). The most common types of flue gas dryers are rotary and flash dryers. The commercial scale steam dryer types are tubular dryer, fluidised bed dryers and pneumatic conveying dryers. [13]

High velocity cyclone dryer. A special technology for sludge drying is cyclone drying.[14] This method is based on a high velocity cyclone dryer where sludge drying can be performed at low temperatures (<90 °C) enabled by a high-capacity fan. The feed material is fed to the inlet air stream and the air-material suspension is directed to the cyclone where changes in pressure and radial velocity induce water vaporisation and possible particle grinding and separation phenomena. The bulk of the dried material (accept fraction) is recovered from the bottom of the cyclone while the fine particles (reject fraction) are captured from the humid exhaust air stream in a separate baghouse filter unit. A slit inside the cyclone is used to control the flow distribution to the filter unit.

Densification

Baling, briquetting, pelletizing and extrusion are common ways to densify different types of biomass. Baling is typically used to store and transport agricultural materials such as straw, while briquettes and pellets are usually made for transport, storage and combustion of solid biofuels. Pellets are generally considered to have better handling properties compared to briquettes. Densification offers several advantages, i.e.: improved handling and conveyance efficiencies, controlled particle size distribution for improved feedstock uniformity and density, fractionated structural components for improved compositional quality, and conformance to pre-determined conversion technology and supply system specifications.[15]

In all these compaction techniques, the starting materials are solid particles. The individual particles are still identifiable to some extent in the final product. Briquetting, pelletizing and extrusion represent compaction i.e., the pressing together of particles in a confined volume. If fine materials which deform under high pressure are pressed, no binders are required. The strength of such compacts is manifested by van der Waals' forces, valence forces, or physical interlocking. Natural components of the material may be activated by the prevailing high pressure forces to act as binders. Some materials might however need binders even under high pressure conditions.[16,17]

Baling. Bales are commonly round (1.5 m wide by 1.8 m diameter) or rectangular (0.9x1.2x2.4 m). Typical bale densities are 140-180 kg m^{-3}.[18] Usually bales are used for transport and storage of agricultural materials such as straw and energy crops.

Briquetting. Typical technologies for briquetting are the piston press and the screw press. In the reciprocating press type biomass is pressed in a die by a reciprocating ram at a very high pressure. In a screw extruder press, the biomass is extruded continuously by a screw through a heated taper die. In a piston press, the wear of the contact parts e.g., the ram and die is less compared to the wear of the screw and die in a screw extruder press. The physical dimensions of briquettes can vary from cylindrical to brick formed depending on the technology used. Typical densities of single briquettes are 1-1.4 kg m^{-3} and the bulk density for briquettes is often < 700 kg m^{-3}.[16, 19]

Pelletisation. The simplest way to enable more efficient usage of the food waste residue as a source of energy is to process it by a pelletisation process. The most common type of pelletisers consists of a perforated die with one or more rollers. By rotating the die and rollers, the feedstock is forced through the perforations to form densified pellets. Factors affecting the quality of the pelleted product are, moisture content, particle size and shape, chemical composition of raw material and type of processing equipment.[20] Utilisation and optimisation of different residues from agricultural production has been the topic of many investigations. Agricultural residues investigated include the following: olive cake,[20] spelt wheat hull,[21] grape pomace,[22] grasses,[23] etc.

Extrusion. During extrusion, biomass is transported with a rotating screw through a barrel and against a die, resulting in a significant pressure gradient and friction due to shearing of the biomass. The effects of wall friction and internal friction in the material increase the temperature of the biomass. The heated biomass is further forced through the extrusion die to form briquettes or pellets.[16]

Results can also be improved by the combination of extrusion/extraction with chemical treatment. A pre-treatment in a dilute acid medium at low temperature will open up the cell wall structure by hydrolysis of certain components, particularly hemicelluloses. This combination of extrusion/extraction and dilute acid pre-treatment has successfully been tested to increase yields of hemicellulose in the hydrolysate on extruded rice straw.[24] Combined alkaline thermo-mechano-chemical pre-treatment followed by injection of enzymes into a twin-screw extruder called "bio-extrusion", has been developed with sweet corn residue, a co-product of industrial corn grain canning; blue agave bagasse from the manufacture of tequila, oil palm empty fruit bunch, a residue from palm oil manufacture and barley straw.[25]

High pressure pre-processing and extraction

Hydrothermal technologies for pre-processing

Hydrothermal processes are broadly defined as chemical and physical transformations at high temperature and pressure.[26, 27] In this section, special attention is given to key hydrothermal technologies, in particular; liquid hot water (i.e. autohydrolysis), steam-explosion, ammonia-assisted subcritical H_2O and the novel high-pressure CO_2-H_2O process. Liquid hot water, steam-explosion and high-pressure CO_2-H_2O processes are reviewed here with respect to the hydrolysis of biomass/waste components, such as hemicelluloses, starch and lignin, and their effect on saccharification process yields as well. Additionally, the effect of subcritical H_2O on the hydrolysis of poly-

saccharides (cellulose and hemicelluloses) into respective sugars and depolymerisation of lignin is also described.

Hydrothermal extraction of biomass has fostered considerable interest due to the range of conditions that can be imposed and the reactions that can be carried out. Besides acting as a solvent, water can also acts as a reactant and catalyst.[28] During the hydrothermal extraction of biomass, water is present under "Subcritical" conditions at temperatures between 100 and 240 °C. However, the changes that occur as the temperature rises to, and above these conditions need to be considered in order to understand the efficacy of hydrothermal pre-treatment under subcritical conditions.

Subcritical water is considered to be water at temperatures greater than 100 °C, and below the critical point (Tc = 374 °C at a pressure of 22.1 MPa).[29] In the last decades, subcritical water extraction has attracted a lot of attention due to its safe and environmentally-friendly character, competitive solvating properties, excellent selectivity and economic viability. Above the critical point, water will change to "supercritical" where it will exhibit liquid- and gas-like properties, and will not show any phase transition with changes in temperature and pressure.[28] Subcritical water differs from both ambient water (water at room temperature) and supercritical water in a number of ways and several properties are of interest when processing biomass.

The dielectric constant, (also known as relative permittivity) (ε), of a liquid is a dimensionless constant that indicates how easily a material can be polarised by the imposition of an electric field. The constant may be defined as the ratio between the ability of the liquid to carry an alternative current to the ability of a vacuum to carry the current ($\varepsilon = \frac{\varepsilon_s}{\varepsilon_0}$), where ε is the dielectric constant, ε_s is the static permittivity of the material and ε_0 is vacuum permittivity. At 20 °C, water has a very high dielectric constant of ε = 80.2. This is due to its dipole moment which enables it to be polarised in an electric field, and also underlies the ability of water to dissolve ionic compounds by interacting with the charged ions reducing their re-association. However, the dielectric constant of water decreases considerably as temperature increases. At 25 °C (0.1 MPa) the value drops to ε = 78.5. At the subcritical temperature it drops to less than ε = 14. This decrease is due in part to the increase in molecular movement of the water molecules at the higher temperature, thus reducing their ability to interact with charged groups (e.g. soluble ionic species) or to align in an electric field (hence the reduced value of ε). Thus, increasing temperature confers solvent properties to water similar to that of organic solvents such as acetone and ethanol at room temperature. At around 240 °C, the dielectric constant of water is in the region of ε = 35, which is similar to that of acetonitrile (37.5) and methanol (32.7) at room temperature. Hence, the high temperature/pressure during hydrothermal extraction can enhance the solubilisation of hydrophobic non-polar organic compounds. Equally, at the higher temperatures, the solubility of ionic species for example salts decreases.

The ionic product of water (K_w : $K_w = [H_3O^+][OH^-]$) is the equilibrium constant for the dissociation of water (H_2O) into hydroxonium ($H_3O^+_{(aq)}$) and hydroxide ($OH^-_{(aq)}$) ions. Due to the endothermic nature of the disassociation process, as the temperature increases, the ionic product of subcritical water increases; and by 250 °C is approximately 2 orders of magnitude greater than at ambient. This enables water to play an important role in acid- and base-catalysed reactions, of particular relevance to biomass hydrolysis.

Hydrothermal processes are generally divided into four groups[28]:

- *Hydrothermal carbonisation*, carried out at up to about 250 °C for up to 12 hours (although higher temperatures of up to 900 °C may be used). This process can simulate a long-time scale carbonization process and may be used for producing hydrochar[30]
- *Aqueous phase reforming*: use of heterogeneous catalysis at 220-250 °C and pressures of up to about 50 bar to convert sugars and alcohols into H_2 and CO_2[28]
- *Hydrothermal liquefaction* at between 280 and 370 °C, 100-250 bar, to produce primarily water insoluble bio-oils
- *Hydrothermal gasification* using catalysts at between 300 and 500 °C, producing methane and hydrogen, but also CO_2, CO.[28]

Hydrothermal treatments of biomass have been developed because of the ability to rapidly transform the organic material via chemical reactions into other platform moieties that can be readily used in the chemical industry. However, the properties of water within the 100-240 °C temperature range over shorter periods are also highly effective in extracting and tailoring the structure, chemistry and properties of the component biological materials to enable their further exploitation in a more native form.

Hydrothermal pre-treatment of (ligno) cellulose.

Hydrothermal treatment is widely used for the pre-treatment of lignocellulosic biomass in order to make the cellulose more available for enzymatic saccharification.[31] The most common form of this treatment involves steam explosion. This involves subjecting the biomass to high pressure steam usually between 180 and 230 °C for several minutes (5–15 min are most common) after which the reaction vessel is depressurised. Under such conditions the water, which is held in liquid form under high pressure, will be flash evaporated when depressurised possibly providing disruptive shear forces to the biomass. The pre-treated insoluble cellulosic product is then processed (usually enzymatically) to release the glucose for fermentation to other products using micro-organisms such as yeasts and prokaryotes. A key advantage of hydrothermal pre-treatment is that it does not necessarily have to involve any additional acids or chemicals, and much of the thermal energy can be recovered for use in other processing activities within a biorefinery.

There are several hypotheses as to why this steam explosion and related pre-treatments (such as hot-water extraction at similar pressures) improves the downstream enzymatic digestibility of the cellulose. Firstly, it helps to alter and partially remove the protective polyphenolic lignin matrix from around the microfibrils. Some of the lignin is considered to melt at

these extreme temperatures and indeed can re-coalesce in droplet form afterwards.[32] Secondly, hemicellulosic polysaccharides that coat the cellulose microfibrils are partially hydrolysed thus further exposing the surface of the microfibril to enzymes.[33] This hydrolysis is enhanced by the more acidic nature of water at the temperatures used. In lignocellulose from monocotyledonous sources such as wheat straw, this may be augmented by the hydrolysis of phenolic esters such as diferulic acid and related cinnamic acids which cross-link the hemicelluloses with themselves and with lignin.[34] Thirdly, the crystallinity of the cellulose may be reduced facilitating accessibility of cellulases.[33] Furthermore, the particle size becomes reduced resulting in a greater surface area to volume ratio, relevant for enhanced enzymolysis.[34,35] Although the temperatures generally used in this pre-treatment are a lot less severe than those used in the chemical reaction processes described above, at 180 °C and above there is a significant and increasing degree of chemical degradation of lignocellulosic components. Hexoses and pentoses can breakdown to produce furfural derivatives, levulinic acid, acetate and formic acid.[33] Phenolic moieties may also be released from the partially degraded lignin. Such products are generally inhibitory to many microorganisms and retard the downstream fermentation processing. However, they can be removed to a large extent by washing post processing.

There are a number of variants on the steam explosion hydrothermal pre-treatment, all of which will have influence on the reactions and changes that occur. Steam explosion itself may be modulated by the addition of acid to the biomass either through soaking in dilute acid in advance, or perfusing with SO_2 in advance.[36] Equally, the amount of water present (i.e. substrate aqueous concentration) during the actual incubation period will have an influence on the hydrolysis procedure and the extent to which hydrolysed components can diffuse away from the residue. Indeed there is an overlap here between steam explosion pre-treatment and hot water hydrothermal processing without the explosion component. The latter will certainly help to enhance the extraction of the solubilised components including hemicellulosic and phenolic moieties and fermentation inhibitors. One interface between the two processes involves steam exploding into hot water thus benefiting from both the explosion component and the hot water extraction.[37]

Research on hydrothermal pre-treatment of cellulose has also been carried out at temperatures above 240 °C, but below the supercritical temperature of 374 °C. Processing of a wide range of lignocellulosic biomass (e.g. agro food residues) using subcritical H_2O processes with various reactor designs have been demonstrated.[38-41] At these higher temperatures, Deguchi *et al.* found that crystallinity of cellulose disappeared at around 320 °C and 250 bar.[42] At these conditions, the rates of cellulose hydrolysis into glucose are higher than those for degradation of glucose.[43] To prevent degradation of glucose, faster hydrolysis is desired, which can be obtained using H_2O at supercritical conditions.[44, 45] Saka and co-workers found that cellulose is more susceptible to hydrolysis under supercritical H_2O conditions and a high yield of hydrolysed products was obtained while cellulose treated under subcritical conditions is more liable to dehydration.[46]

Hydrothermal pre-treatment for the extraction of hemicellulose

The hemicelluloses class of polysaccharides from lignocellulose are the world's second-most abundant source of renewable polymers after cellulose.[47] Hemicelluloses are polysaccharides that are extracted from cell walls in alkaline solutions, in order to break the hydrogen bonds that create attachments between the hemicelluloses and cellulose.[48] In addition, alkaline extractions will serve to hydrolyse any ester linkages, including diferulic acid cross-links commonly found in cell walls of monocotyledonous plants[48,49,50] which may further attach the hemicelluloses to each other and lignin. Traditional cell wall fractionation processes[51] demonstrate the range of polymer sizes and chemistry that can be extracted in a sequential manner and there are numerous studies on the chemical, rheological and other functional properties of hemicelluloses in food and non-food applications. The hydrolysis of hemicelluloses and starch in subcritical H_2O has been poorly studied when compared to cellulose because these carbohydrates are much more susceptible to hydrolysis under milder reaction conditions[52, 53] resulting in the production of breakdown products. For instance, Rogalinski *et al.* carried out kinetic studies of cellulose and starch hydrolyses and found that hydrolysis of cellulose is much slower than of starch.[54]

Many approaches have been developed to extract hemicelluloses in order to exploit their diverse characteristics and functionalities. For example, industrially produced hemicelluloses are used as viscosity modifiers in food packaging films,[47] additives in paper manufacture,[55] pharmaceuticals both as tablet binders[55] and to exploit their bioactive properties such as immunostimulatory and antitumor characteristics[56,57] Wilde *et al.*[58] discovered that xylans extracted from brewers' spent grain could be used as very high quality foam stabilisers in beverages; arabinoxylans from corn bran have been industrialised for making hard-gels through peroxidative cross-linking of their ferulic acid side chains,[59] xylan hydrolysates (xylo-oligosaccharides) can be used as prebiotics.[60] Hemicelluloses can also be hydrolysed to their constituent sugars and converted into fuel, ethanol and other value added chemicals such as furfural, levulinic acid, xylitol and 5-hydroxymethylfurfural (HMF).[61,33] Recently, Shuaiyang, *et al.*[62] demonstrated that xylan citrate can be used as a potential absorbent for industrial waste water treatment.

Hydrothermal extraction.

Since hydrothermal pre-treatments (developed to enhance the saccharification of lignocellulose) lead to the modification, hydrolysis and solubilisation of varying amounts of hemicelluloses, and because hemicelluloses can potentially provide sources of functional poly- and oligo-saccharides, there is great interest in developing hydrothermal processes to release and recover potentially valuable hemicellulosic moieties. For example, Chen and Liu[63] demonstrated that steam explosion of wheat straw for 4.5 min at 1.5 MPa coupled with ethanol extraction could recover over 80% of the hemicelluloses. Sun *et*

al.[64] demonstrated the potential for steam explosion and alkaline peroxide treatments in sequence for extracting over 80% of the hemicelluloses and up to 99% of the lignin from cereal straw. Wang *et al.*[65] explored the use of steam explosion in conjunction with post-treatment alkaline ethanol extraction to effectively extract hemicelluloses. Sabiha-Hanim *et al.*[66] evaluated steam explosion of oil palm frond between 180 and 210 °C for 4 min. They investigated yield of hemicelluloses in water soluble fractions with and without KOH and achieved up to 65% recovery. However, extraction yield does not necessarily reflect the quality of hemicellulose obtained. In-depth studies on hemicellulose chemistry were carried out by Kabel *et al.*[67] who investigated the impact of pre-treatment severity using steam explosion on the release and decomposition of xylan hemicelluloses from wheat straw in relation to the enzymatic digestibility of the remaining cellulose. They demonstrated that as the severity was increased (which increased cellulose digestibility), larger amounts of xylan were released from the straw and these were accompanied by a greater degree of breakdown to create furfural and related derivatives. Pre-treatment created a range of acetylated xylo-oligomers with a wide size distribution from above 25 to less than 9. Studies using HPSEC (high-performance size exclusion chromatography) and mass spectrometry also showed that higher severities created more xylose oligomers with a Degree of polymerisation (DP) of less than 9. At the higher severities, the xylose broke down considerably, and the creation of furfural compounds was greater. More recently, Merali *et al.*[34] performed a comprehensive analysis of xylan polymer chemistry and extractability from cell walls of pre-treated wheat straw. The results showed that hydrothermal pre-treatment at 190 and 200 °C extracted about 50% of the xylan. The remaining xylan could be sequentially extracted from the residues in increasing strengths of alkali. The alkali-soluble xylan was found to be significantly depolymerised by the pre-treatment, and more readily extractable from the cell wall residue either in hot water, or in alkali. Detailed assessment of the molecular weight profiles of alkali-extracted hemicelluloses showed that a large proportion of them displayed molecular weights in excess of 50 KDa, highlighting their potential for exploitation. These studies reflect the view of Josefsson *et al.*[68] who highlighted the difficulty in controlling the degradation of hemicelluloses, lignin and cellulose during such processing. Aguedo *et al.*[69] investigated the solubilisation of enzymatically-resistant arabinoxylans from destarched wheat bran using hydrothermal microwave processing in pressure vessels. They demonstrated that this scalable approach could provide a rapid solubilisation of hemicelluloses in a range of forms, including polysaccharides, oligosaccharides and monosaccharides with variable yields and proportions depending on the severity. Importantly, the approach also enabled a certain degree of control over the production of breakdown products such as HMF and furfural.

Examples of polysaccharides extracted in hot water

Commercial quality hemicelluloses. Yao *et al.*[70] evaluated hydrothermal alkaline extraction of bagasse for extraction of hemicelluloses using pH-corrected water. Using surface-response methodology, they demonstrated that hydrothermal extraction in 4M NaOH resulted in the release of high quality xylan. Strand *et al.*[71] improved recovery and quality of hemicelluloses from wood extracts using activated carbon treatment ultrafiltration. Removal of lignin and other extractives on activated carbon before ultrafiltration increased the capacity of filtration by 1.5 x and facilitated the production of higher purity and higher concentrations of high molecular weight hemicelluloses from spruce. This was in part due to the selective absorption of 4-O-me-GlcA-containing moieties to the activated carbon, probably due to complexation with phenolics, and resulted in a slightly lower recovery of hemicelluloses albeit of higher quality.

Hemicelluloses for films and barriers. Some hemicellulosic polysaccharides have the potential for use in the production of pure or composite films and barriers, such as those used in food packaging (e.g. Ren *et al.*,[72] Kesonan *et al.*[73]). Recently, Azeredo *et al*.[74] explored the use of wheat straw hemicelluloses in the production of films and barriers using citric acid as a cross-linking agent. In that study, the hemicelluloses were extracted by sequential extraction in alkaline peroxide and recovered by precipitation in ethanol. The resulting xylan/glucomannan product was soluble in water and films with a range of properties were successfully produced. There is little or no information on creating films and barriers using hemicellulose solely extracted by steam explosion, probably because of the high degree of hydrolysis that occurs. Azeredo *et al.* (unpublished) have carried out alkaline extraction of post-hydrothermally treated wheat straw to produce films, thus extending their work presented above. More directly relevant, however, is the use of pH-modulated hydrothermal treatment for extracting hemicelluloses for films which has been successfully demonstrated by Svard *et al.*[75] They used a combination of temperature (industrial autoclave up to 140 °C) and alkali (0.5M NaOH) to extract hemicelluloses from oilseed rape (OSR) straw and successfully formulated xylan-containing films with strain-to-break ratios of >60%. It is likely that such hydrothermochemical approaches could form a good basis for hemicellulose exploitation. Nevertheless these studies have not yet been integrated with the saccharification and fermentation biorefining of lignocellulose.

Extraction of hemicellulosic oligosaccharides. As indicated above, hydrothermal pre-treatments can break down and solubilise hemicelluloses into smaller polymers and oligomers. Oligomers in particular are of interest as potential sources of prebiotics. Prebiotics are microbial substrates that are able to improve the host health by stimulating the proliferation and/or metabolic activity of beneficial bacteria in the colon.[76] There is an increasing body of work describing the successful hydrolysis and extraction of hemicellulose-derived prebiotics (oligo and polysaccharides). For example, Gullon *et al.,*[77] subjected wheat bran to a two-stage process (aqueous extraction followed by hydrothermal treatment) to produce xylan-derived oligosaccharides. These were evaluated for prebiotic activity and demonstrated the ability to enhance bifidobacterial proliferation to the same level as fructo-oligosaccharides. Kurdi and Hansawasdi,[78] used hydrothermal treatments

(135 °C) for producing hemicellulosic oligosaccharide mixtures from rice bran and cassava pulp, rich in galactose, glucose and mannose. These have been explored as potential sources of prebiotics, demonstrating bifidogenic effects. Other related research has highlighted the potential to add further value through fractionation. For example, Onumpai *et al.*[79] showed that pectic oligosaccharides prepared from commercial pectin demonstrated structure-function relationships in relation to their prebiotic activity providing a good evidence base to potentially add further value to lignocellulosic derived non-cellulosic components through sub-fractionation and tailored hydrolysis.

There is considerable additional research that focuses only on the hydrothermal extraction of oligosaccharides and monosaccharides, providing more information on the conditions required, and the effects of different substrates. A large body of work surrounds the steam explosion/hydrothermal or autohydrolysis treatments developed for solubilisation of bamboo hemicelluloses as oligo- and mono-saccharides.[47,80] Aoyama *et al.*[81] showed that over 55% of bamboo xylan could be extracted and recovered in this way. Further work has explored the use of catalysts to enhance the effect of hydrothermal extractions.[82] These included organic acids, salts and Lewis acids. $CaCl_2$ and Lewis acids effectively reduced the temperature necessary. Other examples include Shao *et al.*[83] Xiao *et al.*[84] showed that hydrothermal (hot water) extraction could increase yields of xylo-oligosaccharides to nearly 50%. The studies on hydrothermal extraction of bamboo in water alone, or in the presence of catalysts or acids, also showed that whilst extraction of the hemicellulosic polymers is tractable, the solubilised moieties are mainly in mono- and oligomeric forms thus limiting their exploitation, and negating the potential for developing the use of whole polymeric forms, or producing industrial xylans. Other "subcritical" extraction approaches with other biomass have shown similar problems for example in the extraction of sugarcane bagasse using microwave heated water to 160 °C (Zhang *et al*.).[85]

However, the Coimbra group[86] have extracted polymeric mannans from coffee grounds using microwave hydrothermal extraction at up to 230 °C. In this study, a range of polysaccharides with MWt of up to 17KDa were obtained. In addition, they managed to produce a range of arabinoxylan polysaccharide fractions with DPs of up to 40 using microwave extraction. Hence, soluble hemicellulosic polysaccharides can be recovered from some feedstocks by hydrothermal extractions. The differences in quality and molecular weight may relate to the structure in the native cell wall. Also, the possible release of catalytic reagents such as acetyl groups (present on xylans) may further reduce the pH during extraction and thereby increase the extent of acid-catalysed depolymerisation. It is noteworthy that the Coimbra group[86] used quite short extraction periods (2-3 min).

Hydrothermal extraction of other components. Because of the hydrophobic nature of lignin, although significant quantities may be released and solubilised from the cell wall by hydrothermal extraction at up to 240 °C, it is likely to recoalesce/precipitate after cooling, and is thus difficult to separate from the feedstock. However significant research has been conducted to try to address this problem. Chen *et al*.[87] used hydrothermal liquefaction to convert rice straw into a soluble mixture of products and compounds. From this, solubilised phenolic compounds could be recovered using a modified adsorption resin. Ravber *et al*.[88] have developed a pilot scale process to isolate phenolic compounds from larch wood waste using pressurised hot water. A semi-continuous process was developed to recover components that could be used as natural ingredients for producing adhesives, biocidal coatings etc.

The depolymerisation of lignin into valuable products in subcritical H_2O has also been examined and this is a challenging and intriguing approach due to the highly cross-linked phenol-based structure of lignin. Both temperature and reaction time play an important role in lignin depolymerisation. A number of studies on the effect of subcritical H_2O as well as the addition of organic solvents as catalysts (e.g. phenols, ethanol and mixture of ethanol and CO_2) to subcritical H_2O medium have been reported.[89-91] High temperatures promote the depolymerisation of lignin while long reaction times facilitate the reaction between produced compounds (e.g. guaiacol) and high molecular weight polymers.[89] These undesired reactions can be avoided by the simple addition of phenol or methanol.[45] Kanetake *et al*. investigated the hydrothermal depolymerisation of pure lignin at temperatures between 350 °C and 400 °C.[92] A wide range of products namely phenols, catechol and cresols, some of which are produced from secondary hydrolysis of methoxyl groups were obtained. Zhang *et al*. examined the influence of hydrothermal processes on organosolv efficiency.[93] The liquid and solid residue yields were 79 % and 37%, respectively, and the major products were phenol, 4-ethylguaiacol and methyl dehydroabietate. Liu *et al*. investigated the processing of walnut shell under alkaline-catalysed conditions at temperatures between 200 °C and 300 °C.[94] A wide range of several phenol derivatives originating from hydrolysis of methoxyl groups such as 1, 2-benzenediol, 3,4-dimethoxyphenol and 2-methoxy-phenol were found. Furthermore, Karagöz *et al*. identified the same phenolic compounds (4-methyl-1,2-benzenediol, 3-methyl-1,2-benzene-diol, 2-methoxy-phenol and phenol) from sawdust and rice husk with subcritical H_2O at 280 °C for 15 min at an unknown pressure.[95] Yoshida and co-workers applied subcritical H_2O for hydrolysis of rice bran at 220 °C for 30 min and a great variety of phenolic compounds (e.g. gallic, caffeic, ferulic, vanillic, sinapic and syringic acids) were found.[96]

Thus, significant information has been provided on the potential to co-exploit the non-cellulosic components of lignocellulose that may be tailored using the pre-treatments applied in optimising the enzymatic saccharification of cellulose. However these complementary procedures and processes have yet to be developed in the synergistic manner required for a successful Biorefinery.

Ammonia-assisted processing.

A variety of different pre-treatments have been examined, and only a few have met the pre-conditions necessary for industrial

exploitation. One especially appropriate process, AFEX (ammonia fibre expansion),[97] is currently discussed. The AFEX process has been found to be adequate for low lignin biomasses such as residues from agriculture, e.g. straw or grass. Alizadeh *et al*.[98] Teymouri *et al*.[99] and Murnen *et al*.[100] were able to reach a theoretical 90% glucose yield from switchgrass, corn stover and miscanthus. However, for high lignin biomass such as that from poplar wood the method is less adequate.[101]

Table 1. A comparison of ammonia assisted pre-treatment of corn stover and wheat straw. Effect on carbohydrates yields, solid protein extracts, and residual solids (g / 100 g dry weight biomass).

	NH3 (liquid)99	NH3 (25 wt.%)111
Biomass	Corn stover	Wheat straw
NH_3:Biomass	1:1	5:1
H_2O:Biomass	0.6:1	-
T [°C]	90	200
τ [min]	5	5
p [psi]	300	551
Yields		
Glucose [g]	38.5	38.4
Xylose [g]	18.5	15.9
Arabinose [g]	1.2	1.3
Protein extract (solid] [g]	2	2
Residual solids [g]	38.9	35
Possible location	Combination with chemical site	Combination with agricultural site

Due to the mild reaction conditions, the production of fermentation inhibitors is avoided, and this makes the process suitable for production of e.g. products such as ethanol, and processes such as simultaneous saccharification fermentation (SSF). Krishnan *et al*.[102] and Shao *et al*.[103] each achieved more than 90% theoretical ethanol yield from the fermentation of *Saccharomyces cerevisiae* 424A (LNH-ST)[104] in bagasse and corn stover hydrolysates, without having to decontaminate them and without needing to provide additional sources of nutrition. Jin *et al*. reached 71% ethanol yield[105, 106] using simultaneous saccharification and ethanol fermentation of corn stover through *Clostridium phytofermentans* (ATCC700394).[107] Furthermore, AFEX provides the opportunity to recover proteins for animal nutrition as an integrated by-product.[108] Unlike other alkali-based pre-treatments, the AFEX process allows a nearly complete recycling of the ammonia used, which is important in relation to the acceptability of the process and thus for commercial exploitation.[109, 110]

However, the AFEX process described in the above references uses liquid ammonia for the reaction, which demands a high level of expenditure on apparatus and running costs. This is the greatest obstacle to industrialise the process. Recent research has thoroughly investigated the AFEX process with aqueous ammonia (25% NH_3 w/v) as a simpler and less expensive variant of the traditional AFEX process. The effects on the glucose, xylose, and arabinose conversion rates during subsequent enzymatic treatment of corn stover and wheat straw are shown in Table 1.

These results make it clear that the AFEX process can be carried out with both aqueous ammonia (25% w/v) and liquid ammonia. Conversion rates of more than 90% can equally be reached. The classic AFEX process with liquid ammonia is used extensively in large chemical industrial plants because the necessary infrastructure is already present there. Under these circumstances, the classic AFEX process is preferred for industrial use. The method using aqueous ammonia, on the other hand, can be used as a simple and cheap method in non-centrally organised agricultural structures.

CO_2-assisted processes.

Similarly to subcritical H_2O, supercritical carbon dioxide ($scCO_2$) has gained special importance in the processing of biomass.[112] This is mostly due to the fact that molecules of CO_2 have similar size to both H_2O and ammonia hence CO_2 can penetrate small pores of biomass. At supercritical conditions, CO_2 is able to penetrate into small pores of recalcitrant structure of lignocellulosic biomass resulting in structural modifications. This improves the susceptibility of both polysaccharides (cellulose and hemicelluloses) to enzymatic bioconversion.

Additionally, the expansion that occurs when CO_2 is quickly released promotes the disruption of the cellulose structure, which decreases the cellulose crystallinity and consequently increases the accessibility of hydrolytic enzymes to a larger surface area of biopolymers.[113] It is also important to highlight that biomass contains water as moisture. Therefore, the presence of H_2O and CO_2 results in the in-situ formation of an acidic environment, due to the generation of carbonic acid, which dissociates as follows:

$$CO_2 + 2H_2O \leftrightarrow HCO_3^- + H_3O^+$$
$$HCO_3^- + H_2O \leftrightarrow CO_3^{2-} + H_3O^+$$

This acidic environment (pH slightly above 3) promotes the acid-catalysed hydrolysis of biomass-derived hemicelluloses into C_5-sugars (mainly into oligomers).[114-116] Additionally, besides the chemical effect, the physical interaction plays an important role as well. The physical phenomenon is based on the interaction of liquid hot water with polysaccharides while at the same time CO_2 acts as a catalyst increasing the diffusion of water molecules into pores of biomass causing a biomass swelling effect.[117] The in-situ generated acidic medium does not constitute an environmental problem because simple depressurisation of CO_2 increases pH value of the liquor.[114] Thus, it can be concluded that high-pressure CO_2-H_2O technology offers benefits similar to mineral acid-based processes however without the typical drawbacks, such as formation of undesired dehydration products (i.e. furfural, 5-HMF), and the need of acid neutralisation after the reaction.

In an effort to assess the influence of CO_2 on high-pressure CO_2-H_2O pre-treatment, a combined severity factor ($CS_{P_{CO_2}}$)[118] was proposed aiming to estimate the pH value from temperature and partial pressure of CO_2 according to the following equation:

$$CS_{P_{CO_2}} = \log(R_0) - 8.00 \times 10^{-6}T^2 - 0.00209T + 0.216 \ln(p_{CO_2}) - 3.92$$

where $CS_{P_{CO_2}}$ is the combined severity factor determined from partial pressure of CO_2, R_0 is the severity factor,[119] T is the reaction temperature (°C) and p_{CO_2} is the partial pressure of CO_2 (atm). The proposed combined severity factor permits the integration of all the most important factors of high-pressure CO_2-H_2O processing which influence the sugar formation through enzymatic hydrolysis. Esmailzadeh and co-workers investigated the effect of $scCO_2$ on wet and dry wheat straw.[120] They found that in the presence of water, the CO_2 pre-treatment led to a superior overall sugar yield (208.4 g/kg of wheat straw) in comparison to dry $scCO_2$ pre-treatment (149.1 g/ kg of wheat straw). Narayanaswamy *et al*. concluded that for wet corn stover (75 % w/w) at 120 °C, 240 bar for 60 min, the glucan to glucose yield increased significantly (2-fold) in comparison to dry biomass.[121] Liu *et al.* examined the effectiveness of $scCO_2$ in the pre-treatment of various agro-food residues.[122] They found that the most important factors leading to high sugar yields were temperature, moisture and presence of CO_2. The most recent studies about the pre-treatment of agro-food residues with high-pressure CO_2-H_2O technology are depicted in Table 2.

Another field of research where CO_2 was used efficiently is enzymatic hydrolysis under high pressure.[123, 124] Park *et al.* demonstrated that when cellulases (from *Trichoderma reesei*) were applied with $scCO_2$ pre-treatment (162 bar, 50 °C for 90 min) 100 % of cellulose hydrolysis yield was obtained.[124] They found that cellulases were highly stable under $scCO_2$ conditions (even up to 20 times) and their reaction rate was improved as compared to those employed at atmospheric condition. Paljevac *et al.* showed an improvement of residual activity of immobilised cellulase up to 461 % in a high-pressure CO_2-H_2O system at 100 bar, 35 °C for 24 h.[125] Lee at al. demonstrated that both α-amylase and glucoamylase are stable in $scCO_2$ at pressures up to 93 bar, 50 °C for 48 h while under scN_2 a decrease on enzyme activity by over 30 % was observed.[126] The engagement of CO_2 and H_2O brings benefits such as an increase in polysaccharide stability and lower production of undesired products such as furanic and phenolic compounds. Bogel-Lukasik and co-workers reported the use of high-pressure CO_2-H_2O in the hydrolysis of hemicelluloses and the production of C_5-sugars from wheat straw.[114-116, 127] A pentose yield of 94% (mostly in oligomer form) was obtained at 210 °C, 60 bar of initial CO_2 pressure and at non-isothermal conditions. The

Table 2. An overview of high-pressure CO_2-H_2O pre-treatment effect on enzymatic hydrolysis yield of various agro-food residues.

Residue	Reaction conditions			Moisture	Glucan to glucose yield (%) of biomass		Ref.
	T(°C)	P(bar)	t(min)	(%)	processed	Untreated	
Sugarcane bagasse	80	250	120	65	74.2[a]	19.6[a]	128
	180	50	100	-	86.6	-	129
	136	68	60	-	42.8	9.5	130
	180	206	60	80	61.3	13.4	131
Corn stalk	170	200	150	50	25.5[a]	16.6[a]	132
Corn cob	170	200	60	50	62[a]	12[a]	132
Wheat straw	185	120	30	23	53.4[a]	-	120
	225	54	0[b]	-	82.2	34.3	116
Rice straw	110	330	30	-	32.4	27.7	133
Corn stover	160	200	60	60	30[c]	12[c]	121
	150	240	60	75	85	36	134

[a] Total reducing sugar yield (%); [b] Non-isothermal reaction condition; [c] Glucose yield (g/100 g of dry raw material).

addition of CO_2 to hydrothermal medium resulted in a higher yield of xylose oligomers in comparison to water-only reactions at optimal reaction conditions.[135] Pang *et al.* studied various methodologies such as butanediol, ammonia, H_2O_2, hot lime water, NaOH and $scCO_2$ to process raw cornstalk. Among the technologies investigated, butanediol and $scCO_2$ allowed the extraction of 77% hemicelluloses from cornstalk, and in the case of CO_2, it occurred without co-extraction of lignin.[136] Others works investigated the pulp produced in $scCO_2$ with 1-butanol/H_2O mixture as co-solvent using sugarcane bagasse as feedstock.[90] Pasquini *et al.* found that when using CO_2 at 70 bar and 190 °C for 105 min with 60:40 mixture of 1-butanol/H_2O as co-solvent a delignification yield of 94.5 % was achieved.

Other potential use of CO_2-assisted hydrothermal processes is the production of furfural. The employment of CO_2 as phase-splitting media helps to produce furfural. in the presence of THF yielding 83 mol % of furfural in case of pure xylose used.[137] In case of wheat straw biomass the overall furfural yield was 43 mol %.[138] that is in the same range as currently used industrial processes with environmentally hazardous catalysts.[139] The reaction approach of this process is depicted in Figure 1.

Similar to hemicelluloses, starch is easily susceptible to hydrolysis under high-pressure CO_2-H_2O conditions.[140, 141] Thangavelu *et al*. studied the effect of CO_2 addition (dry ice) to microwave hydrothermal hydrolysis of sago pith.[142] They reported a maximum glucose yield of 43.8 % when CO_2 was added at 900 W and 2 min of irradiation. In addition, Miyazawa and Funazukuri reported an increase in glucose production (14-fold) from

starch when CO_2 was added (CO_2: starch ratio of 9 w/w) at 200 °C for 15 min and at unknown pressures.[143]

Moreschi *et al*. reported high yield of starch-derived sugars from ginger bagasse (above 97.1 %) when high-pressure CO_2-H_2O system was used (200 °C and 150 bar).[141]

Although the use of hydrothermal technologies in processing of agro-food residues has been already broadly studied, the development of high-pressure CO_2-H_2O processes is still in its infancy. So far, very promising results have been reported and further studies on these sustainable processes are needed for the development of novel applications of $scCO_2$ in the processing of various kinds of bio-feedstocks.

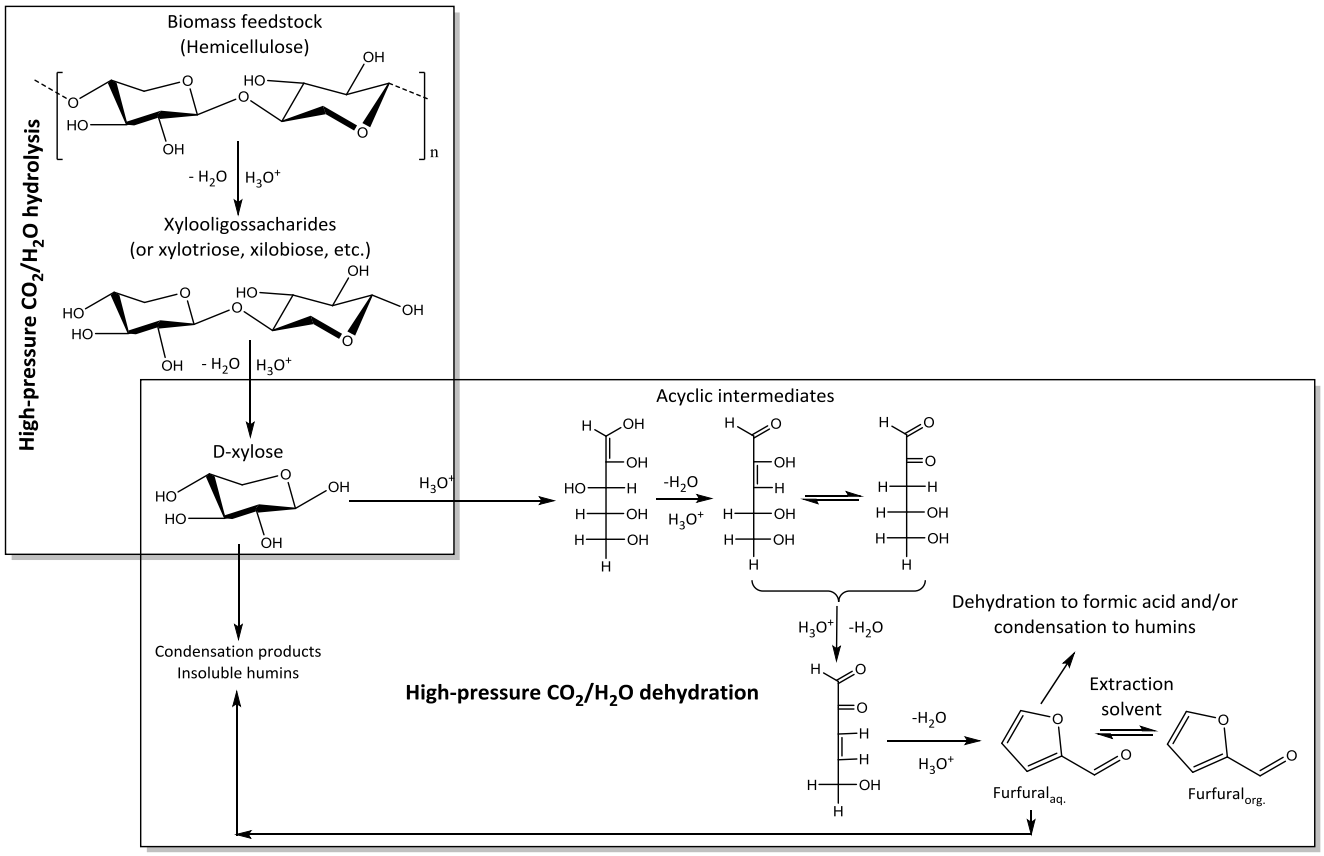

Figure 1: The reaction pathways involving high-pressure CO_2-H_2O extraction of hemicelluloses from biomass and CO_2-catalysed dehydration of pentoses to furfural in the presence of an extracting solvent. Reproduced from ref. [138] with permission of RSC.

High hydrostatic pressure treatment

Currently, consumers demand for safer, more natural and minimally-processed foods that possess the sensory, nutritional and functional properties of fresh products. This request has led researchers and manufacturers to develop new processing and conservation technologies. Within these new technologies, high hydrostatic pressure (HHP) is one of the top-10 most popular emerging technologies applied in the field of food science.[144-146]

High Pressure Processing is a cold pasteurisation technique in which products, already sealed within its final package, are introduced into a vessel and subjected to a high level of isostatic pressure (300–600 MPa) transmitted by water. Pressures above 400 MPa at cold (+ 4 °C to 10 °C) or ambient temperature inactivate bacteria, virus, yeasts, moulds and parasites, extending the products shelf-life significantly and guaranteeing food safety. Some virus families can present a low susceptibility to HHP, in particular Hepatitis A virus or Norovirus, and require pressures above 400 MPa and longer time than 1 min to obtain a complete inactivation.[147, 148] This technology also reaches the commercial sterility by combining HHP with elevated temperature (about 60 °C).[149] HHP is a natural, environmentally friendly process that extends product shelf-life similar to classical thermal treatments, such as pasteurisation, do. However in addition, it maintains the fresh food quality while the sensory (taste, flavour) and nutritional properties remain almost unchanged in the final product.[150, 151] This offers a unique chance to produce fresh-tasting, safer and long shelf-life food products.

The effects of HHP on the nutritional and bioactive compounds have been studied in some foods, such as the extractability of phenols from onions,[152,153] carotenoids and tannins from persimmons,[154] bioavailability of minerals, antioxidants and starch from apple and carob bean,[155, 156] extractability of anthocyanins from grape by-products[157] and solubilisation and functionality of dietary fibre from the soybean by-product okara.[158] To the authors` knowledge, the two latest reports are the only

previous studies on the effects of HHP in vegetable by-products. However, the described properties of HHP could be particularly interesting to recover valuable bioactive substances from by-products, as these compounds are already over-processed and further thermal treatments could cause an excessive loss of their functionality.[145, 159]

Dietary fibres (DF), one of the first ingredients showing health benefits, have been used by the food industry since the mid-1970s. In this regard, agrofood by-products are mainly composed of the insoluble residues from plant cell walls, which make up the insoluble dietary fibre (IDF) fraction (cellulose, hemicelluloses, lignin plus associated bioactive compounds). Different approaches have been developed to modify dietary fibre, in order to increase the amount and availability of solu

ble dietary fibre (SDF) by degrading IDF. Regarding health effects, SDF is associated with lowering of blood lipids and slowing down of glucose intestinal absorption, while IDF is generally related with the proper functioning of the intestinal tract.[160] Common treatments are mainly chemical, such as the use of alkali to release antioxidant polysaccharides,[158] enzymatic,[161] or physical ones such as micronisation technology, microfluidisation, ultrafine grinding, high-pressure homogenization, and blasting extrusion, all of which improve the physicochemical and functional properties of DF by decreasing particle size, rather than by increasing SDF content.[162-165] However, Mateos-Aparicio *et al.*[158] show an increase in SDF (therefore, an improvement in SDF to IDF ratio) by combining hydration, HHP-treatment and mild temperature, thus making the treated sample more valuable. HHP-treatment should be considered in order to improve 1) the functionality of vegetable residues rich in insoluble dietary fibre and/or 2) the bioavailability of phytochemicals, i.e. polyphenols, carotenoids, etc. for producing new food supplements or functional food ingredients.

HHP requires high initial capital investment. Nevertheless, regarding the costs per weight or volume unit of product, -due to its smaller water and energy needs-, HHP implementation is comparatively cheaper and has lower energy cost than traditional thermal treatments, such as pasteurisation. Moreover, it is a non-contaminant and environmentally clean technology, as water is used as the pressure transmitting fluid. The production scale will always be a key factor before a final decision on capital investment is made. Until recently, the high volume of by-products generated was a limiting factor for the use of emerging technologies, but this problem is now overcome due to the development of new generation HHP systems. In fact, one the latest and most productive HHP system shows throughputs of over 3,000 kg of product per hour.[166.]

In conclusion, HHP technology represents a highly-efficient and environmentally friendly alternative as well as an interesting tool for food industries. Therefore food industries that decide to implement this technology will be able to stabilise their own by-products and improve the availability of bioactive substances -without facing the losses associated with thermal treatments. Furthermore, they will be able to reuse their by-products as ingredients for their own production. To meet the demands of the 21st century consumer (convenience foods, higher sensory and nutritional quality, additive free/natural, functional products, etc.), food companies must innovate by using the latest non-thermal technologies, and HHP processing is currently one of the most relevant.

Supercritical carbon dioxide extraction, subcritical water extraction and pressurised liquid extraction

The extraction of added-value molecules from food waste has been effective using green solvents (such as carbon dioxide and water) and green extraction techniques. The following section will highlight the key areas in the green extraction of natural products from food waste.

Supercritical fluid extraction.

In the past few years, there has been a growing interest in the recovery of bioactive compounds from natural sources for the development of nutraceuticals, functional foods and cosmetics.[167, 168] Supercritical carbon dioxide ($scCO_2$) has been thoroughly investigated due to its numerous advantages over traditional organic solvent extraction: it is renewable, non-toxic and easily recyclable.[169, 170] Furthermore, it is a highly tuneable extraction solvent; slight adjustments to the applied temperature and pressure result in a significant change in solvent density, which in turn causes a variation in the density-dependent solvent properties including partition coefficient, solubility parameters and dielectric constant, making $scCO_2$ a highly selective solvent.[169] The addition of small amounts of a polar modifier (such as ethanol) can lead to a marked improvement in extraction yields due to an increase in solvent polarity.[171] It is possible to carry out supercritical fractionation using fractional separators reducing downstream processing of the extracts. Furthermore, no solvent residues remain in the extracts making them suitable for a number of applications including food, pharmaceutical and personal care applications.[172]

In terms of food waste, literature describes the use of supercritical fluid extraction to extract high-value waxes, essential oils, high-molecular weight sesquiterpenes that are not soluble in water, as well as other molecules.[170] In particular, supercritical extraction of epicuticular waxes from wheat straw, flax straw, corn stover and sugarcane agricultural residues have been investigated.[172-182] These studies looked into the optimised extraction and characterisation of hydrophobic components constituting the waxes. Typical groups of hydrophobic compounds found in the $scCO_2$ extracts from these biomass residues include long-chain hydrocarbons, saturated and unsaturated fatty acids, *n*-policosanols, fatty aldehydes, wax esters, sterols, steroid ketones and triterpenoids.[173-182] These molecules can be utilised in a wide array of applications including cosmetics, cleaning products, flavour and fragrance, insecticides, degreasers, lubricants, nutraceuticals and pharmaceuticals.[183-193] $ScCO_2$ wax fractions from corn stover were found to be effective as anti-foaming agents in detergent formulations, which could be a potential replacement for the current non-renewable anti-foams which are widely known to have a number of negative impacts such as eutrophication (phos-

phates), carcinogenic products, and persistent in the environment (silicates).[177, 194] Recent work has demonstrated the economic viability of $scCO_2$ extraction of corn stover wax, with the lowest cost of production found to be €4.56 per kg of wax.[178] Data obtained from global wax reports in 2015 indicate that the price of the non-petroleum waxes beeswax, carnauba wax and candelilla wax, in the US, were found to be €7.66/kg of wax, €7.15/kg of wax and €2.68/kg of wax respectively; while the average price of all non-petroleum waxes imported in the US was found to be €5.75/kg of wax. Therefore the supercritically extracted waxes from maize stover fall within this range. Obviously, the price of the wax would vary greatly depending on the purity of the wax product as well as the application. Supercritically extracted waxes would be higher-quality grade waxes as $scCO_2$ is more selective than conventional organic solvents, which extract considerable quantities of unwanted co-extractives such as pigments. The price of the supercritically extracted waxes could therefore be higher.[195]

Previous work has also looked into extracting β-carotene and lycopene as well as other carotenoids from tomato-processing waste using $scCO_2$ with or without the presence of co-solvent.[196-205] β-carotene and lycopene have numerous health benefits, the latter having antioxidant and anti-cancer properties.[196, 198] Winemaking is also a source of different wastes that can potentially be valorised. $ScCO_2$ (with and without a modifier) extractions of by-products from the wine industry have also been investigated, whereby catechin and other phenolic compounds were successfully isolated from grape seeds with higher yields when compared to traditional solid-liquid extraction.[167, 206] Studies on the supercritical extraction from olive-oil by-products (extraction of tocopherols from olive pomace) and soybean-oil by-products (extraction of antioxidants) were also conducted.[167, 207, 208]. Extraction of essential oils (such as *d*-limonene) from orange peel using $scCO_2$ has also been investigated.[209-211] It is possible to isolate and obtain essential oils of high purity by supercritical fractionation.[212] During extraction from biomass, essential oils and epicuticular waxes are normally co-extracted resulting in two added-value products mixed together. At very low temperatures (ca -5 °C to 5 °C), waxes are completely insoluble in carbon dioxide and crash out while essential oils remain soluble which allows for fractionation of the two products.[212] This cannot be done for conventional organic solvent extraction and further energy-intensive purification steps are required.

Since CO_2 is nonpolar and lipophilic in nature, it is unable to extract compounds with high molecular weight such as anthocyanins, large polyphenols (MW≈600g/mol) with important recognised functional and bioactive properties. For this reason, the use of suitable co-solvents (modifiers) has been proposed to enhance the solubility of these target compounds and/or to increase the extraction selectivity. Another strategy to overcome this problem is the application of enhanced solvent extraction (ESE). This technique involves the use of CO_2, water and/or organic solvents at elevated temperatures (40–200 °C) and pressures (3.3–20.5 MPa) and has been applied with success to the extraction of polar solutes including anthocyanins from elderberry pomace.[213, 214] Subcritical fluid extraction, using ethanol as a co-solvent, was already used for extraction of phenolic compounds from sour cherry pomace.[215] Adil *et al.* used combinations of pressure, temperature, ethanol concentration and extraction time as variables in order to find the optimal conditions for the recovery of total phenolic compounds and antioxidants.[215]

The combination of $scCO_2$ and ESE with mixtures of CO_2 and ethanol and/or water has also been applied to the separation and fractionation of specific bioactive compounds: terpenes, carotenoids, sterols, polyphenols and betalains with potential application as bioactive agents. Serra and co-workers studied a fractioned high pressure process to recover a powerful anticancer agent from the surpluses of a traditional Portuguese cherry.[216] The combined process comprises a first step with $scCO_2$ followed by a second ESE step where different mixtures of CO_2 and EtOH were tested (10–100%, *v/v*). The authors concluded that the extract obtained with CO_2:EtOH (90:10,*v/v*) exhibited the most powerful biological activity, with perillyl alcohol and the polyphenols sakuranetin and sakuranin being the major compounds present in the extract.[216] For the terpene perillyl alcohol, the sole application of $scCO_2$ was shown to be an effective extraction process, namely with orange and citrus peel.[217, 218]

$ScCO_2$ has also been applied for the isolation of glucosinolates and isothiocyanates from several cruciferous vegetables (members of *Brassicaceae family*), such as cabbage, rocket salad and broccoli leafs.[219-224] In fact, over the past few decades, several epidemiological studies have established a strong positive correlation between a diet rich in these vegetables and a reduced risk of chronic diseases such as diabetes, cardiovascular diseases and cancer.[225-227] In particular, the claimed role of cruciferous vegetables on cancer chemoprevention is consistently associated to glucosinolates hydrolysis products (isothiocyanates). Examples of isothiocyanates include, benzyl isothiocyanate, phenethyl isothiocyanate, sulforaphane or allyl isothiocyanate, which have been widely studied in a large number of in vivo and in vitro models. More recently, $scCO_2$ has also been studied for the extraction of phenethyl isothiocyanate (PEITC) from watercress market surpluses and wastes.[228] The results showed that PEITC was the major isothiocyanate compound present in watercress extracts with high selectivity.

Another high pressure CO_2-assisted process (HPCD) applied for the extraction and separation of bioactive compounds is the process described by Nunes et al 2015.[229] In this case, the authors applied a two-step process for the extraction of betalains from *Opuntia spp.* fruits with the aim of producing a natural red colorant. Betalains are water-soluble vacuolar nitrogen-containing pigments with high added value due to their double function as a colorant and an antioxidant. The first step of the integrated process consist of a High Pressure Carbon Dioxide (HPCD) pre-treatment of dried prickly pears at 375 bar, 55 °C for 60 min followed by HPCD assisted-water extraction. For the optimised conditions the authors found that the betalain extraction yield was increased 2-fold when compared to conventional water extraction.

$ScCO_2$ extraction of animal food waste has also been investigated such as in the extraction of carotenoids (astaxanthin) and lipids from crustacean waste (shrimp and crab waste).[230-236] Rodriguez *et al.* looked into the supercritical extraction of fish oil from fish by-products which is of high-value to the food and pharmaceutical industries due to the high levels of omega-3 polyunsaturated fatty acids.[237] They found that supercritical fluid extraction is advantageous over conventional solvent extraction as it prevents lipid oxidation and decreases the amount of pollutants extracted.[237]

When looking at supercritical extraction from biomass, it is important to not only focus on the extracts, but also investigate the effects that $scCO_2$ have on the biomass. One of the key drivers for investigating supercritical extraction of food waste is the potential to incorporate it as part of a holistic biorefinery. Recent studies have demonstrated the $scCO_2$ extraction of lipophilic molecules from corn stover and wheat straw as part of a holistic biorefinery.[172, 177] In the former case, it was found that supercritical extraction of corn stover not only leads to the extraction of added-value products but it also enhances the downstream processing of the biomass leading to increased sugar release following hydrolysis when compared to non-$scCO_2$ extracted corn stover. A 40% increase in ethanol production, following fermentation of the sugars, was observed for the $scCO_2$ corn stover.[177]

Subcritical water extraction

CO_2 is non-polar and is therefore ideal for lipophilic molecules. For molecules that are more polar, water is seen as an attractive solvent, in particular subcritical water extraction. In the last decades, subcritical water extraction has attracted a lot of attention due to its safe and environmentally-friendly character, competitive solvating properties, excellent selectivity and economic viability. The term subcritical water refers to liquid water at temperatures between the atmospheric boiling point and the critical temperature (374° C) and at pressures sufficient to maintain it in a liquid state. Similar to $scCO_2$ extraction, this extraction technique offers high selectivity, fine-tuning of solvent polarity and targets specific classes of compounds.[238] The polarity of water drops substantially with an increase in temperature, thus heating water to its critical temperature causes its dielectric constant to drop to 13, offering a wide polarity range (~13-80). In contrast, $scCO_2$ is non-polar offering manipulation possibilities within the range of 1-2 of dielectric constant. In waste management, a particularly attractive application is when subcritical water is used as a reactive medium. Water in its subcritical and critical state substantially potentiates hydrolysis, oxidation, and, in general, decomposition reactions. These reactions can be exploited for the valorisation of agricultural and food industry waste. Consequently, enormous quantities of food and agricultural waste that are generated worldwide have the potential to be used for isolation of sugars, amino acids, organic acids, oils, etc. by using this emerging green technology.

However, it is important to consider the high reactivity of subcritical water, especially when the final goal of the process is to extract valuable compounds, avoiding their degradation. In some cases mild hydrolysis may be desirable for liberating target compounds from their bound forms.

In food waste management, the most reported applications of subcritical water extraction are related to phenolic compounds and different plant wastes, e.g. apple by-products, potato and mango peel, bitter melon (*Momordica charantia*), etc.[239-243] Some authors have focused on the optimisation of extraction parameters for the efficient isolation of particular phenolic compounds from plant sources. Cvetanovic *et al.* investigated the influence of the most important extraction parameter for the highest yield of apigenin, whereas Xu *et al.* focused on baicalin.[244, 245] Antraquinone damnacanthal, pharmaceutically attractive due to its anticancer properties, was isolated by subcritical water extraction from the roots of great morinda (*Morinda citrifolia*).[246] Other antraquinones were extracted by the same technique from the roots of black mulberry.[247]

Water polarity drops with an increase in temperature, thus subcritical water can also be competitive in the recovery of fragrance and flavour compounds from plant sources, such as savoury and peppermint, coriander, rosemary and clove.[248-251] When comparing with other techniques commonly used for the recovery of aroma constituents, such as hydrodistillation and $scCO_2$ extraction, it was found that subcritical water extraction demonstrated better yields, especially for polar flavour compounds.

Limited work has been conducted on other applications of subcritical water for the isolation of added-value compounds from food waste. However, Goto *et al.* proposed a hybrid technology for citrus peel, in which a packed bed of peel was first extracted by $scCO_2$ to recover essential oils, followed by subcritical water in a gradient mode to extract pectins of different molecular weight.[252] In the study of Shalmashi *et al.*, subcritical water extraction was used to recover caffeine from tea waste.[253] The highest yields were obtained at 175 °C while pressure showed no significant influence.

Taking into consideration competitive features of subcritical water extraction and advantages that this technique offers the number of applications in food waste valorisation is expected to increase in the near future.

Pressurised Liquid Extraction

Pressurised Liquid Extraction (PLE) involves the use of a variety of solvents and solvent mixtures. From a Green Chemistry point of view however, the use of ethanol, aqueous ethanol as well as other emerging solvents such as ethyl lactate and *d*-limonene is preferred.[254] In general, the selection of the solvent for extraction is performed in agreement with the polarity of the target components. In this regard, the use of green-PLE is halfway between $scCO_2$ and subcritical water. This technique has been widely employed for the recovery of bioactive compounds from different natural matrices.[255, 256] Since PLE utilises pressurised solvents maintained at high temperatures in their liquid state under an oxygen-free environment, the recovery of labile bioactive components is also possible. In general, PLE processes provide significant enhancements compared to traditional solvent-based extraction procedures; including faster extractions, higher extraction yields and recoveries, as well as

lower volumes of solvents utilised.[254, 257] The application of high temperature results in an increase in mass transfer rates, which corresponds to an enhancement in the solubility of the analytes in the solvent as well as a decrease in solvent viscosity.

This extraction procedure has been also exploited for the recovery of bioactives from different food wastes and food-related by-products; including sterols, phenolic compounds, carotenoids and aromatic aglycones.[254] Vegetal materials have been mostly studied. Different approaches have been explored for the recovery of bioactives from olive oil industry-related by-products. Several important phenolic bioactive compounds such as oleuropein were recovered using aqueous ethanol or ethanol alone at high temperatures from olive leaves.[258, 259] The same approach was also studied for the extraction of similar compounds from olive oil filter cake.[260] Olive oil phenolic compounds have been pointed out as possible anti-proliferative compounds as well as antioxidants, among other interesting bioactivities.

Pressurised liquid extraction has also been investigated with by-products from the wine industry. High proportions of ethanol in water at temperatures reaching 120 °C were reported as suitable for the recovery of anthocyanins from red grape pomace, consisting of skin, stems and seeds of grapes after processing.[261] Similar solvent compositions and temperatures have also been recently employed to recover glycosidic aroma precursors from the same by-product.[262]

Other food wastes studied include potato peels for the extraction of phenolic compounds, *Agaricus bisphorus* residues to recover sterols and carrot by-products to obtain carotenoids, among others.[263, 264] Both extraction time and temperature had a significant effect on the ethanolic PLE of carotenoids from carrot by-products.[265] After 20 min of extraction, more than 80% of total carotenoids were recovered at 60 °C using two extraction cycles. Moreover, the use of a dispersing agent was pointed out as very important to increase extraction efficiency. Interestingly, other studies showed that much higher temperatures were the most-appropriate to extract carotenoids using mainly ethanol, like lutein from green tea wastes.[266] These data suggest the need to closely study the full range of temperatures available for each particular application in order to always maintain good extraction efficiency.

New bio-derived solvents, including *d*-limonene and ethyl lactate, widely considered as Generally Recognised as Safe (GRAS)[267] have only been scarcely explored. Ethyl lactate is an agrochemical and economically viable alternative to traditional liquid solvents, which is produced by fermentation of carbohydrates. It is fully biodegradable, non-corrosive, non-carcinogenic and non-ozone depleting. Undoubtedly, the employment of this kind of solvent is of significant interest from a Green Chemistry perspective. This solvent has already been demonstrated to be efficient for the extraction of caffeine from coffee and tea as well as for the recovery of phenolic compounds from *Cystisus scoparius*.[268] On the other hand, *d*-limonene has been observed as the most favourable solvent for the recovery of thymol, a bioactive monoterpene, from *Thymus vulgaris* compared to other solvents such as pressurised ethanol or ethyl lactate.[269]

The use of novel green solvents may expand the range of applications explored up to now although the possible use of deep eutectic solvents (DESs) could also be exploited. DESs are formed by mixing two naturally-occurring components, namely associated hydrogen-bond acceptor and a hydrogen-bond donor, usually having a much lower melting point that their individual components. DESs have been reported to be environment-friendly, economically-viable, promising alternatives to traditional volatile solvents, since they are easily prepared from natural compounds, and thus, their potential for use in PLE processes is worth exploring.[270]

Integrated biochemical and low temperature chemical processes, applied on the recalcitrant lignin-like fraction in bio-wastes.

Current biomass treatment technology,[271, 272] mainly focused on the production of biofuel by fermentation, such as biogas and bioethanol, adopts a variety of pre-treatment methods to remove lignin from the fermentable fraction and/or processes the residual lignin fraction by combustion, pyrolysis, hydrocracking, or aerobic fermentation. These processes, respectively, convert the chemical energy to thermal and electric energy, produce hydrocarbons and other platform chemicals, and compost which is used for landscaping and/or soil fertilisation.[273] Yet, the bio-waste lignin fraction has further potential[274] which can be exploited by low energy consumption chemical technology. The valorisation of lignin in this fashion would contribute important economic and environmental improvements to current waste treatment practices. This section shows how coupling known biochemical and new chemical processes leads to the generation of added value products from the recalcitrant lignin fraction of bio-wastes.

Bio-wastes Biochemical Processes.

Major biochemical processes applied to bio-wastes are anaerobic digestion and composting. There are important environmental and economic aspects related to the technological features of these processes.

Environmental Aspects. Composting and anaerobic digestion may be classified as recycling when compost (or digestate) is used on land or for the production of growing media. If no such use is envisaged it should be classified as pre-treatment before landfilling or incineration. In addition, anaerobic digestion (producing biogas for energy purposes) should be seen as energy recovery. Composting is the most common biological treatment option (some 95% of current biological treatment operations). Anaerobic digestion is especially suitable for treating wet bio-waste, including fat (e.g. kitchen waste). It produces a gas mixture, mainly methane (50 to 75%) and carbon dioxide in controlled reactors. As long as leakage to the atmosphere is avoided, using biogas as a biofuel for transport or directly injecting into the gas distribution grid can reduce greenhouse gas (GHG) emissions most significantly, then compared

to other transport fuels. The residue from the process, the digestate, can be composted and used for similar applications as compost, thus improving overall resource recovery from waste. The use of compost and digestate as soil improvers and fertilisers offers agronomic benefits such as improvement of soil structure, moisture infiltration, water-holding capacity, soil microorganisms and supply with nutrients. The environmental impact of composting is mainly limited to some greenhouse gas emissions and volatile organic compounds. The use of digestate has an additional limitation connected to the amount of ammonia produced during anaerobic digestion as a consequence of organic N mineralisation.

Economic Aspects. The currently practiced technologies to treat bio-wastes are burdened by process costs which are not compensated by the value of the obtained products. In Europe, 3,500 composting and 2,500 anaerobic digestion facilities operate. The potential of compost production from most valuable inputs (bio-waste and green waste) is estimated at 35 to 40 Mt.[275] Compost marketability is rather poor. The product is proposed for use in agriculture, in land restoration or landfill cover. Usually, compost for agriculture is sold at a symbolic 1 €/ton price. However, well-marketed compost of recognised quality may reach 14 €/ton.

The ultimate trend to optimise the economy and reduce the environmental impact of MBW treatment is to build plants integrating the above processes. A typical example is the plant operated by ACEA Pinerolese Industriale in North West Italy (schematics in Figure 2).[276] A review on the number and types of plants worldwide, which perform anaerobic digestion, alone or coupled to composting, is given in literature.[277] The ACEA plant processes MBW collected from an area of 2,200 km^2 populated by 800,000 inhabitants distributed over 100 municipalities and amounts to about 50,000 tons $year^{-1}$. The plant contains four sections, two for the treatment of solid wastes by anaerobic (AN) and aerobic (AE) digestion respectively, the third for treating Urban sewage wastewaters (WWT) and the last being a landfill area equipped for biogas collection (LBG). The four plant sections are interconnected to maximise biogas and compost yields from MBW, thus minimising bio-refuse disposal to landfill. In essence, the municipal solid waste organic (humid) fraction waste entering the AN process is fermented to yield biogas and a solid digestate (D) containing residual organic matter not converted to biogas. The D material is mixed with green home gardening and park trimmings wastes (GW) and/or with sewage sludge (SS) coming from the WWT process. The bio-residues mix is fermented under aerobic conditions to yield compost. The total plant biogas production is more than enough for covering the plant energy consumption. Exceeding electrical and thermal energy produced by biogas is sold to the electrical network and to nearby residential and commercial districts. In spite of these desirable features, the process economy of the plant, as well as that of all other waste management plants spread around the world, is not profitable due to operational costs exceeding the market value of the energy and/or materials produced.

Possible Bio-waste Chemical Processes and Added Value Chemical Products

Low temperature chemical processes are options which can be used alone or combined with biochemical and/or thermal processes. Chemical processes require green solvents. No solvent is greener and more available than water. Recent work[278] has shown that low temperature hydrolysis allows obtaining useful lignin-like soluble polymeric products from biomass. Contrary to biochemical and thermo-chemical processes, low temperature hydrolysis does not disrupt the natural molecular structures, but converts them in soluble fragments saving the original carbon types and functional groups as much as possible. The process requires low energy consumption and/or amount of equipment needed. It does not require secondary waste treatment. Several soluble bio-based polymeric substances with molecular weight ranging from fourteen to several hundred kDa have been obtained by acid and/or alkaline hydrolysis at 60-100 °C from different urban and agriculture biowastes, as collected and after anaerobic and/or aerobic biodegradation.[278, 279] It has been reported that the acid hydrolysates[279] have at least one order of magnitude lower molecular weight than the alkaline hydrolysates.[278] All products contained aliphatic and aromatic C types, and several acid and basic functional groups.

The acid hydrolysates contained mainly soluble saccharide polymers (SSP). The alkaline hydrolysates contained mainly soluble lignin-like polymers (SLP). Composted MBW contain more lignin-like matter than the original collected wastes. This is the likely reflection of microbial biodegradation, whereby the pristine polysaccharide matter is converted to carbon dioxide and water, while the lignin remains non-metabolised.

The performance of the above SSP and SLP has been studied in diversified fields of the chemical industry, agriculture and animal husbandry. The SLP have been proven to perform as valuable biosurfactants. They are black products, due to the presence of lignin-like chromophore moieties. Their black colour spoils their performance in detergency and dyeing.

Room temperature oxidation of SLP has not been investigated so far. According to literature[280, 281] ozonisation of native lignin destroys double bonds and aromatic rings, leaving the side chains intact in the form of carboxylic acids.

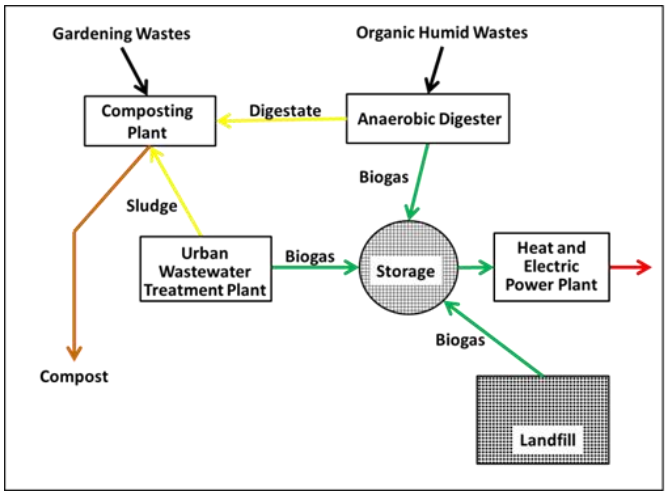

Figure 2. Schematic of a Municipal Bio Waste (MBW) treatment plant. Feed: Gardening, organic humid and water wastes. Products: Compost, biogas, heat and electricity. Process: Anaerobic and aerobic fermentation

In this fashion, the reaction in Figure 3 can ultimately lead to the formation of 4 C atoms dicarboxylic moieties, -(HOOC)CH-CH(COOH)-. Application of this reaction to SLP is likely to convert the pristine aromatic ring to aliphatic carboxylic moieties. Thus, new decolourised biosurfactants might be obtained. Higher oxidation products might be aliphatic polycarboxylic macromolecules, potentially valuable for the manufacture of biodegradable polymers and/or added value platform molecules to recycle to the chemical industry.

Products performance in agriculture. At the current state of technology, the most feasible and rewarding applications of the above SSP and SLP seem to be in agriculture and anaerobic digestion. Added to cultivation soil, the SLP have been found to significantly increase growth and productivity of several plants, i.e. tomato and red pepper,[282] corn,[283] beans,[284] radish,[285] and ornamental plants.[286] They have also been proven to be efficient plant disease suppressants. Both SSP and SLP have been tested for manufacturing blended films with synthetic polyethylene copolymers. The blends exhibit higher mechanical strength than the neat synthetic polymer.[279, 287, 288]

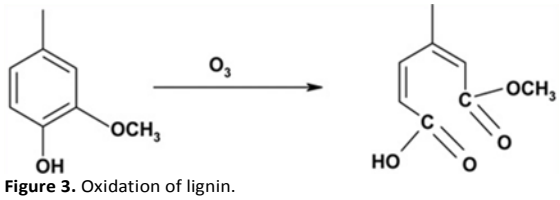

Figure 3. Oxidation of lignin.

These findings prospect a double use for SSP and/or SLP in agriculture, i.e. in form of mulch film and/or as plant growth biostimulants.

Products performance in MBW anaerobic digestion. The improvement of current municipal bio-wastes anaerobic fermentation processes is pending upon the achievement of two main objectives, i.e. enhancing the biogas CH_4/CO_2 ratio and reducing the mineralisation of organic N.[289] The latter has relevance for the environmental impact of the process digestate reuse or disposal. In both cases, ammonia has an important role. Ammonia inhibits methanogenic bacteria which are especially sensitive to this compound. Ammonia is collected with the digestate which is normally recycled as fertiliser to farmland. Ammonia emission and/or nitrate leaching can occur due to inappropriate handling, storage and application of the digestate as fertiliser. Addition of 0.05-2 % SLP to MBW anaerobic fermentation slurries has been found to decrease the ammonia content of the fermentation digestate by favouring the oxidation of ammonia to N_2.[290, 291] These findings suggest a virtuous bio-waste cycle according to the following scenario: the bio-wastes entering a conventional waste management plant (Figure 2) will produce a digestate which is composted. The compost is then hydrolysed to SLP and the product recycled to the anaerobic digestion reactor to yield an eco-friendly digestate with reduced ammonia content. This scenario offers a feasible opportunity to reduce the investment risk by starting with the production of soluble bio-based organic substances (SBO) for in-house use. Construction and operation of the SBO production facility (finalised to producing digestate with lower ammonia content than the feed slurry has), would also allow for the production of excess SBO at very limited risk. The SBO could find use in diversified field[276] of the chemical industry, plastic manufacture[279, 287, 288] and agriculture.[282-285, 292] Estimates on operating costs and how feasible is the implementation of the proposed processes and products at commercial production and use level are reported for the hydrolysis of municipal biowaste compost carried out by conventional and microwave heating,[278] and for some case study applications of the SLP as active principles for agriculture,[286] auxiliaries for ecofriendly biowaste anaerobic fermentation,[290, 291] and components for the manufacture of bio-based blend plastic articles.[279, 287, 288] All these estimates confirm that the conversion of the composted municipal biowaste organic matter to SLP can yield revenue from SLP sales in the chemical and agriculture market, which are several order of magnitudes higher than the revenue obtained by the sale of the pristine compost. Moreover, this revenue may largely compensate process costs, potentially release the tax pressure on citizens and generate new business opportunities and jobs.

Ionic liquids in the pre-treatment and extraction of food residues

Ionic liquids (ILs) are salts solely composed of ions with melting points below 100°C. The most common properties of ILs are high thermal stability,[293] negligible volatility, non-flammability[294] and tuneable properties such as hydrophobicity, polarity, acidity and basicity, which mainly governs the solubility power of ILs.[295, 296]

The application of ILs in waste and residue processing allows surpassing the recalcitrance of these materials altering their morphological structure. Hence these materials will under IL treatment be more susceptible to other processes, such as extraction, fractionation and/or conversion to a great variety of products.[297] An example is lignocellulosic biomass processing with ILs that allows efficient fractionation into main compo-

nents, such cellulose, hemicellulose, lignin and phenolic compounds.[298-304] Besides the ability of ILs to dissolve and to pretreat, the solvent power and high selectivity of ILs also allows for the extraction of specific targeted biomolecules from biomass as demonstrated in literature.[305] In fact, the heterogeneity of food waste generally leads to the disadvantage of adopting multi-step fractionation strategies to obtain target compounds.[306] This limitation can be overcome by using tailored ILs to reach high-selectivity extraction.

In this review the main achievements in the processing of food waste, namely crustacean shells,[307-309] citrus and potato peels,[310-312] poultry feathers[313, 314] and peanut hulls are discussed.[315, 316] In these works, ILs are used as either pretreatment or as an extraction agent to obtain value-added biomolecules in a more sustainable manner.

Crustacean shells are a source of considerable amounts of chitin, which is a long chain polysaccharide that can be used to produce various bio-polymers. The dissolution of chitin in ILs was successfully achieved and the mechanism was considered to be similar to dissolution of cellulose in IL media.[317, 318] Among several examined ILs, [emim][OAc] (1-ethyl-3-methylimidazolium acetate) demonstrated to be the most efficient to dissolve and to extract chitin from shrimp shells.[308] High basicity of acetate governs the dissolution of long-chain chitin in IL and 94% chitin was dissolved in [emim][OAc].[308] Further recovery of chitin from IL was achieved after adding water as an anti-solvent helping to precipitate the biopolymer.[308] One of the limitations in this process are minerals which can also be dissolved in IL compromising the purity of regenerated chitin.[309] This problem was solved by the addition of a citric acid solution during the chitin extraction from crab shells with [amim][Br] (1-allyl-3-methyl-imidazolium bromide). The chitin precipitation and simultaneous removal of $CaCO_3$, the main mineral constituent of crab shells, was achieved with success.[309] Besides the interest in chitin, other biomolecules with high commercial value can be extracted from crustacean waste. For instance, astaxanthin was selectively extracted from shrimp waste with different ILs/methanol solutions.[307] In this case, the efficiency of IL to extract astaxanthin was correlated to two distinguished properties: **i)** a high miscibility of IL with methanol, which allowed better penetration of IL into the shrimp biomass and **ii)** a moderate hydrophobicity of IL (tuned by the alkyl chain length of IL cation) to better interact with astaxanthin. Among examined IL, the 1-butyl-3-methylimidazolium based, e.g. [bmim][Br] (1-butyl-3-methylimidazolium bromide), were most efficient for astaxanthin extraction. The employment of a "task-specific" IL, namely [C_3NH_2mim][Br] (1-propylamine-3-methylimidazolium bromide), in the extraction of astaxanthin was also examined. This IL enhanced the extraction yield of this terpenoid, since this IL maintained the properties of [bmim][Br] as well as protected astaxanthin from oxidation, due to the amine group attached to the IL cation.[307]

The variety of compounds presents in fruit peels demands high selectivity of the processing and extraction of biomolecules from these wastes. Orange peel is a source of essential oils, among which, one of the principal component is limonene and ILs were employed with the objective to extract this terpene.[311] The adopted strategy implied total dissolution of orange peels in ILs exposing essential oils to be further recovered by distillation. Similarly to lignocellulosic biomass, orange peels were totally dissolved in [emim][OAc] in just 3 hours. Subsequently, the resulting mixture was distilled and a two-phase distillate consisting of essential oils and water was obtained allowing easy separation of the essential oils through decantation. A maximum extraction yield of limonene of 0.74 g/100 g biomass was achieved with [emim][OAc]. Lower yields were obtained with other examined ILs that only partially dissolved the orange peel. It means that complete dissolution guarantees the release of essential oils from the peel matrix.[311] In fact, the ability of ILs to dissolve fruit peels principally lies in the formation of a strong hydrogen bond network. A similar observation was proposed for the dissolution and extraction of pectin from lemon peels with ILs.[310] Several ILs were examined and a maximum 19.91 % yield of the initial mass of pectin was attained with [bmim][Cl] (1-butyl-3-methylimidazolium chloride), where intermolecular strong hydrogen bonds between [Cl] anion and hydroxyl groups of the polysaccharide were established.[310, 318] Another type of valorisation based on direct conversion of potato peel polysaccharides into reducing sugars using ILs was approached.[312] Brønsted acid such as [sbmim][Cl] (1-(4-sulfobutyl)-3-methylimidazolium chloride) IL with 20 wt.% water solution was applied as a solvent and catalyst. It results in a 43% reducing sugar yield from wet potato peel sludge (67% water content). In this process, water was needed to dissociate the sulphonic acid functional group of IL, which in turn hydrolysed the starch from the potato peels.[312]

Poultry feathers are another food waste that presents potential as a raw material for valorisation with ILs. The literature studies demonstrated the application of ILs to treat chicken and duck feathers and to extract keratin,[313, 314] a protein, which has properties similar to antioxidants or pectin and has the potential to be applied in the formulation of novel polymers.[319, 320] A first strategy is based on the use of a hydrophobic IL, such as [OHemim][NTf_2] (1-hydroxyethyl-3-methylimidazolium bis(tri-fluoromethanesulfonyl)imide), to dissolve non-polar feathers.[314] Due to the strong disulphide bond structure of keratin, the efficiency of IL extraction was relatively low, thus an alkaline reducing agent ($NaHSO_3$) was added to the mixture to break those covalent bonds. An enhanced extraction of keratin was achieved, mainly when higher amount of $NaHSO_3$ was added to the solution. The second strategy for keratin extraction from duck feathers with several ILs was presented elsewhere.[313] The [amim][Cl] and [bmim][Cl] demonstrated to dissolve feathers and to extract keratin in only 1 h (Figure 4). Water was then added to the resulting mixture acting as anti-solvent to precipitate keratin. In fact, high concentrations of water interferes with IL/keratin interactions allowing for the precipitation of keratin, similarly to cellulose regeneration from IL.[313]

Other works used peanut hulls as raw material for the extraction of phenolic compounds with ILs.[315, 316] the ability of [bmim][Br] to extract flavonoids from peanut hulls assisted by ultrasonic irradiation was studied and optimised.[316] The total flavonoid yield rose with an increase of IL concentration up to

a certain point, at which high IL viscosity started to compromise the diffusion of IL in the peanut hull matrix.[316] Another work focused on the selective extraction of luteolin from peanut hulls using imidazolium-based ILs.[315] Preliminary studies of luteolin dissolution in ILs showed that the hydrophilic ILs have better ability to dissolve luteolin and the dissolution is anion dependent. In fact, the most efficient examined IL, [bmim][NO_3] (1-butyl-3-methylimidazolium nitrate), demonstrated higher ability for luteolin dissolution than common organic solvents, such as alcohols, acetone and hexane. Once more the viscosity of IL limited the extraction yield of the polyphenol. Therefore, water was added to the IL improving the mass transfer in [bmim][NO_3]-mediated extraction. A maximum 79.8% luteolin yield was attained at optimal conditions determined.[315]

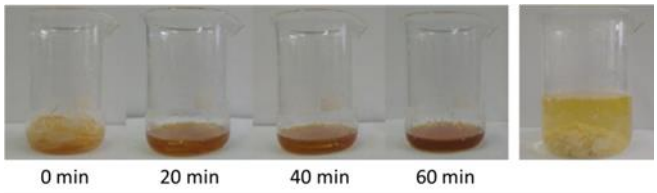

Figure 4. Dissolution of feathers in IL over time and subsequent regeneration (precipitation) of keratin after the addition of water to the IL solution. Adapted with permission from.[313]

In conclusion, the tailored properties of ILs allow for designing "task-specific" ILs to process particular food waste and to selectively extract desired biomolecules. A more profound study about the extraction must be still carried out to increase the value from food waste. Moreover, the recovery of targeted biomolecules and products from IL and subsequent IL recovery is highly desired to make the process with ILs more economically and environmentally sustainable.

Microwave assisted pre-treatment and extraction

In recent years, much attention has been given to the use of microwave energy instead of conventional heating for the extraction of natural products such as essential oils, pectin, pigments, phenolics, and other organic compounds.[321] The main benefits of this technology include decrease in extraction time, solvent usage and consumed energy, high heating rates, higher extraction yield, higher selectivity and better quality of the target products.[322] By considering these advantages, microwave heating can be a good way to recover and synthesise valuable products from a wide range of biomass types. Table 3 summarises the waste source, target product and microwave assisted extraction conditions.

Microwave technique for assisted pre-treatment and extraction

Usually, microwave-assisted extractions (MAE) or pre-treatments are ensured in polar media (typically water, alcohols, acetone or mixtures) with a reaction time comprising between a few seconds and a few minutes. The longer reaction times (typically 30 min) are observed for pre-treatment of lignin-containing materials. MAE experiments are well described in the literature on small scales using laboratory devices (from 1 to 10 mL in batch conditions) but higher scale equipment is more and more encountered (with parallel vessels and global volumes up to 1 L per batch). The temperature range is below 100 °C for MAE of phenolic compounds or valuable carbohydrates, avoiding their thermal degradation but pre-treatment experiments required reaction temperatures of 140-190 °C in closed vessels conditions.

Examples of food waste valorisation

Citrus fruit wastes. Citrus fruit by-products are processing wastes obtained from citrus juice extraction that account for 50 % of whole fresh fruit weight. These by-products are a good source of pectin, phenolic compounds and essential oils.[323] Thus, when compared to the traditional methods, microwave assisted extraction methods for essential oil and phenolic compounds or pectin which preserve the quality of products, reduce the extraction time and therefore the energy consumption. A number of methods have been studied in recent years. Attard *et al.* studied the microwave process at 200 W different times using hexane as the extraction solvent,[324] while Uysal *et al.* focused on the solvent-free microwave extraction (85 W for 20 min) of essential oil from citrus fruits wastes.[325] Higher extraction yields were obtained than when using Soxhlet extraction and conventional hydrodistillation in these studies. According to Bagherian *et al.* the microwave field power and heating time improved the qualitative and quantitative characteristics of extracted pectin from grapefruit peel.[326] Sancheaz-Aldana *et al*. have also studied the conventional and microwave methods to obtain pectic extracts from Mexican lime pomace and bagasse.[327] For the microwave assisted method, bagasse or pomace was placed in a reactor with 60 mL of 1% citric acid solution and the solution was subjected to MAE at 800 W irradiation power for 5 min. They reported that the yield of pectin from pomace was greater than that from bagasse and the extraction method had an impact on the molecular weight and polymerisation of pectin compound. Furthermore a method for the isolation of pectin, *d*-limonene, a flavour compound, a flavonoid, a soluble monosaccharide, a decomposition product of a monosaccharide and cellulose from citrus material using microwave assisted hydrothermal low temperature treatment of citrus material was patented by Clark *et al.*[328] They described a microwave assisted citrus peel biorefinery, which processes the main compounds of citrus fruit wastes all together, without pre-treatment or adding acid and minimising waste. Citrus fruit wastes have also been studied for the microwave assisted extraction of phenolic compounds. Wang *et al*. optimised the extraction process using 80% ethanol as the extraction solvent and they demonstrated that the optimal conditions were 3 min. of extraction time, 25:1 (ml/g) as the liquid to solid ratio and 560 W of microwave power,[329] while Hayat *et al*. focused on the use of methanol/water mixtures.[330] Under these conditions 5.81% of extraction yield is obtained, which was higher than reflux and ultrasonic methods. According to Ahmad and Langrish antioxidant activities of the extracts can also be modulated as a function of microwave conditions.[331]

Olive oil processing wastes. During the olive oil production process, large amount of wastes are generated such as olive cake, leaves and olive mill waste water. These wastes are an important source of added value compounds including polyphenols, fatty acids, pigments, tocopherols, phytosterols, volatile and aromatic compounds, which have the potential to be used as food additives and/or nutraceuticals.[332] Olive cake is the remaining pulpy material after removing most of the oil from the olive paste which contains pieces of skin, pit and pulp. In addition it still contains oil which can exceed 8% and the use of the extraction by solvent allows its valorisation by recovery of the residual oil.[333] Application of microwave assisted extraction has been reported for the extraction of residual oil from olive cake by Amarni and Kadi.[333] The authors optimised the extraction conditions by using hexane as a solvent and compared this method with a conventional solvent extraction (CSE). They reported that, compared to the CSE, MAE gave better yields within very short process times. The results obtained with this method indicated that the microwave power and exposure time enhanced extraction ability. Pérez-Serradilla *et al.* have studied MAE for the simultaneous isolation of polar and nonpolar compounds from alperujo using methanol–water and hexane as solvent system.[334] The authors reported that the proposed method allows the phenolic compounds and fatty acids to be leached in a shorter time and the composition of extracts was statistically similar to those obtained from reference methods. Additionally, MAE was used to extract phenolic compounds from olive leaves. Japón-Luján *et al*. optimised the extraction conditions such as irradiation power, time and extractant composition and compared this method with a conventional extraction method.[335] They observed a reduction in the time required for the extraction to reach completion (from 24 h to 8 min at 40 °C. Extraction of phenolic compounds from olive leaves with MAE was also performed by Rafiee *et al*.[336] and Taamalli *et al*.[337] using various solvents. The authors reported that the amount of extracted phenolic compounds varied significantly with extraction time, solvent and temperature. When compared with conventional methods higher extraction yields and phenolic concentration were obtained with MAE as a result of these studies.

Brewer's spent grains. Brewer's spent grains (BSG) are interesting lignocellulosic materials for microwave-assisted treatment. They are the main side-products from breweries and they represent the barley malt residues obtained after wort manufacture (about 20 kg per 100 L of beer produced). These BSG are a source of polysaccharides and ferulic acid.[338] BSG have thus been studied either for the MW-assisted selective extraction of arabinoxylans and arabino-oligosaccharides under dilute alkali conditions[339] or for the production of reducing sugars by hydrolysis under more drastic reaction conditions.[340]

Apple pomace. Apple pomace is a convenient food side-product for MAE investigations, notably for the extraction of pectin with modulated structures and physico-chemical properties.[341] Nevertheless, the state of the art mentions extensive works on the selective microwave-assisted extraction of polar blends of polyphenols (chlorogenic acid, caffeic acid, syrigin, procyanidin B2, (-)-epicatechin, cinnamic acid, coumaric acid, phlorizin and quercetin). Bai *et al*. optimised the MAE process using ethanol as the extraction solvent,[342] while Rezaei *et al*. focused on the use of ethanol/water mixtures.[343] Under these conditions a 90% polyphenols recovery is recorded, which was higher than conventional maceration or Soxhlet protocols. According to He *et al*., the antioxidant activity of the extract can also be modulated as a function of the MW conditions.[344] More recent works revealed that various apple cultivars can provide polyphenols mixtures with completely different profiles and antioxidant activities after MAE.[345]

Wheat and Triticale straws. Application of microwave on wheat straws was first reported as a method to increase subsequent enzymatic hydrolysis rates in a bioethanol production approach[346] or aiming to improve the solubilisation of straws for subsequent methane generation.[347] Thermochemical conversions, including hydrogen,[348] bio-gas[349] and bio-oils[350] were also extensively studied under microwave assistance. A MW-assisted process is also reported to ensure the selective production of furfural and 5-hydroxymethylfurfural from C-5 and C-6 containing carbohydrates.[351,352] Recent works report the selective solubilisation and extraction of hemicelluloses and lignin using alkali conditions[353] or the delignification of straws using ionic liquids.[354] The maximal microwave extraction yield of lignin (about 90%) was reported by Monteil-Riveira using the ethanosolv (EtOH/H_2SO_4) protocol. Recovered lignin was found to be less contaminated by residual carbohydrates than those recovered under conventional heating.[355]

Winemaking waste streams and residues. The winemaking processes generate huge amounts of wastes and by-products, including grape pomace (solid remains generated after the juice has been pressed out of the grapes and maceration) and wine lees (mostly dead yeast resulting from the different decanting steps of wine after the fermentation of the must). Although variable in composition both by-products still contained high concentrations of interesting functional and bioactive compounds, in particular secondary metabolites of grapes including phenolic acids, flavan-3-ols and anthocyanins.[356] Grape pomace is constituted by stalks, peels and seeds, the former constituting about 15% of this solid waste. In the last decade, apart from the application of MW to intensify the extraction for analytical purposes, MAE has been applied to different winemaking residues as an alternative extraction process of polyphenols.[357] In 2001 Hong and co-workers[358] applied MAE using methanol as a solvent for the extraction of phenolic compounds from grape seeds. Different process parameters were studied in order to optimise the extraction process and they reported that neither the time nor the power had a significant effect on the overall percent mass yield and on the polyphenol content of the extracts (when compared with conventional solid-liquid extraction). Nevertheless they attributed these findings to the low solvent polarity, as an increased yield and polyphenol content was observed during the MW extraction when they changed the polarity of the solution with the addition of water. Later, Li *et al.* also applied MW for the extraction of polyphenols from grape seeds but using hydroethanolic (EtOH:H_2O) mixtures as a solvent.[359] They reported that in comparison with other extraction methods, MAE provided

comparable or better extractions, in a shorter time of operation which is measured only in minutes, as opposed to hours as required by alternative methods. One key finding reported by the authors was that the applied microwave power did not influence the yield and extraction efficiency.

More recently, grape pomace, due to its moisture content, has been more extensively studied as a raw material in MW-assisted extraction. Casazza[360] compared MAE with other non-conventional extraction methods including ultrasound-assisted extraction (UAE) and high pressure and temperature extraction (HPTE) for the recovery of polyphenols (flavonoids and o-diphenols) from the Pinot-Noir grape pomace using methanol as a solvent. The highest flavonoid content was obtained with high pressure and MAE extraction. Peralbo-Molina[361] also compared MAE of polyphenols from grape pomace, with conventional maceration extraction (CME), ultrasound-assisted extraction (UAE), and superheated liquid extraction (SHLE). The solvent used was the same among the aforementioned three extraction techniques; water, ethanol mixtures (50:50%, v/v) and ethanol was acidified with 0.8% (v/v) HCl. In this case, the authors concluded that the two extraction techniques based on the use of auxiliary energy (MAE, UAE) yielded lower efficiencies (in terms of total polyphenols content) than CME and SHLE. The application of MW to Pinot Noir-grape pomace for the extraction of the stilbene *trans*-resveratrol was evaluated by Wang[362] who applied an orthogonal experimental design to determine the best extraction conditions using methanol, ethanol, acetone and ethyl acetate as solvent. The author concluded that the maximum yield was obtained for ethanol and for an 1:20 mass:solvent ratio, 30 min and 55 °C. Brahim *et al.*[363] investigated MAE using water for the extraction of polyphenols, in particular tannins, from red grape and white grape pomace. One of the extraction parameters was the application of Na_2CO_3 (in different concentrations). The authors demonstrated that the optimal conditions for the grape biomasses investigated were 100 °C, 1.25% Na_2CO_3 and 8 min concluding that MAE gave significantly higher yields as compared to traditional extraction, greatly improving the rate of phenolic compounds extraction with strong reduction of the reaction time. Pedroza and co-workers[364] investigated the application of MAE for recovery of total phenolic compounds from dried waste grape skins using a domestic microwave oven and compared this with solid-liquid extraction (SLE) carried out for 2 h at 60 °C. Aqueous ethanol (60% v/v ethanol) was used for all the extractions and an equivalent yield of total phenolics was achieved with SLE and MAE but. In the case of the latter, a total extraction time of 1 sec and an irradiation time of 83 sec at 900 W was observed (compared with an extraction time of 2 h using SLE).

MW-extraction was also applied to wine lees in order to recovery a high polyphenols extract by Perez-Serradilla *et al.*[365] The authors applied a mixture of ethanol 75%, hydrochloric acid 1% in water as solvent and subjected the lees to MAE at 200W irradiation power for 17 min. The selected MAE extraction time was compared with the 24 h conventional method extraction time and was enough to obtain better extraction efficiency (in terms of % dry residue).

MW has also being applied as a pre-treatment (microwave assisted pre-treatment, MAP) before the solid-liquid conventional extraction[366] and the author concluded that a microwave pre-treatment highly improves solid-liquid extraction velocity contributing for the intensification of the target compounds extraction.

Brassicas surpluses. Cruciferous vegetables (members of Brassicaceae family) such as broccoli, cabbage, watercress, rocket salad and cauliflower are recognised as important sources of biologically active ingredients with a broad spectrum of biological actions, such as flavonoids, phenolic acids and glucosinolates (GLs).[367] Brassicas by-products (from industrial and market processing) and market surpluses are rich sources of bioactive compounds, in particular glucosinolates that could be converted in isothiocyanates (ITCs) and phenolic compounds.

Despite MW-processing is reported as not suitable for the extraction of volatile compounds[368], work has been done concerning the recovery of ITCs-rich extracts from brassicas using this non-conventional technique. Tanongkankit *et al.*[369] investigated the application of MAE of sulforaphane from cabbage leaves (dichloromethane and water as solvent extraction) and concluded that MAE increased the content of the extractable bioactive (sulforaphane) at shorter processing time (3 min compared with 30 min for conventional extraction). In another work by Chaisamlitpol and co-workers[370], the authors demonstrated the applicability of the MW-assisted process to extract GLs from fresh cabbage leaves. It was found that MAE (100 W, 5 min) applied to the brassicas -biomass with ethanol as a solvent promotes the production of extracts richer in GLs.

Jokic´ *et al*.[371] also studied the application of a MW-assisted process but in this case for the extraction of polyphenols from broccoli. Mixtures of methanol/water, 50–90%, v/v were applied as a solvent and temperature, power and time were studied as process variables in order to optimise the polyphenols, flavonoids and antioxidant content. The application of MAE was also investigated for the extraction of bioactive compounds from cabbage outer leaves by Pongmalai *et al.*[372] The authors compared the ultra-sound extraction (US) and MAE using 99% of ethanol, concluding that to extract the same amount of sulforaphane, MAE was faster than US.

MW as an option for pre-treatment before other extraction techniques has been applied to watercress market surpluses in order to improve the extraction of isothiocianates.[373] In this case, only few seconds of MW is applied before the application of conventional or high-pressure extraction.

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Table 3. Microwave assisted extraction of bioactive compounds, their sources and processing conditions.

Type of MAE open vessel (OV) Closed vessel (CV)	Type of waste	Solvent use	Conditions			Target product
			Time (min, sec)	Sample size (g)	Power (W) / Temp (°C)	
CV	Orange peel	Hexane	30 min	1	200 / 110	*d*-limonene (11.1% yield)[324]
OV, distillation	Grapefruit peel	Solvent-free	20 min	250	85 / -	Essential oil (0.44% yield)[325]
OV	Grapefruit peel	Water (pH 1.5)	6 min	6	900 / -	Pectin (27.81%)[326]
CV	Lime bagasse or pomace	1% citric acid solution	5 min	2	800 / 120	Pectin (16.9±0.03% for pomace and 8.40±0.02 for bagasse)[327]
OV	Grapefruit peel	80% ethanol	3 min	2	560 / -	Flavonoids (5.81%)[329]
OV	Mandarin peel	66% methanol	49 sec	5	152 / -	Phenolic acids (1162.84 µg/g dry weight)[330]
CV	Mandarin peel	Water	3 min	1	400 / -	Phenolic acids (TPC 23.2 mg GAE/g FW)[331]
OV	Olive cake	Hexane	2 min	50	720 / -	Residual oil (4.95%)[333]
OV	Alperujo	Methanol-water/ Hexane	14 min	2	200 / -	Phenol compounds and fatty acids[334]
OV	Olive leaves	80% ethanol	8 min	1	200 / -	Oleuropein and related biophenols[335]
OV	Olive leaves	Water, 80% ethanol, 50% ethanol, acetone	15 min	ns	900 / -	Phenolic compounds (88.298 mg TAE/ g)[336]
OV	Olive leaves	80% methanol	6 min	ns	1200 /80	Phenolic compounds[337]
CV	Brewer's spent grains (BSG)	H_2O/ NaOH 0.5%	15min	1	- /100	Ferulic acid (1.31 wt.% yield)[338]
CV	BSG	H_2O/KOH (0.1 M)	2 min	ns	140 / 210	Arabinoxylans + arabinoxylo-oligosaccharides (62% yield)[339]
CV	BSG	H_2O/HCl or HAc (0.1 M)	10-60 min	ns	160 / 210	Free reducing monosaccharide (35% yield)[340]
CV	BSG	H_2O/NaOH (0.5 M)	10-60 min	ns	160 / 210	Reducing oligosaccharides (49% yield)[340]
OV, distillation	Apple pomace	HCl pH 1.01 (solid:liqid ratio 0.069)	20.8 min	2	500 / -	Pectin (16wt. % yield)[341]
CV	Apple pomace	Ethanol	53.7 sec	5	- / 70	Polyphenols (yield: 62.68 mg GAE/100 g)[342]
CV	Apple pomace	Ethanol/H_2O (65/35 v/v)	5-20 min	ns	90-180-360 / -	Polyphenols (mixture)[343]
CV	Apple pomace	70% acetone or 60% EtOH	30-180 sec	1	100-900 /-	Polyphenols (mixture)[345]
CV	Wheat straw	H_2O/HCl pH 0.1-1.6 (1:5–1:200 solid:liquid ratio)	1-30 min	ns	140-190 /-	Furanic compounds (2-furfural and 5-hydroxymethylfurfural) (45 to 48% yield)[352]
CV	Wheat straw	81% EtOH; 0.5 N H_2SO_4	30 min	1	-/125	Lignin[355]
CV	Grape seeds (from grape pomace)	Methanol	200 sec	1	30 / -	Total polyphenols conc.[358] Yield 13.5% (392 mg TAE/g of crude extract)
CV	Grape seeds (from grape pomace)	Ethanol (10%-90%)–water mixtures	2-32 min	ns	100-200/ -	Total polyphenols concentration[359] (96.3 mg GAE/g grape seeds)
CV	Pinot Noir dried milled grape marc	Methanol	60 min	ns	60 / 110	Total polyphenols[360] (86.2 mg GAE/g dry weight) Flavonoids (46.8 mg CE/g dry weight)
CV	Red and white Grape skins	50% (v/v) aqueous Ethanol acidified with 0.8% HCl	10 min	2	140 / -	Polyphenols[361] Antioxidant Activity
CV	Pinot Noir-grape pomace	Methanol, ethanol, acetone and ethyl acetate	30 min	10	1000 / 55	Trans-resveratrol (% yield 90.87 with ethanol as solvent)[362]
CV	Red and white grape pomace	Water. Na_2CO_3 solution (1.25-2.5%)	8 min	20	-/100	Total polyphenols concentration [363]
OV	White grape pomace	60% ethanol	Time to boil	37.5	100-900 / -	Total polyphenols conc.[364]
CV	Wine lees (from first fermentation process)	Ethanol 75%, hydrochloric acid 1% in water	17 min	2	200 / -	Total polyphenols conc.[365] %Dry Residue, %Total Polyphenols (53.2mgGAE/100gdM) ORAC value (6250 µmolTE/100gDM)

CV/OV (pre-treatment)	Grape pomace (tempranillo)	Ethanol:H_2O (50:50%), pH 1	30-120 sec	15	300 / -	Total polyphenols concentration [366] (12mg/g dry weight)
OV	Cabbage leaves	Dichloromethane and H_2O	1.5-3 min	5	130, 260, 390 / -	Glucosinolates[368] (sulforaphane)
CV	Cabbage leaves	Ethanol	5 min	ns	100 / -	Glucosinolates[369]
CV	Broccoli	Methanol/H_2O, 50–90%, v/v	1-27 min	0.3	100-200 / -	Total Phenolic Compounds[371], Total flavonoids content, Antioxidant activity
OV	Cabbage outer leaves	99% Ethanol	2 min	ns	100 / -	Bioactive Compounds[372] (sulforaphane 1.72 mg/100 g dry mass), Antioxidant Activity
OV (pre-treatment)	Watercress (surpl.)	Water	7 sec	10	750 / -	Tot. isothiocyanates (ITCs), Phenethyl ITC)[373]

Ultrasound assisted extraction of polysaccharides from food waste

The food industry controls the selection process, cleaning, and preparation of raw plant materials for further processing. This industrial processing gives rise to remnants that could be re-used, since they are a good source of dietary fibres, pectins and phytochemicals.[374]

Due to the demands of final consumers for safe and high quality food products as well as the expectation of manufacturers for sustainable methods of food industrialisation, new techniques based mostly on non-thermal principles are being developed. These technologies include for example: pulsed electric fields (PEF), power ultrasound (PUS), high hydrostatic pressure (HHP), supercritical fluid extraction (SFE) and high voltage electric discharges (HVED).[157, 375-378]

Ultrasound (US) has many benefits for a variety of applications in industry. By definition ultrasound is the sound determined with frequency range from 18 kHz-10 MHz.[379]

In practical applications frequency dependence determines its activity i.e. as lower frequency is applied more rapid changes occur (Figure 5).

The frequency range from 18 kHz-100 kHz is known as power ultrasound (PUS). The range between 100 kHz – 2 MHz is known as transient area while the range between 2 MHz – 10 MHz is characterised as Non-destructive Ultrasound (NDT), which is used as a diagnostic technique. Ultrasound waves are created or generated with piezoelectric or magnetostrictive transducers which transfer low sound frequencies into frequencies within the US range. Vibrations are amplified in the process and transferred to a sonotrode. The sonotrodes are either directly immersed into the liquid (direct sonication) or attached to the bottom of the ultrasonic bath (indirect sonication).[380, 381]

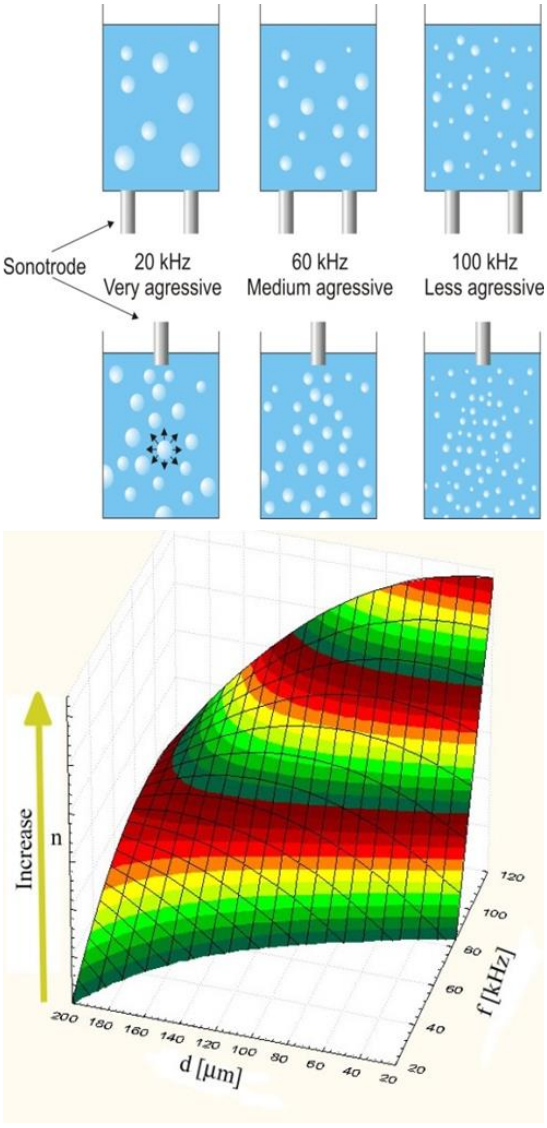

Figure 5. Cavitation dependence on applied frequency.[378.]

Ultrasound-assisted extraction (UAE) is a technology based on the creation of cavitations that lead to tissue disruption. Disruption allows the diffusion of inner cell material without any significant increase in temperature, thus avoiding thermal degradation of the contained valuable compounds.[382]

To increase the yield of the extracted compounds, optimisation of the frequency, propagation, nominal input power, amplitude is required, as well as the selection of the geometry of the system (e.g. length and diameter of the probe). Therefore,

the selection of ultrasound conditions including choice of solvent and plant operating characteristics is of utmost importance.

Hromadkova *et al*.[383] reported the production of xylans from corn cobs using ultrasound (100 W and 10 min) in solutions of NaOH, followed by precipitation with ethanol. It was found that the efficiency of the ultrasound-assisted extraction allowed for similar yields at lower extraction temperature and substantially shorter extraction times when compared to conventional procedures. They also observed that the biological activity of the sonically extracted xylans was a bit higher than that of the classically extracted preparations.

Hromadkova *et al*.[384] obtained pectin, mannan, xylan and glucan from *Valeriana officinalis* L. using water as the solvent and with an ultrasound intensity of 1W/cm^2. They observed that the thermomechanical effect of ultrasounds depends on the type of tissue used and that it seemed to be lower for the roots than for the leaves.

Grassino *et al*.[374, 385] compared the yield of pectin extracted from tomato waste using convectional extraction and ultrasound-assisted extraction. The yield of pectin was high with both approaches, however, duration of extraction with conventional extraction was 24 hours in comparison with UAE which lasted for 15 min only.

Table 4 summarises the main important results of the last five years with respect to pectin extraction from plant tissues. Most of the articles listed in the table report the advantages of ultrasound including the use of less energy, shortening of processing time and significant increase of product yield. The reason for the latter is that plant cells might be completely cracked as a result of acoustic cavitation leading to larger contact area between solvent and material. Furthermore, the collapse of the bubbles promote the interpenetration of the solvent into the plant cells dissolving most of the pectin present increasing the extraction yield. In particular, Bai *et al*.[386] observed that there is an optimum time for ultrasound application in jujube waste with the purpose of increasing the yield; for larger application times, insoluble substances that were produced, could lower the permeability of the solvent decreasing the yield. Wang *et al*.[387] observed that the ultrasounds contributed to the purity of pectin extracted. As can be concluded from the research of Bai *et al*.[386] and Bagherian *et al*.[388] the combination of ultrasounds with microwaves also helped to obtain better yields of pectin probably due to the assistance of ultrasounds resulting in a more efficient heating.

Table 4. Applications of ultrasound (US) for the recovery of pectin from food wastes. US=Ultrasound, MW=Microwave.

Food waste	Operational conditions	Yield (target compound)	Other stress factors for extraction	Benefits of US	Ref.
Jujube waste	Power: not informed. Frequency: not informed. Time: 17.66 min Solvent: distilled water. Liquid-solid ratio: 10.03 mL/g. pH of 1.97.	20 g/kg	MW: Irradiation time of 52.73 sec., power of 560 W.	An increase in yield with ultrasound application.	386
Grape-fruit peel	Power: 12.56 W/ cm^2. Frequency: 20 kHz. Duty cycle of ultrasound pulse: 50% (2 sec. on: 2 sec. off). Temp.: 67 °C. Time: 28 min Solvent: deionised water and pH adjusted to 1.5.	US: 27%. Conventional extraction: 23%.	---	Extraction time (56 min) and temp. (67°C) for ultrasound procedure lower than those for conventional technique (90 min and 80 °C).	387
Grape-fruit	Power: not informed. Frequency: 24 kHz. Peel albedo/water ratio: 1 g/30 mL. Sonication: Intermittent. Time of sonication: 30 min	US+MW: 32g dried pectin/100 g dried peels. MW: 28g dried pectin/100 g dried peels.	MW: irradiation time of 6 min, power of 900 W.	An increase in yield with the comb. of US and MW and higher intrinsic viscosity of pectin obtained with combined procedures.	388
Prickly pear peel	Power: 1350 W. Frequency: 20 kHz. Time: 10 and 15 min Solvent: aqueous solution of 0.5% EDTA.	60 g/kg	---	Higher productivity than that of convectional extraction.	389
Grape pomace	Power intensity: 0.05W /mL. Frequency : 37 kHz. Solid-liquid ratio : 10g/100 mL citric acid solution. Temp.: 75 °C. Time: 60 min Solvent: citric acid solution with pH 2.0.	32 %	---	Yield obtained after US appl. was higher (25.6 %) compared to same cond. But without US. Also, the pectins formed had a higher average MW.	390

Techniques for the extraction of polyphenols

Nowadays, the need to look for new sources of antioxidants used in the pharmaceutical, cosmetic and food industries has promoted research on new techniques for extraction of these compounds from agricultural and food wastes. Large amounts of polyphenols, in fairly high concentrations, are presented in wastes generated by the cork industry[391] and vegetable oil production among others.[392] Currently, cork boiling wastewater (CBW) and olive mill wastewater (OMW) are being studied as a promising source of valuable by-products and have been selected as a case study because it is representative of a group of effluents with high levels of phenolic compounds. Several studies carried out concerning the recovery of these by-products showed that multi-stage membrane processes for

CBWs and OMWs and precipitation for CBWs are promising techniques to achieve this goal.

Multi-stage membrane processes

Application of membrane technologies to the treatment of CBWs and OMWs is of interest due to their several advantages, mainly low energy consumption, low environmental impacts and no phase change. Membrane-driven processes are good techniques to remove organic matter of different sizes (as phenolic compounds), from small solutes by nanofiltration to macromolecules (through ultrafiltration) or suspended solids by using microfiltration. The retention properties of membranes are expressed as Molecular Weight Cut-off (MWCO) and the main limitation is membrane fouling, which is related to the decrease of the permeation through a membrane as a function of time. This decline is caused by several phenomena, taking place during the filtration process and therefore, the pre-treatment, membrane cleaning and the improvement of operating conditions is essential. This is why membrane filtration is preferably applied in crossflow or tangential flow mode. In this kind of filtration, the wastewater flows through the feed channel and along (tangent to) the surface of the membrane as well as through the membrane. The feed it is separated into two parts, namely thepermeate and the concentrate, where the target compounds have been retained. Most of the rejected material from the membrane surface is removed by the passing flow and the fouling is minimised.

Cork boiling wastewater

Cork is a versatile product that has different uses, of which the most important one is the production of wine cork stoppers. Portugal is the leading producer, with 49.6% of the total production, followed by Spain with a 30.5%. The cork industrial process includes a stage in which cork planks are immersed in boiling water for one hour in order to improve their physicochemical characteristics. In addition, the same water is repeatedly used for several boiling cycles (10–30 times). Cork boiling wastewater (CBW) is a black liquor containing suspended solids (4.5–5.5 g/L) and high chemical oxygen demand (COD, 0.6–0.9 g/L) due to the polyphenols content. Due to the toxicological properties of these effluents and the high volumes produced (400 L/ton cork)[393] they must be treated before its discharge into public courses by sophisticated treatment processes.[394] The phenolic fraction in CBWs also contains other interesting compounds, e.g.: gallic, protocatechuic, vanillic, syringic, ferulic and ellagic acid.[391] Thus, CBW is a natural source containing high levels of bioactive substances with useful properties for several industry branches such as nutraceutical applications.[395, 396]

Literature shows information about the treatment of cork wastewater by multi-stage membrane processes, mostly nanofiltration (NF), ultrafiltration (UF) and microfiltration (MF) techniques:

Minhalma *et al*.[397] proposed a flocculation/flotation/ultrafiltration integrated process for the treatment of CBWs in order to reduce the membrane fouling. The flocculation/ flotation pre-treatment led to the enhancement of the UF permeate fluxes and several UF membranes ranging from 4.5 to 86 KDa were used. The same authors[398] studied an ozonisation/ultrafiltration integrated process with five ultrafiltration membranes which covered a range of molecular weight cut-offs, from 4 to 98 KDa. The ozone pre-treatment led to a reduction of 11% in TOC and 51% in the total polyphenols content with an enhancement of the UF permeate fluxes. Benítez *et al*.[399, 400] performed experiments using MF, UF and nanofiltration (NF) membranes to compare the quality of the wastewater treated and they focused on the separation of ellagic acid. UF membranes achieved a removal efficiency of 73.2% COD and 98.6 % ellagic acid and NF processing provided the best results although presented the higher membrane resistances to the flux, yielding the higher rejection coefficients of 95.5% COD and 100 % ellagic acid.

Other studies focused on the reuse of the permeate and recovery of total polyphenols as tanning agents by using the concentrate from the leather industry. Geraldes et al[401] studied the NF process, and TOC rejections coefficients had an average value of 95%. Teixera *et al.*[402] proposed a membrane-based process based on four polymeric NF membranes, producing a permeate with a TOC rejection of 88-99%. Oliveira *et al.*[403] presented a study using a NF membrane with COD, BOD5, colour and TOC rejection values remaining above 90%.

With reference to studies about the separation of specific phenolic compounds by membrane treatments, there are some studies carried out; Benítez *et al*.[404] studied the purification of aqueous ellagic acid solutions by 3 UF membranes with a best recovery of 63.2%. They also studied the ultrafiltration (UF) of aqueous solutions containing mixtures of three phenolic compounds (gallic acid, acetovanillone, and esculetin) by a tangential UF.[405] Minhalma *et al*.[406] carried out the identification and quantification of phenolic compounds in cork wastewater, which are responsible for membrane fouling (gallic acid, protocatechuic acid, vanillic acid, syringic acid, ferulic acid and ellagic acid). A UF system with two cellulose acetate UF membranes was applied. They concluded that ellagic acid is almost totally retained with a 6000 Da membrane. Good recoveries were obtained for the rest of phenolic compounds with this membrane: >90% (gallic acid), >80% (protocatechuic acid), >70% (vanillic acid), >60% (syringic acid) and >90% (ferulic acid).

A sequential system of five membranes: MF(0,3 µm)-UF(100 KDa-20 KDa-5 KDa)–NF (150-300 Da) to remove the majority of polyphenols and avoid membrane fouling was proposed by Yuste *et al.*[407] DQO, TOC, TP and 7 specific phenolic compounds were studied in all permeates and concentrates. Removal of COD (96, 24%), TOC (865, 60%) COT and total polyphenols (nearby 100%) was achieved. At the same time, the best combinations of MF-UF-NF were applied to obtain the best separations of target polyphenols, with good recovery of ellagic acid (>90% with MF-UF 100KDa), protocatechuic acid (>90% with MF-UF 20 KDa) and >90% for gallic acid and the rest of phenolic compounds (MF-UF-NF).

In conclusion, treatment by multi-stage membrane processes shows a general decrease in the pollutant content (COD, TOC, phenolic compounds) of permeates, with the decrease of the

membrane MWCO applied. The best results are achieved with NF (alone or combined with MF/UF) and 99% removal of COD, TOC and TP, but this process suffers from strong fouling in the membrane, caused by organic matter. Sequential process (MF-UF-NF) improves the yield, mitigating fouling and separating phenolic compounds by molecular weight cut-off. However, most of the authors focused on separating the phenolic compounds as a concentrate for tanning industry although the ellagic acid was easily separable by MF/UF. Few articles studied separation of specific phenolic compounds by membranes and only 2 studies proposed integrated systems of several membranes for cork wastewater.[406, 407] The last application[389] of sequential system of MF-UF-NF membranes showed a promising solution to purify cork wastewater and at the same time, extract specific phenolic compounds with useful properties, generating added-value for the cork sector.

Olive mill wastewater

Olive processing has been an important and traditional industry for Mediterranean countries. Olive mill wastewater (OMW) is the liquid effluent of the olive oil process. OMW is characterised by an intensive dark colour, high levels of organic matter (COD; 40-220 g/L,) pH 3-6, and high levels of polyphenols (0.5–24g/L).[408] The management of this wastewater is a critical problem in some regions due its pollution and huge quantities produced. However, OMW has been studied as a cheap source of phenolic compounds with strong antioxidant properties. The main polyphenols present in OMW are tyrosol, hydroxytyrosol and oleuropein[409]. Olive mill wastewater has phenolic compounds of different molecular masses ranging from low molecular weight phenolics such as benzoic acid and derivatives (MW up to 198) to high molecular weight phenolics (MW up to 416). Therefore, the use of membrane technologies to separate the low molecular weight biophenols, recover and concentrate them using NF and RO has been proposed. There are several studies that focus on the treatment of OMWs by membranes with reference to extraction of phenolic compounds.

Mudimu *et al*.[392] made a comprehensive review about recovery of polyphenols by membrane processes from OMWs`, highlighting the use of MF-UF-RO, UF-NF-RO and Direct Contact Membrane Distillation (DCMD) with recovery of hydroxytyrosol, tyrosol and other compounds as oleuropein, caffeic acid, protocatechuic acid and DHPEA, p-HPEA, 3,4-DHPEA-EDA and verbascoside.

In conclusion, the efficiency of multi-stage membrane processes to recover specific polyphenols (tyrosol, hydroxytyrosol amongst others) from OMWs has been successfully investigated, with final concentrates ranging between 0.5 and 30 g L^{-1} total polyphenols. However, there are some problems associated with fouling and the use of small-scale experimental setups (results can be different in real conditions).

Precipitation

The use of typical coagulants such as trivalent aluminium and ferric chloride has been proposed to remove organic matter from cork wastewater, including phenolic compounds, due to the large amount of total solids and colloidal matter present in this wastewater. Normally, most of these coagulation/flocculation processes for cork wastewater are used to remove organic matter (including polyphenols) as a pre-treatment without using the polyphenols extracted for any added value purposes.

Dominguez *et al.*[410] determined the optimal conditions for the use of iron (III) as a coagulant in the treatment of cork processing wastewater and the influence of the different operating variables on the settleability parameters: The organic matter removal was in the range of 35−65% for COD, 55−90% for polyphenols, and 40−90% for aromatics. The same study was done using aluminium as the coagulant obtaining similar results.[411] Peres *et al.*[412] used $Ca(OH)_2$ to adjust the pH to 8.5 and improving coagulation with $FeCl_3$. The removal of chemical oxygen demand (COD), total polyphenols and aromatic compounds of the effluent was 45, 71 and 58%, respectively. Yuste *et al.*[407] studied the use of $Ca(OH)_2$ as a coagulant itself and not only as a way to adjust pH. A comprehensive study of calcium dosage, pH, conductivity and mixing time was conducted in order to determine the optimal conditions to remove COD and phenolic compounds. Reductions in the ranges of 30-49% for COD and 83-89% for total polyphenols were achieved. Precipitated polyphenols have potential as a promising source of by-products (biogas, fertilisers).[395]

To summarise, coagulation/flocculation with aluminium or iron is often used as a pre-treatment for cork wastewater but not as a method to extract useful polyphenols. The use of calcium in a basic medium gives good yields with regards to the reduction of COD and total polyphenols and the extracted phenolic compounds have promising potential for new uses (biogas, fertilisers). Calcium is a nutrient so its use doesn´t have significant effects on the environment and permits a better use for by-products. In addition, the removal of polyphenols makes the treated wastewater less polluted for further treatment.

Characterisation and techniques for on line process optimisation/control of added value chemicals in food waste.

Waste materials from the agricultural and food industries are produced in large quantities. Environmental concerns and stricter legislation have limited the way in which waste products can be disposed of, and industry has to carefully evaluate what to do with these products. The growing interest in recovering added value chemicals from waste requires considerable efforts in terms of chemical analysis in order to answer the important question: what is in the waste/by-product and how much of it is there? This question can only be answered by the use of various techniques for chemical analysis. The techniques required encompass sampling, extraction, identification and quantitation of the chemicals in these often very complex materials. The analytical methods should be available in the laboratory, but many of them could be integrated into the industrial processes.

The three parts presented here are:

- General definitions of process monitoring and control
- Chromatographic techniques for the laboratory and at-line process monitoring
- Vibrational spectroscopy techniques for online monitoring and control

General definitions of process monitoring and control

Industrial processes may be subdivided in 2 categories: batch and continuous processes. Batch processes such as brewing beer or making cheese, start with a feedstock which after some time leads to an end-product with the desired qualities and properties. In a continuous process, raw materials are continuously entering the reactor/machine and the final material is coming out all the time. Examples include paper or plastic manufacturing. In both types of processes, monitoring of product quality is needed. In a continuous process, the end product has to be within tolerance limits for a number of parameters. For batch monitoring, the end product has to be within some tolerance limits. However, the process can also be monitored while it is on-going and it is possible to determine how far from the endpoint the process is.[413-416]

Industrial process control can be off-line, at-line, on-line, in-line or non-invasive. Offline means that samples are taken from the process and brought to the laboratory for analysis which is very slow. There are still many industries where a sample is taken from the process and analysed in the laboratory once a week or once a day. At-line means that an instrument is available close to the process, so the samples can be analysed quickly. In on-line measurement, usually an instrument is connected directly to a product stream or bypass so that continuous or semi continuous measurement is possible. It is also possible to have a customised instrument integrated into a process control system. This is called in-line. In this case, the measured data are used automatically to modify process settings without a human operator checking all the time. Non-invasive means that a stream in a pipe is measured without any contact between equipment and the sample. There is also a relationship between the complexity of the measurement and the analysis done. Simple variables such as temperature, pressure and flow rate can easily be integrated for measurement in-line or noninvasively. More complicated measurements such as spectra often require on-line measurement, many times in a bypass. Table 5 gives some properties of different analysis techniques for industrial processes. A general term that is often used is process analytical technology (PAT). Some books about PAT are available.[417-420]

Table 5. Definition of process monitoring types.

Analyser	Sample taken	Transport of sample	Frequency of measurement	Speed
Off-line	manually	to laboratory	rarely	slow
At-line	manually	to local analyser	regularly	medium
On-line	automated	none or bypass	often	fast
In-line	integrated	none	very often	fast
Non-invasive	no contact	none	very often	fast

Chromatographic techniques for the laboratory and at-line process monitoring

Chemical analysis and characterisation are essential in order to gather information, not only about the presence and concentration of specific components in the waste, but also of other compounds that potentially can disturb the processing of the material. In addition, for on-line process optimisation and process control in processing agricultural residues and food waste of diverse origin, analysis of reference samples (for use in e.g. NIR calibrations), is essential. Finally, purity/quality control of the added value compounds recovered by chemical analysis is important to optimise the added value of the compound/product isolated.

General aspects on analytical methods. For organic waste valorisation, tools of modern analytical chemistry play a crucial and decisive role.[421-428] Qualitative, semi-quantitative and quantitative analytical measurements have involved gravimetric, volumetric, electro analytic and spectroscopic analysis.

The materials to be analysed are often heterogeneous and therefore correct sampling and sample handling strategies need to be used since very small samples injected into an analytical instrument should represent kilograms or tons of waste. Many mechanical operations for mixing, grinding, subsampling etc. are available.[429-431]

Once a representative sample of the waste is present, it is often necessary to extract a fraction of interest in order to purify and concentrate the analytes of potential interest. For this purpose, a multitude of traditional and novel extraction methods are at the disposal of the analyst. Thus, as an example, early sample preparation strategy employed for characterisation of bio diesel from biomass involved filtration, centrifugation and phase separation.[429, 430, 432]

The analytical techniques are based on two principles: separation and identification/quantitation. Chromatography in all its forms is an excellent separation technique. The chemical fractions separated by chromatography have to be identified and there needs to be a quantitative determination. This can be taken care of by spectrometry. Spectroscopic analyses have well known potential for revealing the identities of constituents in conjunction with chromatography. Qualitative analytical data often require as many analytical techniques as possible to reveal the unequivocal identity of unknowns.[433]

Chromatographic separation, identification and quantification of biomass constituents. A broad range of chromatographic techniques are used in food waste analysis. The separation techniques as such are well described in the literature and will not be explicitly covered here.[422-427]

Furthermore, technical descriptions of detectors mentioned in the various examples below are found in the literature. Most frequently used for qualitative and quantitative determination of organic compounds are various mass spectrometric techniques that are well applicable to hyphenation with chromatography, electrophoresis and other column separation techniques.[424, 426, 428]

Applications. High performance thin layer chromatography as a preparative tool has recently been applied for the determination of sugars, i.e., separation of anhydrosugar, levoglucosan and cellobiosan in bio oil,[434] while gel permeation chromatography (GPC) has been utilised to extract smaller molecules from macromolecules or biomolecules. GPC could also be applied for separation of phenols from lignin to characterise pyrolytic lignin and also to establish if higher molecule weight lignin derived compounds are present.[435] Nowadays, liquid-liquid extraction commonly used in the past has been replaced by more efficient techniques like as single-drop micro-extraction, hollow-fibre mediated liquid phase micro-extraction, etc. Solid-phase micro-extraction – SPME and head space SPME have the potential to extract volatiles and semi-volatiles.[433] Solid-phase extraction – SPE thanks to its versatility, simplicity and efficacy has been used regularly; normal phase (silica and alumina), reversed phase (C_{18} and HLB (hydrophilic lipid balanced)) and ion exchange phases MAX and MCX (mixed-mode, reversed-phase/strong anion (cation)-exchange respectively). Other non-conventional SPE adsorbents like florisil, zirconia, nano-composites and phenyl substituted have the potential to segregate classes of compounds for better and more-detailed identification.[436] Moreover, development and modification of SPME fibres, molecularly imprinted polymers and nanostructures (e.g., carbon nanotubes and graphenes with extraordinary geometry, morphology and surface area) are a few potential areas that have offered high efficiency and selectivity in extraction. Therefore, miniaturised sample extraction procedures are accepted by researchers worldwide because of their green approaches, convenient set up and high enrichment factors.

Phenolic compounds. Soxhlet extraction[437, 438] and ultra-sonic bath treatment[439, 440] have been utilised for sample preparation, i.e. methanolic sample extraction mostly due to measurements of antioxidant activity,[438, 439, 441, 442] total phenolic contents,[438, 439, 443-445] polyphenols,[439] total flavonoid contents,[439] etc. However, in order to extensively characterise the antioxidant potential of extracts there is a need for combining several different methods. Thus, methanolic solution of DPPH (2,2-Diphenyl-1-picrylhydrazyl), hydroxyl, and nitric oxide radicals have been widely used for testing the scavenging ability of investigated extracts. It must be noted that the Folin-Ciocalteu[445, 446] method applied for measuring total phenolic content has several analytical interferences. In this method the reagent mixture of phosphotungstic and phosphomolybdic acids also reacts with other non-phenolic reducing compounds leading to an overestimation of phenolic content. However, pronounced antioxidant activity, manifested with radical scavenging and reducing power, could be due to high phenolic content. It should be highlighted that in the previously mentioned methods absorption at selected defined wavelengths are measured by the spectrophotometer without knowing which individual phenolic compounds are presented in the investigated extract. Nevertheless, these methods are widely used prior to liquid chromatography quantification of phenolic compounds.[438, 439, 447-449] However, quantitative determination of individual phenolic compounds could be done using high performance liquid chromatography (HPLC) with different detectors such as with diode detection,[449], mass spectrometry (MS), MS/MS,[438, 440, 450] and ultraviolet/visible UV/Vis.[439] The individual separation of phenolic compounds: gallic acid, protcatechin, catechin, gentisic acid, chlorogenic acid, vanillic acid, syringic acid, caffeic acid, epicatenchin and benzoic acid was performed on an ultra-base C_{18} column by described procedure,[449] while others analysed complex samples in negative mode by Turbo-ion-spray tandem mass spectrometry coupled with liquid chromatography (HPLC-MS/MS) and equipped with an API source.[440] The identification and quantification was simplified thanks to the high selectivity of tandem mass spectrometry in MRM (Multiple Reaction Monitoring). They identified and quantified 19 phenols of which 6 belonged to the biophenols, and were all presented in considerable amounts except elenolic acid and 4-nor-oleuropein aglycone. Detailed identification and quantification of phenolic acids and flavonoids was done by RP-HPLC-UV/Vis.[439] Chromatograms were recorded using different wavelengths for individual compounds: 280 nm for hydroxybenzoic acids and ellegic acid, 320 nm for hydroxycinnamic acids, and 360 nm for flavonoids. Separation was further explored by HPLC analysis on a Luna C-18 RP column with a C18 guard column. In total 18 phenolic acids and flavonoids were quantified. However, identification of anthocyanins[439] was done by HPLC-DAD-ESI/MS^n using retention times, molecular mass and MS^2 ion fragments while RP-HPLC-UV/Vis chromatograms were used for quantitation.

Analysis of complex matrices. For a complex matrix, e.g. biomass derived fuels, selection of an appropriate analytical strategy depends on the desired information to be derived from investigated samples. Among all the techniques of analytical chemistry, spectroscopy is widely used. There are a large number of reports in which the use of Gas chromatography (GC) and HPLC with various detectors is described for characterisation of volatile polar and non-polar and highly polar organic compounds, respectively, while for molecular weight distribution GPC is widely employed. Flame ionisation (FID) and thermal conductivity (TCD) detectors are universal with sensitivity for a wide range of compounds and broad linear dynamic range. GC-FID is very precise and accurate and thus, is recommended for characterisation[451] and concentration, determination of components in biomass derived fuels like as bio-oil,[452] while for characterisation of uncondensed gases from pyrolytic

processes GC-FID/TCD is favoured. GC x GC and multi-dimensional GC has been applied for pyrolytic products and volatile organic compounds from lignocellulosic biomass.[453]

Mass spectrometry (MS) coupled to gas chromatography (GC) provides explicit identification of the constituents of a sample thanks to the large commercial mass spectral databases available.[436] Small organic molecules such as phenols, aldehydes, alcohols, organic acids, ketones, polycyclic aromatic hydrocarbons have been characterised by GC-MS[437, 454, 455] to determine the pyrolysis yield. GC-MS analysis with electrospray ionisation in positive and negative mode showed 320 peaks and revealed molecular mass distribution and chemical structure of biofuel derived from lignins.[456] A disadvantage that could be associated with GC-MS analysis of bio oil is the lack of reference standards or recommended working parameters due to a change of bio oil compositions derived from different feedstocks. For determination of molecular weight distribution utilisation of GC-TOF-MS is reported in electron ionisation (EI) mode.[457] High resolution mass spectrometry (HRMS) with an Orbitrap analyser has also been utilised for separation and determination of over 100 compounds with sufficient resolution.[458] Additionally, as it has been previously mentioned for determination of antioxidant activity, i.e. for phenols separation and determination, HPLC[438, 440, 449, 450] is widely used. Furthermore, phenols have been the targeted analytes in bio oil as they caused chemical instability of the one. Therefore, HPLC[433, 436, 444, 446, 456, 459] with different detectors, particularly with UV and RI detectors, have been reported for analysis of polar water soluble constituents of bio oils. Moreover, as comparative tools, Fourier transform infra-red spectroscopy (FT-IR) and nuclear magnetic resonance (NMR) could be successfully used to reveal the varieties of functional groups and nuclei, respectively. Hence, spectroscopy provides necessary data in molecule level understanding. Additionally, the gathered data from spectroscopic analysis could be subjected to the multivariate analysis[460-463] as an important statistical tool used to: (a) characterise syngases obtained under different conditions during co-gasification of crude glycerol and olive kernel, (b) compare syngases obtained by co-gasification and co-pyrolysis of crude glycerol and olive kernels, (c) assess general information common for different gasification systems, comparing the syngas from co- gasification of crude glycerol with olive kernel with those produced by other non-woody and woody biomass gasification processes,[464] (d) contribute to the mapping of potential biodiesel feedstocks, considering also their geographical availability and the plant (grain/seed) oil contents, which might be of special interest for practitioners interested in alternative and inedible oil sources.[465]

Vibrational spectroscopy techniques for online monitoring and control

Near infrared spectroscopy. Near infrared (NIR) spectroscopy uses overtones and combination tones of vibrational frequencies in the infrared. The range is 800 to 2500 nm or 4000 cm^{-1} to 12500 cm^{-1}. The near infrared spectra rarely show sharp peaks that can be used to identify constituents. They show convolved wide peaks, but the information about the constituents is still there.

NIR spectroscopy is a very flexible technique. It can be applied in transmission and in absorption. The radiation source is a simple quartz halogen lamp running at a low voltage. A number of monochromators have been used: interference filters, gratings, interferometry combined with Fourier transformation, tuneable filters and more. As detectors, PbS, PbSe, GaAs, InGaAs, and HgCdTe have been used. Some detectors have to be cooled to get a good signal to noise ratio. Sometimes a single detector is used, but lately detector arrays with up to 250 or 500 detector elements have been available. Using an array makes for quicker measurement, often without using moving parts. Some monochromators and detectors have a limited range so the spectrum may be limited to 960 - 1660 nm. The number of variables created in the NIR range has increased over time. Early filter instruments had 19 filters, newer Fourier transform instruments can produce thousands of wavenumbers or wavelengths. This means that NIR spectroscopy requires multivariate data analysis. Figures 6a and 6b show a schematic setup of a laboratory spectrometer. A number of modifications, usually implying use of high quality fibre optics and special software are needed to do process measurements at regular intervals.

A typical average spectrum for a cereal sample is given in Figure 7a. The spectrum is very complicated. It is not possible to exactly identify materials by their peak positions and it is certainly not possible to use peak height or area for quantitative purposes. Some pure materials, especially in the dry state, have NIR spectra that are easier to understand. Figure 7b is a spectrum of a dry polymer. It is easier to discover peaks for identification.

The range of wavelengths covered by NIR allows quantification of all major organic constituents in a sample: water, proteins, carbohydrates and fats. But NIR is not limited to these constituents. A few books give a good introduction to the NIR topic with reference to numerous applications,[466-472] and some introductions for multivariate data analysis.[473-475]

The most interesting property of near infrared measurement is that it is quick, requires little or no sample preparation and penetrates a few mm into a sample. Many other techniques that may have a better wavelength or wavenumber resolution have the disadvantage of requiring longer sample preparation and of longer measurement time.

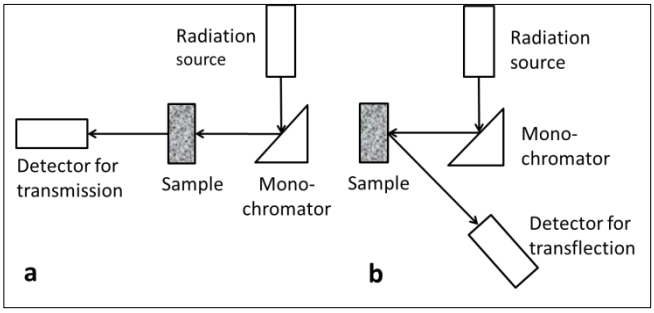

Figure 6a. The basic setup of an NIR spectrometer for transmission through a sample. **b.** The basic setup of an NIR spectrometer for transflection from a sample.

NIR for process monitoring. The speed and lack of laborious sample preparation make NIR very useful for at-line, online or inline monitoring.

Figure 8a shows a schematic drawing of a typical online monitoring setup. The liquid/gas flows through a pipe with quartz windows mounted on both sides. These quartz windows are connected to fibre optics bundles coming from and going through the NIR instrument. The measurement is in transmission. For this reason, such a setup is often used with a bypass. A problem is keeping the quartz windows clean. Figure 8b shows an inline setup. A reflecting mirror sits in the pipe and radiation from and back to the instrument passes through different fibre optic bundles. Contamination can also be an issue here.

A number of useful review articles have been written and are worth mentioning.

It is no surprise that food applications are very common. Giovenanza *et al.*[476] gave a good overview of using optical techniques in the visual and NIR range for controlling fruits and vegetables. They also give examples of NIR imaging. A nice explanation of the multivariate techniques and a long list of general food applications are presented by Porep *et al.*[477] A long list of pharmaceutical applications is given by Fonteyne *et al.*[478] An overview of brewing applications is given by Sileoni *et al.*[479] The elaborate paper by Watari[480] is a classic example of process monitoring in the polymer industry. A general overview

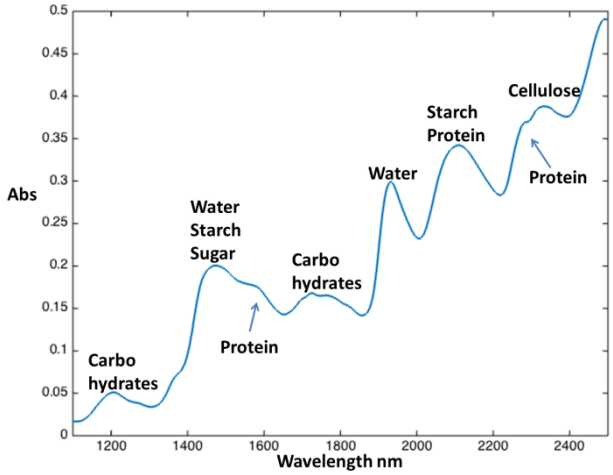

Figure 7a. A typical average transflectance spectrum for a number of cereal samples. Some peaks are identified, but the peaks are often convolved.

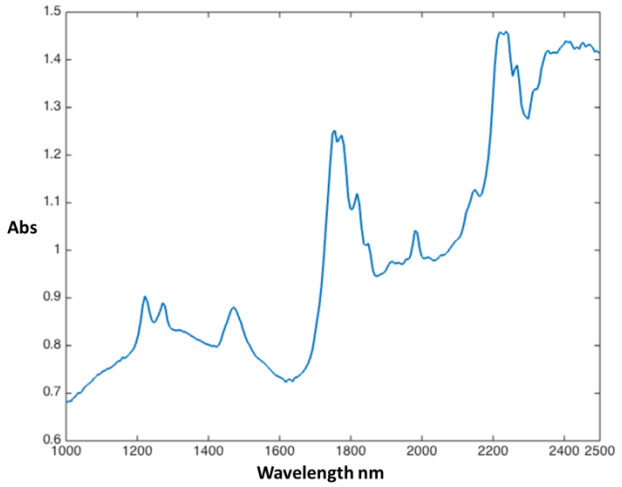

Figure 7b. A typical average transflectance spectrum of a dry polymer (polystyrene).

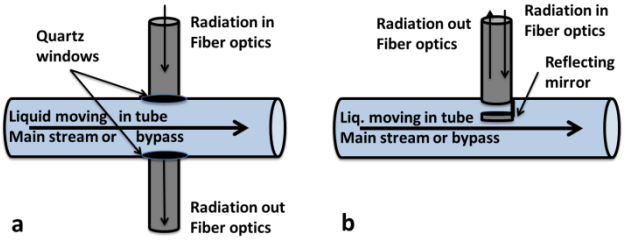

Figure 8a: A typical setup for online measurement. **b**: A typical setup for inline measurement.

from Swarbrick[481] compares the complementary techniques NIR and Raman. An example from online monitoring of a process stream is used to show how such data is analysed. The data set consisted of 33 samples (daily averages) x 256 wavelengths (1018 - 2032 nm). The raw data up to 1900 nm are shown in Figure 9. The spectra all look identical. Before analysis the wavelengths above 1880 nm were removed leaving some 211 wavelengths. After mean-centring of the data PCA analysis was carried out. The first 2 components explained 97.6% and 2.1% of the total sum of squares.

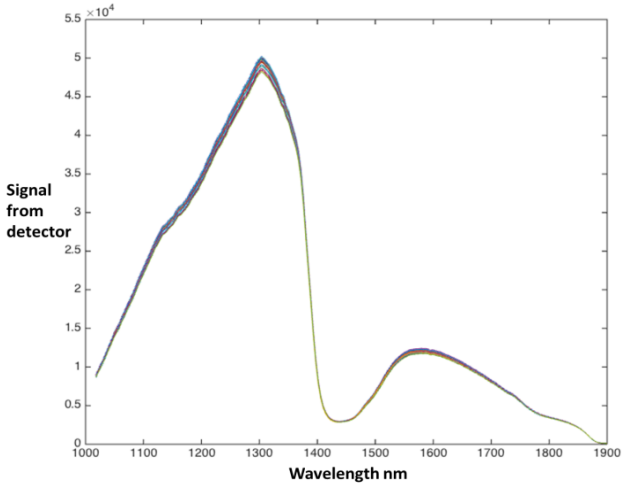

Figure 9. The 33 NIR spectra from online monitoring of a process stream.

This is 99.7% for the 2-component PCA model. Figure 10 shows component 1 and Figure 11 shows component 2. The first component shows fluctuations around a constant level and then a quick decrease in signal. The second component shows a periodic behaviour with an approximate period of 10 days.

Interesting observations from this example are that NIR can be used to monitor processes. It was actually possible to get spectra with 10 min intervals but for this simple example only daily averages were used. The NIR spectra themselves showed little difference, but the PCA analysis was able to extract useful information by 2 components that explained 99.7% of all the data. The first component showed a drastic change in the process after about 25 days. The second component showed a periodic behaviour.

In many industrial situations, NIR can be used to monitor a process without interpretation of spectra. One just has to define normal operating conditions and then check whether these are valid or not.

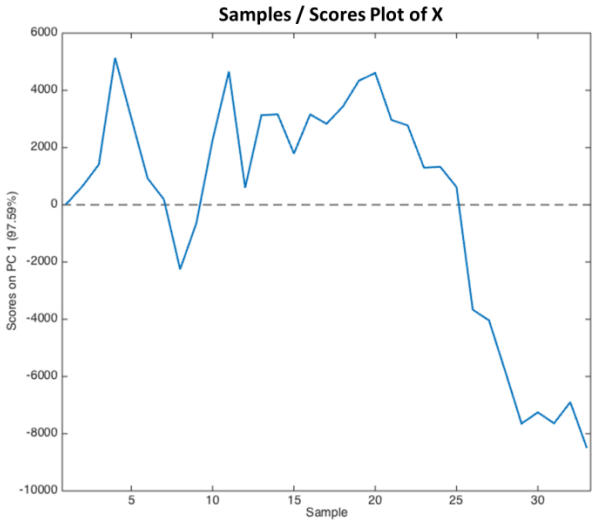

Figure 10. Component 1 of the process example. Horizontal axis is days. A drastic change after 25 days can be noted.

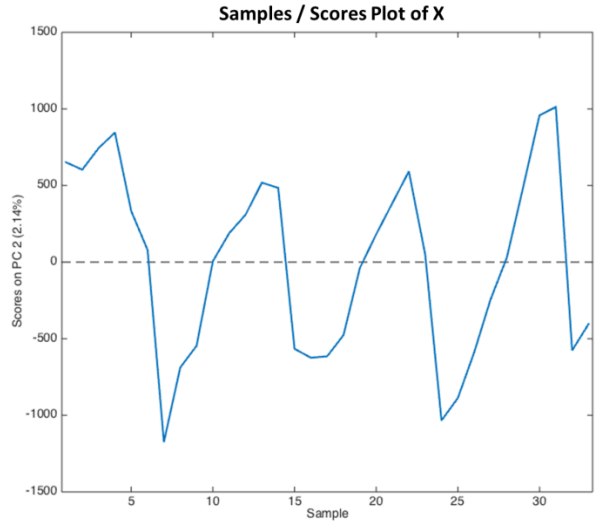

Figure 11. Component 2 of the process example. The horizontal axis is days. A periodic behaviour can be seen.

Simulated Moving Bed Chromatography separations of complex process mixtures

Separation steps usually account for more than 40% of the total manufacturing costs in the chemical industry, therefore they are of paramount importance in cost reduction.[482] Despite some inherent drawbacks, liquid chromatography is generally accepted as an efficient and versatile separation tool for the purification of various chemicals and biochemicals.[483] Chromatography was initially developed for separation and purification of compound mixtures of vegetal origin. Its application in the pharmaceutical industry, biotechnology and in the production of fine chemicals fields is still growing. At present it is the most powerful high-resolution technique for the production of many different compounds of high purity from a laboratory to an industrial scale.[484] The two major disadvantages of classical batch chromatographic separations are the discontinuity of the process and the product dilution.[485]

Simulated moving-bed (SMB) technology is a multi-column continuous chromatographic separator, based on the simulated counter-current movement of a liquid and a stationary solid phase packed into the columns.[486] The idea of SMB dates as far back as the 1840s in England to the Shank's system for leaching.[487] The first recorded SMB chromatographic technique was developed in the petrochemical industry in the late 1940s[488] and has been widely used industrially in petrochemical refineries since the 1970s, in high-fructose corn-syrup processing since the 1980s, and enantiomer separations in the pharmaceutical industries since the 1990s.[484, 489]

The concept of SMB technology relies on adjusting the bed transport rate in between the propagation velocity of the fast moving (weaker binding, 'cat') and slow moving (stronger binding, 'turtle') components (Figure 12).[489] It was designed to simulate the solid phase movement of the corresponding true moving bed (TMB) process, in which the fluid and solid phases flow counter-currently to each other.[490, 491] It continuously separates or purifies feed streams using very much the same chromatography mechanisms, including adsorption, ion exchange, size exclusion, hydrophobic interactions, chiral interactions, affinity, or a combination of these mechanisms.[484] It can effectively separate binary mixtures, i.e. two target compound mixtures, therefore industrial applications to date are often binary separations. However, some processes require a ternary or pseudo-ternary split. This is often more so when two products need to be recovered separately from the feed stream, or when a single desired component is buried in the middle of a chromatographic sequence of undesirable components, as with insulin purification. Insulin is first separated from fast-moving impurities (high-molecular-weight proteins) in a first SMB; then it is separated from a slow-moving impurity (zinc chloride) in a second SMB.[484] Separation costs can be higher than US$ 200/ kg^{-1} when using batch lab scale chromatography, whereas on a large-scale the use of continuous chromatographic systems such as a SMB can reduce this figure to as low as US$ 0.1 kg^{-1}.[482] The original concept of SMB was commercialised as the Sorbex technology and it was branded for *p*-xylene as Parex. Typically, Parex systems have production

capacities in the range of 21,000 to 1,600,000 metric tonnes per annum.[492]

Methods for purifying compounds from complex streams

Distillation, liquid–liquid extraction, crystallisation, membrane separation and chromatography are common processes for downstream purification of natural products. Among these, chromatographic separation is considered simple and effective in separating bioactive components from crude extracts.[493] For example, the conventional organic acid recovery from crude streams usually includes their precipitation with calcium carbonate and sulphuric acid recovery to produce the free acid, resulting in the production of a large amount of gypsum (calcium sulphate) as a by-product. To avoid generation of the gypsum waste, many other techniques, such as electro-dialysis, reactive distillation, and ion exchange, have been studied as potential methods to recover organic acids and nowadays emphasis is given to SMB.[494]

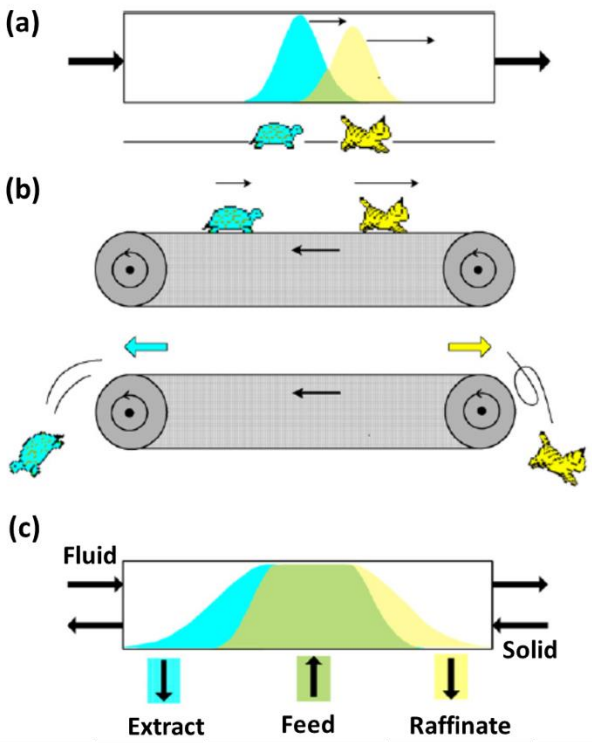

Figure 12. The cat-turtle analogy for the better understanding of the elution (batch chromatography) and counter-current (SMB) chromatography. (a) representation of elution chromatography, (b) Analogy of elution and counter current chromatography with the cat and turtle and (c) representation of counter current chromatography.[489]

Basic SMB principles

In conventional batch preparative chromatography, a feed mixture is first loaded into a column (or a series of columns) filled with the stationary phase, and the feed pulse is then eluted with a desorbent (the mobile phase) isocratically (no change in the desorbent composition) or otherwise (Figure 13). A solute in the feed, which has a high affinity for the sorbent, has a high partition coefficient. This means that a larger fraction of the solute exists in the sorbent phase than in the mobile phase. Since only solutes in the mobile phase migrate downstream in the column, the average migration velocity of a solute is proportional to its fraction in the mobile phase.[484] For this reason, a higher affinity solute (turtle) migrates more slowly than a low-affinity solute (cat), resulting in separation of the various feed components in the column.[484, 489] It is generally difficult to achieve high product purity and high yield simultaneously.[484]

In true moving bed (TMB) chromatography, the stationary phase moves in a counter-current direction to the solid phase. The column is divided into four zones by the inlet (feed A+B, desorbent D) and outlet (raffinate B, extract A) ports (Figure 13 top). In zones 2 and 3 the separation takes place, while zones 1 and 4 are required for the regeneration of the stationary and mobile phase, respectively.[489, 495, 496] In particular the TMB, enhances the mass transfer driving force, allowing a better use of the adsorbent, permitting increased productivity values (higher processed throughput using less packing material). The TMB also permits the achievement of high-purity products, even in cases of low resolution (reduced selectivity) as well as less dilute product streams and thus enables reduced solvent recovery duty (eluent/desorbent), the opposite of traditional batch elution chromatography.[489, 495, 496] Nonetheless, with this counter current mode of operation, it is necessary to move both the fluids as the solid phases. This solid movement around the columns presents considerable technical problems, such as mechanical erosion of the adsorbent (with subsequent formation of fines and thus high-pressure drops), equipment abrasion caused by resin particles, difficulties in maintaining plug flow for the solid (particularly when using beds with a large diameter) etc.[486, 495, 496] Such issues clearly restrict the implementation of TMB and reduce it to nothing more than a concept. To avoid these limitations, a discretisation of the TMB unit in several fixed bed columns has been proposed. In this latter strategy, though a sort of counter current movement is created relatively to the fluid, there is no real solid movement. Hence, this technology is called simulated moving bed (SMB) (Figure 13).[496]

So in principle, SMB lies in a simulated counter-current movement of liquid and solid phases, which is achieved by periodic switching of the positions of feed and eluent inlets and extract and raffinate outlets (Figure 13 bottom) in a closed loop of recycled columns.[489, 496, 497] These positions delimit four operational zones with typical concentration profiles of more - and less-retained components, in which different constrains must be met. The feed and eluent (desorbent) are injected at the beginning of section or zones 3 and 1, respectively. At the end of these zones, the raffinate and extract are collected.[497] Valves between the columns are switched open or closed at timed intervals to introduce the inlet streams and withdraw the outlet streams between the separation zones, simulating counter clockwise rotation of the columns. Under appropriate conditions, continuous separation of sample components can be achieved with extremely high purity and yield. The optimisation of flow rates and column switch times enables a higher level of separation to occur with less solvent consumption, making SMB chromatography a powerful tool for separating

binary mixtures.[498] The four sections or zones have to meet the following constraints:

– Section 1 (between the desorbent and the extract) in this part regeneration of the eluent occurs – the more firmly retained product A (extract) must be completely desorbed.

– Section 2 (between the extract and the feed) the less firmly retained product B (raffinate) must be completely desorbed.

– Section 3 (between the feed and the raffinate) the more firmly retained product A (extract) must be completely absorbed.

– Section 4 (between the raffinate and the desorbent) in this part regeneration of the adsorbent takes place -the less firmly retained product B (raffinate) must be completely absorbed.[486, 495, 496]

A classical SMB system consists of 4 to 24 columns distributed between the 4 zones, in addition to 3 to 5 pumps and valves which connect the different streams between the columns. In general a 4 column SMB should be sufficient to test and optimise the conditions for any given separation problem. The optimal number of columns per zone must be determined in the simulation of SMB process. The rule is more columns per zone results in a better separation, while too many columns per zone make the system too complex. If an infinitive number of columns per zone are used the SMB approaches the TMB.

Important parameters for the operating conditions are:

– The feed concentration

– The number of columns per zone

– The column length

– The column diameter

– The particle size

All these parameters can be determined and optimised by measuring data on a laboratory scale.[486]

A powerful short-cut SMB design method is the "Mazzotti-Morbidelli Triangle Theory".[499] This design theory provides a method for selecting the flow rates in each separation zone and facilitates the determination of optimal and robust operating conditions of SMBs suitable for achieving the desired separation. A major feature of this approach consists of the fact that the typical overloaded operating conditions of the SMB can be taken into account, i.e. whenever highly non-linear and competitive adsorption behaviour is exhibited. This makes this approach superior particularly when compared with others, which are based on empirical extrapolations of the linear adsorption isotherms to design the non-linear SMB operations.[486]

Indicative case studies in waste valorisation. The literature provides a long list of potential SMB applications such as purifications of organic acids,[494, 500-503] amino acids,[504-506] and pharmaceutics,[507] which include enzymes,[485] monoclonal antibodies,[508] paclitaxel (a chemotherapeutic drug),[483] ascomycin derivative (an anti-inflammatory drug),[509] biosynthetic human insulin,[510, 511] and many others.

Some more recent applications of SMB in the generation of high yield and purity food ingredients are given in more detail below.

Tomato based Umami active fraction. The use of SMB for the industrial scale separation of the umami fraction from tomato serum was recently described.[512] Monosodium glutamate coupled with taste active nucleotides is a frequently used ingredient to add umami taste in foods. The separation of monosodium glutamate and taste active nucleotides from glucose and citric acid was achieved with two subsequent SMB steps each having 8 columns separated in 4 zones using a strong cation exchange resin (UKB530, or UBK550).

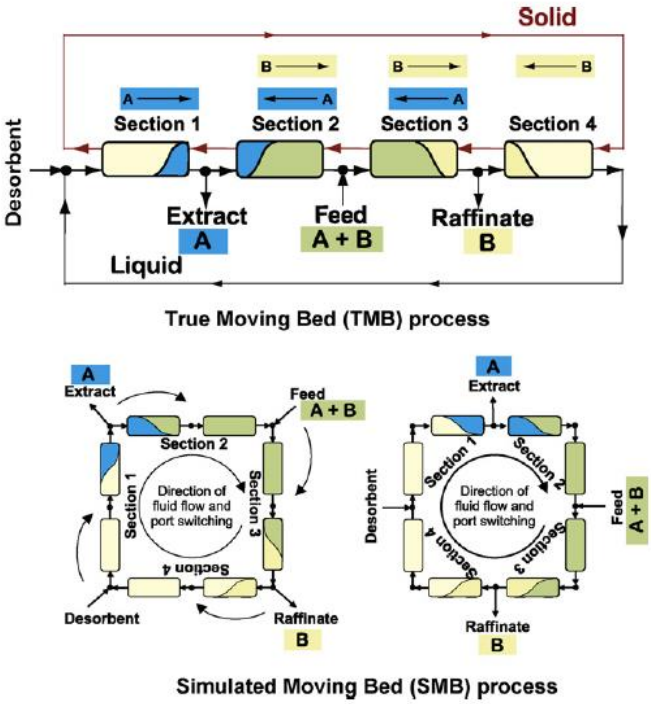

Figure 13. Schematic representation of TMB (top) and SMB (bottom) units for the separation of a binary mixture (A and B).[489]

Isolation of potato proteins. With regards to valorisation of starch production by-products, SMB chromatography has been applied to potato juice to harvest proteins. The potato starch industry produces large amounts of potato juice waste, 0.7–7m^3 per ton potato. Typically, this effluent contains 2–5% solids with a protein content of around 35%. The process often involves a pre-concentration step by reverse osmosis, subsequent heat coagulation of the proteins followed by a separation and drying step. The resulting protein product has a salty, bitter taste and low functionality and is mainly used for animal feed. It was shown by Anderson *et al.*[513] that SMB is able to offer various possibilities under different process strategies harvesting up to 80% of the protein needing very little extra water besides that already present in the juice.[513]

To summarise, the basic SMB binary separation technology is well established in industries with high value products such as pharmaceutical industries but also in industries with medium value products such as petrochemical and sugar, where SMB has provided significant cost savings over traditional batch chromatography. Novel concepts into the respective field are promising even further cost reductions.

SMB technology will surely have an important role in the emerging biorefining industry, where the target compounds are mostly of medium to low value. However, serious chal-

lenges still exist due to the complex characteristics of biorefinery feed streams and the multicomponent separation requirements, whilst ensuring low separation costs at the same time.

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