H2020-BBI-PPP-2015-2-1 **BBI.VC3.D5-2015** - Valorisation of agricultural residues and side streams from the agro-food industry.	

Title: Agri and food waste valorisation co-ops based on flexible multi-feedstocks biorefinery processing technologies for new high added value applications.

Acronym: AgriMax

Grant Agreement No: 720719

Deliverable 1.1	**Report on the state-of-the-art review.**
Associated WP	**WP 1**: Inventory and Specifications of the waste processing & derived biocompounds
Associated Task(s)	**Task 1.1:** Update review of the state-of-the-art and waste inventory **Task 1.2:** Definition of requirements of bio-waste derived compounds for the target applications
Due Date	31/01/2017
Date Delivered	17/02/2017
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Deliverable Version	1.0
Dissemination Level	**PU**

Contents

1. Introduction

Approximately one third of all food produced globally is wasted every year throughout the whole value chain from farmers to consumers. According to FAO, this is about 1.3 billion tons per year [1]. Within the European Union approximately 700 million tons of agricultural waste are generated annually [2]. These wastes can be reused in other production processes and are potential sources of bioactive compounds such as carotenoids, phenolics, essential oils or β-glucans [3-7]. The extracted bioactive compounds have a potential use as functional ingredient or additive in the food industry. Besides, they are known for their health properties, antioxidant, antimicrobial activities, thickening ability as well as for their potential use as a natural food colorant [8-13]. Moreover, tissues from by-products may contain varying concentrations of flavor volatiles that may be recovered and used in the food and beverage industry [14, 15]. Other valuable ingredients might be the content in dietary fibers including polysaccharides and lignin or proteins that can be used as functional food ingredient increasing the nutritional value and providing useful properties in food [16-18]. To extract significant amounts of valuable compounds contained in these wastes, AgriMax will combine affordable and flexible processing technologies (ultrasound assisted and solvent extraction, filtration, thermal and enzymatic treatments) for the valorization of side streams from the horticultural culture and food processing industry to be used in a cooperative approach by local stakeholders. A selection of case-scenarios previously developed to large lab or pilot scale by the participating RTOs has been carried out. Their industrial transfer in new applications as food additives, packaging and agricultural materials among others, the project will disclose the holistic potential of four new agro-value chains (residues and by-products from the culture and processing of tomato, cereals, olives, potato). Many of the by-product generated along the production cycle will be valorized in a cascade manner to reach over 40% of high value use of the waste. This will lead to additional production of active ingredients in lower concentration, but also fibers, biogas and fertilizers from the left biomass. The latter will be used in closed loop in the culture of the crops used in the project to prevent soil impoverishing.

This deliverable summarizes the state-of-the-art processing technologies and application possibilities of bio-waste derived compounds from tomato, cereals, olives and potatoes. An overview about relevant patents is given in the appendix.

2. Valorization of potato residues

2.1 Extraction of phenolic compounds from peels

Phenolic compounds can be classified as secondary plant metabolites. This term describes substances that are formed by plants during their secondary metabolism. They are not essential for the survival of plants. Phenolic substances can have antioxidant, antimicrobial, anticarcinogenic and several other beneficial health effects [19-22]. Whilst whole potatoes are a relatively poor source of polyphenols many studies have demonstrated that these secondary metabolites are enriched in the peel of most cultivars. This is not surprising given their role in the tuber as an allelochemical to prevent attack by fungi and other microbes. This fact coupled with the abundance of potato peel as a by-product of potato processing has meant that a large number of studies on the extraction of phenolic compounds from potato peel have been published. In fact the topic has formed part of a number of review articles dedicated to the valorization of agro-industrial products particularly the work of Balasundram, Sundram [23] and Wijngaard, Ballay [24].

This section will attempt to summarize and evaluate recent advances and cover both, conventional methods of extraction such as solid/ liquid extraction and novel assisted methods. Table 1 summarizes a selection of studies carried out in the last decade on extraction of phenols from potato peels and details on cultivars, optimal extraction and maximum yields. At the outset it should be stated that a wide range of polyphenol levels in potato peel even for optimal extraction conditions have been reported. For example, levels ranging from 112 to 431 mg/100 g have been published as yield obtained by applying optimal conditions in the past ten years. This is perhaps not surprising given the range of cultivars that have been examined and the lack of standardized post processing conditions and analytical methods. By far the most common method of measuring extraction efficiency is the Folin-Ciocalteu reagent method (also known as the FCR assay) however, some studies have reported on the levels of individual phenolic compounds. In most cases studies reported that ferulic, chlorogenic and caffeic acid are the most abundant phenolic acids in varieties used for industrial processing although a wider range such as gallic acid, protocatechuic acid, coumaric acid, syringic acid, vanillic acid and p-hydroxy benzoic acid have been determined in less common cultivars [25]. The authors reported levels of chlorogenic acid ranging from 0.86 – 2.79 mg/g in dried peel powder of six potatoes varieties growing in Ontario. Chlorogenic acid and caffeic acid were found to be the predominant phenolic acids present in the varieties they examined. In contrast, Wijngaard, Ballay [24] detected that caffeic acid was the predominant phenolic compound in extracts obtained by pressurized liquid and solid liquid extraction (SLE) from peel samples of the lady Claire variety. The maximum levels they reported were 651 µg caffeic acid/g DM in SLE extracts. However, the authors did not analyze chlorogenic acid in their extracts. This is surprising as it usually is the most abundant phenolic compound in potato peels. However, when stored at room temperature or exposed to light, chlorogenic acid can be transformed into caffeic acid and quinic acid [26]. Therefore if researchers are interested in adding value to potato peel waste by isolating chlorogenic acid, the instability of this compound should be taken into account. In addition, when attempting to interpret results from the reported studies, the method used to generate the peel should be considered. In many cases peels were prepared manually which does not reflect the abrasion method used during industrial scale peeling of potatoes.

Simple solid liquid extraction is still the most common method used in studies aimed at extraction of phenolic compounds from potato peels (used in three of eight studies in Table 1). Whilst this method may have some drawbacks particularly in regard to high energy and solvent use, the equipment used is simple and does not require a large capital investment. These are distinct advantages for researchers and industry stakeholder who are not willing to commit a large investment and do not have the expertise to maximize the gains from the novel technology aided approaches described in more detail below. In common with other food by-products, phenolic compounds are best extracted from potato peels with hydro-ethanolic solvents at ethanol concentrations ranging from 70 – 80%. One major advantage of ethanol as extracting solvent is its status as a food friendly solvent. But some studies have used methanol due to its much lower price compared to ethanol. It would be expected that methanol behaves in the same manner as manner as ethanol however it cannot be used as solvent for food due to its toxicity [27]. In some cases, water has been used as extracting solvent. Water is the ideal solvent for food use as it is both food friendly and inexpensive. However, it will only extract water soluble phenolics and the predominant species mentioned above are only sparingly soluble in water [28].

Recently, many authors have recognized the need to develop more sustainable energy efficient methods for recovering valuable compounds from food by-products. This has resulted in a move towards the use of novel technology aided approaches to achieve this goal. Most of these techniques aid extraction of the target compound by facilitating the release of intracellular compounds such as phenolics by breaking cell envelopes. This allows their isolation in the subsequent extraction step with less energy. Both, pulsed

electric field [29] and ultrasound (US) assisted extraction [30] operate by this principle and have been successfully applied for the extraction of phenolics from potato peels using water as solvent. Pereira, Rodrigues [31] applied a novel technological approach, namely ohmic heating to allow the use of water as solvent for the recovery of phenolics from potato peels. Ohmic heating applies a constant electric field, in contrast to a pulsed electric field (PEF) and is more commonly used as a novel method for heating foods. It can also be used to electroporate cells whilst simultaneously heating and thus facilitating increased mass transfer into the extracting solvent. As a result of the fears that it may degrade thermally labile compounds ohmic heating is less commonly reported on as an extraction technique than PEF or ultrasound. However, most phenolic compounds are reasonably heat stable and thus ohmic heating may warrant more investigation with regard to the extraction of phenolics from potato peel. Further emphasizing the increasing use of water as a solvent, Singh and Saldana [32] examined the application of subcritical water (i.e. water at high pressures and temperatures) to extract polyphenols from potato peels. They reported good recovery rates for phenolic compounds (81.83 mg/100 at 180 °C for 30 min) as compared to 3 h extraction with methanol.

In summary, the ideal extraction method for recovering polyphenols from potato peels would have the following characteristics: low energy consumption, little capital investment, water as a solvent, high yield and an easy integration into existing processing lines. Unfortunately none of the methods discussed here fulfill all of these criteria. Therefore potato processors must seek the method that best matches their priorities i.e. extraction yields, sustainability or high through-put.

Since potato peel is also a worthwhile source for phenolic acids such as chlorogenic, caffeic, gallic and protocatechuic acids, several applications using their antioxidant activity have been described [33-35]. According to Viscidi, Dougherty [36] phenolics such as catechin, chlorogenic acid and ferulic acid were mixed with other ingredients prior to extrusion for the manufacturing of rolled oats leading to products more resistant to oxidation. Although processing resulted in a 24 – 26% reduction of the amount of phenolics added, the final products had a higher phenolic content in comparison to the conventional ones.

Table 1: Selection of recent studies aimed at the extraction of phenolics from potato peels detailing optimal extraction conditions, maximum yields, method and cultivar used

Cultivar	Extraction method	Optimal conditions	Levels reported	Authors
Agria (White)	SLE	34 min at 89.9 °C and ethanol concentrations of 71.2%	3.2–10.3 mg/100 g db	Amado, Franco [37]
Russett Burbank (brown)	MWAE	MeOH (67.33%), time of 15 min and a MP of 14.67%	120–390 mg GAE 100/g dry	Singh, Sabally [38]
Lady Claire (cream)	PLE	70% ethanol, 125° C	409 mg/100 g db	Wijngaard, Hossain [39]
Lady Claire (cream)	SLE	75% ethanol, 80 °C, 22 min	431 mg/100 g db	Wijngaard, Ballay [24]
Diamond (white)	SLE	Methanol	112–291 mg GAE/100g db	Mohdaly, Hassanien [40]
Red	Subcritical water extraction	180 °C and extraction time of 30 min	81.83 mg/100 g wb	Singh and Saldana [32]
Vitelotte (Purple)	Ohmic heating assisted	100 °C for 1 sec 200 V/cm, water	84 mg/ 100g product	Pereira, Rodrigues [31]
Vitelotte (Purple)	PEF aided extraction	3.4 kV/cm and 105 ls (35 pulses of 3 ls), water	65.8 mg/100 g fw	Puertolas, Cregenzan [29]

Ramus	UAE	sonicated in a continuous air stream ultrasonic bath for 15 min	593.3 mg/ 100g dw	Samarin, Poorazarang [30]

SLE= Solid liquid extraction, MWAE = Microwave-assisted extraction, PLE= Pressurized liquid extraction, MP = Microwave power (watts), UAE = Ultrasound assisted extraction, PEF = Pulsed electric field, db = dry basis, fw = fresh weight.

2.2 Liquefaction of peels

In general, much research has been conducted to get vegetable residues liquefied, but most studies used various approaches. Lignocellulosic biomass represents a renewable, abundant and cheap source of raw materials for the chemical industry to develop biofuels, chemicals and biomaterials [41]. Several studies applied high pressure and temperatures [42], or used chemicals that will not be authorized for a food product, e.g. 2-ethylhexanol and diethyleneglycol [43]. These approaches are quite energy consuming, and will lead to high cost equipment. Therefore, these processes are not desirable for the AgriMax project.

Since potato peel wastes are rich in starch they are a valuable feedstock for ethanol production. However, prior fermentation the peels have to be hydrolyzed either by acids or by enzymes. Due to their biodegradability, high efficiency and ability to work under mild conditions, enzymes are more advantageous. Moreover, an enzymatic hydrolysis does not require a neutralization step like the acidic treatment [44]. Commonly, alpha-amylase from *Bacillus licheniformis* or from engineered strains of *Escherichia coli* or *Bacillus subtilis* is applied to liquefy the slurries. Depending on the used enzyme, reaction conditions of 55 – 85 °C and pH 5.5 – 6.0 are applied, exemplary for Ternamyl® and Liquozyme® [45, 46]. Several enzyme manufacturers (biocatalysts, DSM, etc) are actually offering plenty more enzymes that can be used to downgrade cellulose, hemicelluloses and pectins. By this means a liquefied product can be obtained which can be used to recover chemicals from vegetable origin. Possible applications of produced ethanol are biofuel or biopolyols [41]. Another possible liquefaction technology is the hydrothermal liquefaction in subcritical water. This procedure results in high values of the ionic product and can be used for different kinds of biomass. This is due to the fact that the density and dielectric constant of water decreases while the hydrocarbon solubility increases [47-50]. Li, Liu [51] applied this process to convert starch of rice, potato and sweet potato into reducing sugars which can be used for fermentation and ethanol production.

2.3 Aroma extraction from liquefied peels

Aroma is the volatile fraction of the product that consists of certain organic chemicals. Those products have a relatively low boiling point. Therefore, they pass out the product matrix and can be recognized by human senses, both taste and flavor [52, 53]. Aroma chemicals are considered as a high added value product, as they can be used in food but also in high value products such as perfume or cosmetics.

Aroma extraction has been developed by human kind since ancient ages [54]. Current methods are conducted in an industrial approach. To avoid great losses of the natural aroma that comes from vegetables, mild conditions (i.e. temperature) are advisable. One of the most used methods is the alcoholic extraction, which is actually used worldwide to recover several substances from their matrices. It consist of blending the raw material, usually chopped or liquefied, with a mixture of water and alcohol, commonly between 50 to 90% of alcohol [55]. The extraction time can vary from 30 minutes to several days. The blend is filtered and the liquid can be used directly or it can be distilled to separate the volatile components more concentrated.

Other interesting volatiles can be extracted by using centrifuges. Particularly, organic volatiles that are hydrophobic, at least partially, can be recovered by this process. When they reach a certain concentration, they can be separated from the water matrix which is normally a liquefied product. For example, those products are called 'cold pressed essential oils'. Essential oils can also be recovered using strong organic solvents, such as hexane or ethyl acetate, but those are not so appreciated by the market [53, 56].

Biotechnological approaches are used to create more volatiles in the product before they are recovered, as it is well known that aroma compounds are produced in secondary paths of vegetable metabolism. Enhancing some pathways of the metabolism, e.g. by using the addition of external enzymes, such as beta-glucosidases, can lead to the production of more volatiles and therefore, recovering a higher quantity [56]. An interesting technology to recover volatiles in mild conditions is the Spinning Cone Colum [57]. The volatiles are extracted by using steam (water) as an extractant at low temperatures under vacuum conditions. A system of rotary and stationary plates is applied to generate centrifugal force which causes the feed material to flow as a thin film on the surface of the cone. By introducing stripping steam the volatile compounds are separated of the liquids and slurries [57].

2.4 Ultrasound assisted extraction of toxic compounds from potato
2.4.1 Alkaloids content in potatoes

There are more than 4,000 varieties of native potatoes [58] which differ in characteristics such as the shape of the tuber or the color, but generally they have high starch content and are rich in minerals (especially potassium, magnesium and iron) and vitamins (B1, B2, B6, and C) [59]. Even if the tubers are a valuable source of nutritional elements, potatoes are also rich in steroidal alkaloids, a class of secondary metabolites commonly found in the plants of *Solanaceae* family. Steroidal alkaloids are associated with defense against bacterial [60], fungal [61] and insect attacks [62]. These compounds are toxic and their adverse effects on human health are typically associated with symptoms such as colic pain, gastroenteritis, diarrhea, vomiting, fever, rapid pulse, low blood pressure, and neurological disorders [63, 64].

The most abundant steroidal alkaloids in potatoes are α-solanine and α-chaconine. Both derived from solanidine by the linkage of two different trisaccharides to the hydroxyl group at carbon C-3 (Figure 1). In particular, α-solanine has a glycosidic chain that consists of glucose, galactose and rhamnose units, whereas α-chaconine has a different glycosidic chain made of two glucose units and one of rhamnose [65, 66]. The composition of the glycosidic chains is supposed to be related to the cytotoxic effects of the two alkaloids [67, 68], even if the cytotoxicity mechanism is still not fully clarified. The two toxins appear to be able to inhibit the human acetyl cholinesterase [69], the calcium transport [70], the transport through cellular membranes [71, 72] and even at low concentrations (micro molar) appear able to damage nerve cells. In vitro experiments showed that a-solanine and particularly a-chaconine are potent cytotoxins, acting rapidly to induce cell lysis [73].
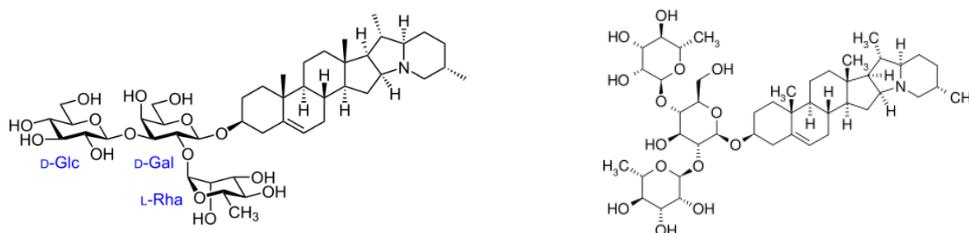

Figure 1: Structures of α-solanine and α-chaconine

Toxins accumulation in potatoes occurs mainly in the peel [67], as it represents the first barrier against pathogens attacks. This layer is also the main waste derived by the potatoes industrial processing, which results in between 70,000 and 140,000 tons of peels worldwide annually [74]. Even if this massive amount of waste could be a suitable feedstock for added value conversions, currently it is only used for animal feed or disposed causing environmental concerns. Potato peels quickly undergo microbial spoilage [59] and their use into valuable application is prevented by technical and economical limitations including alkaloids content.

2.4.2 Ultrasounds assisted extraction of alkaloids from potato peel

In addition to conventional extraction methods, several intensification techniques for the extraction of secondary metabolites from plant tissues have been proposed and tested also to remove alkaloids from potato peels [39, 75, 76]. Among these, ultrasounds-assisted extraction (UAE) is one of the most promising solutions, combining acoustic energy and solvent to extract target compounds from different plant matrices, resulting in an inexpensive, rapid and environmentally friendly process [77-79]. Similar to other secondary metabolites, the extraction of alkaloids, indeed, is hindered by the structure of the plant cell wall that retains these compounds from the solvent.

Ultrasounds generate acoustic waves that propagate into the liquid media causing alternating compression and expansion cycles. If the ultrasounds intensity is high enough, the expansion cycle can create cavities or bubbles in the liquid that suddenly collapse releasing high amount of energy. This phenomenon is called cavitation. The implosion of cavitation bubble can locally reach 5000 K and 200 atm and generates sharp liquid jets of up 280 m/s velocity [80]. The mechanical shear force caused by these jets breaks the plant cell wall (following different mechanism such as fragmentation, erosion, capillarity, detexturation, and sonoporation). This allows a greater penetration of solvent into the sample matrix, increasing the contact surface area between the solid and liquid phase and thus the mass transfer of the target compound toward the solvent [81, 82]. Moreover, ultrasounds can enhance extraction by reducing particle size and increasing the net hydrophobic character of the extraction medium (when the target molecule is non-polar) [83].

A number of parameters can be manipulated to optimize extraction of target compounds using ultrasounds, including extraction time and temperature, ultrasound amplitude and extracting solvent [80]. However, the outcome of the conditions tuning depends intrinsically on the nature of the matrix and the geometry of the system. Therefore, the main process variables can be grouped in physical and medium related parameters. In the first group the characteristics of the mechanic waves such as frequency, wavelength and amplitude are included. As well the influence of power input and the reactor design and shape of the probe can influence the process [84]. The medium related parameters include solvent chemo-physical properties, the reaction temperature, the presence of dissolved gasses and external pressure and the matrix properties.

A comprehensive review on the parameters affecting UAE and its mechanism has been recently published by Chemat, Rombaut [80].

2.4.3 Up-scaling and industrial applications of ultrasounds assisted extraction

As reminded by Vinatoru [85], UAE is a very complex process and what is observed in a volume of some milliliters (typical of lab scale experiments) is not indicative of a volume of one liter and absolutely different than a pilot scale reaction. Therefore, even if the application of UAE at laboratory scale is widely published, a minor number of applications have been commercially introduced. The possible major

problem in the application of ultrasound to industrial processing is the design and development of efficient power ultrasonic systems (generators and reactors) capable of large scale successful operation. Nevertheless, UAE is adopted in industry, for example in the food sector. It is used for extraction, degassing or cutting, but also for the inactivation of enzymes or the sterilization of equipment [80]. The main European manufactures of large scale equipment for UAE are Hielscher (Germany) and REUS (France).

2.5 Production of food microorganisms using pulp and process water

Literature about the use of agro-industrial wastes to produce beneficial microorganisms (e.g. biocontrol agents, baker's yeast, brewer's yeast, probiotic cultures) is only scarcely. Published references deal with the use of these wastes to produce secondary metabolites (e.g. enzymes, organic acids) and single cell protein (SCP). SCP or microbial protein is the dried form of various microorganisms, such as bacteria, fungi and algae. SCP is used as animal feed and as supplemental feed-stuff material. Several agro-industrial wastes have been used as economic substrates to produce SCP, including potato, tomato, oil mill and cereal wastes and wastewater. Other wastes like fruit pomaces, whey, molasses and lignocellulosic biomass have also been widely studied [86-89].

The yeast *Saccharomyces* (*S.*) *cerevisiae* is used for several food applications like brewer's and baker's yeast, wine production, biotechnology processes (e.g. enzyme, acid production, bioethanol), and also as SCP. The metabolism of *S. cerevisiae* is specialized for the utilization of glucose, fructose and sucrose. *S. cerevisiae* cannot be directly applied to convert cellulose. Therefore, pretreatments are required to release glucose from cellulose-rich wastes [90]. The wild-type of *S. cerevisiae* it is not able to metabolize xylose and arabinose, which are contained in lignocellulosic hydrolysates. In addition it is incapable of degrading starch. Moreover, this yeast is sensitive to furfural and hydroxymethylfurfural which are formed during the thermal pretreatment of lignocellulose [91].

Potato wastes are biomasses rich in starch and lignocellulosic constituents. Starch is the storage carbohydrate in plants, and it serves as an important energy and carbon source in biotechnological processes. Starch is made up of long chains of glucose units joined by α-1,4 linkages and joined at branch points by α-1,6 linkages. Many microorganisms, including *S. cerevisiae*, are not able to metabolize starch since they do not produce starch-decomposing enzymes such as α-amylase (which cleaves α-1,4-glycosidic bonds), β-amylase (which cleaves maltose units from the non-reducing end of starch), pullulanase or isoamylase (debranching enzymes that hydrolyze α-1,6-glycosidic bonds), and glucoamylase (which hydrolyzes glucose units from the non-reducing end of starch). Hence, it is necessary either to add starch-decomposing enzymes before fermentation with *S. cerevisiae* or to use a recombinant strain that produces starch-decomposing enzymes in order to utilize this carbon source [92, 93]. Potato wastes and wastewaters have been utilized to produce SCP from various microorganisms and also for the production of secondary metabolites. They have been used alone, enriched with other wastes or supplemented with chemically defined culture media or chemicals. Potato peel has been applied for the production of *S. cerevisiae* biomass [94]. For this peels were dried, ground, sieved and pretreated to convert cellulose into a more available sugar. Similarly, potato wastewaters from the production of starch have been used for the production of *Bacillus thuringiensis* [95]. Starchy wastewater from potato chip factory demonstrated to be as good as synthetic defined medium for the production of the probiotic strain *Streptomyces* [96]. Potato starch (chemically defined, not waste) has been found to be a good nutrient source for the growth of the yeast *Schanniomyces alluvius,* equally [97].

There are several studies on the production of microbial secondary metabolites using potato wastes and wastewaters. For example, potato wastes from the potato chip processing (rotten and substandard potato tubers, potato peel and substandard potato chips) were applied for the production of chitosan by

fermentation with *Rhizopus oryzae* [98]. Enriched potato wastes from potato flakes processing (without pretreatment) were also found to be a good nutrient source for the production of glucoamylase by several strains of *Aspergillus niger* [99]. Pagana, Morawicki [100] produced lactic acid using different acid lactic bacteria and sweet potato waste (peel and water with residual flesh) enriched with sugars. For this purpose, a previous enzyme hydrolysis of the waste was carried out. Further utilization of potato substrates (laboratory simulated wastes) was the production of a biosurfactant by *Bacillus subtilis* [101]. In this case, potato wastes were not hydrolyzed.

2.6 Protein extraction from fruit juice

During the processing of 1 ton of potatoes, it is produced and accumulated from 5 to 12 m^3 of potato fruit juice which contains a protein concentration of 30 – 41 wt% per dry matter (dm) [102, 103]. This leads to more than two million tons of potato fruit juice in the European Union per year [104]. The washed potatoes are rasped or milled and the fruit juice is separated by single- or multi-stage decanters. This aqueous by-product with approximately 5% dry matter mainly contains proteins (~35% of dm), sugar (~35% of dm), minerals (~20% of dm), organic acids (~4% of dm) and other components [105]. The maximum concentration of toxic glycoalkaloids (α-solanin, α-chaconin) amounts up to 100 ppm which is far below the permitted level in food products [106, 107]. The potato protein predominantly consists of patatin, protease inhibitors, high-molecular-weight proteins and is rich in lysine (7.18%) and methionine (1.06%) [108, 109]. As these fractions have high nutritional quality, antioxidant potential and valuable functional properties, its recovery is highly desired especially for use in human nutrition [110-112]. So far, the potato fruit juice is mostly applied as fertilizer by spreading the juice on the fields. However, in winter months this procedure cannot be done due to a reduced biological activity of soil. Therefore, high amounts of wastewater arise. Due to environmental regulations in the European Union, some countries investigated several methods to purify this waste stream and to recover valuable ingredients [104]. Commonly, proteins are extracted through precipitation by steam injection and pH adjustment leading to protein concentrates with yields about 50%. Such a process was developed by Westfalia Separator Industry GmbH and is shown on Figure 2 [113]. However, the recovered proteins possess a low solubility which is disadvantageous for food application [105, 114-116]. This is due to their denaturation at high temperatures which additionally involves a decrease of functionality, e.g. loss of emulsifying capacity, foaming capacity or water binding capacity [117].
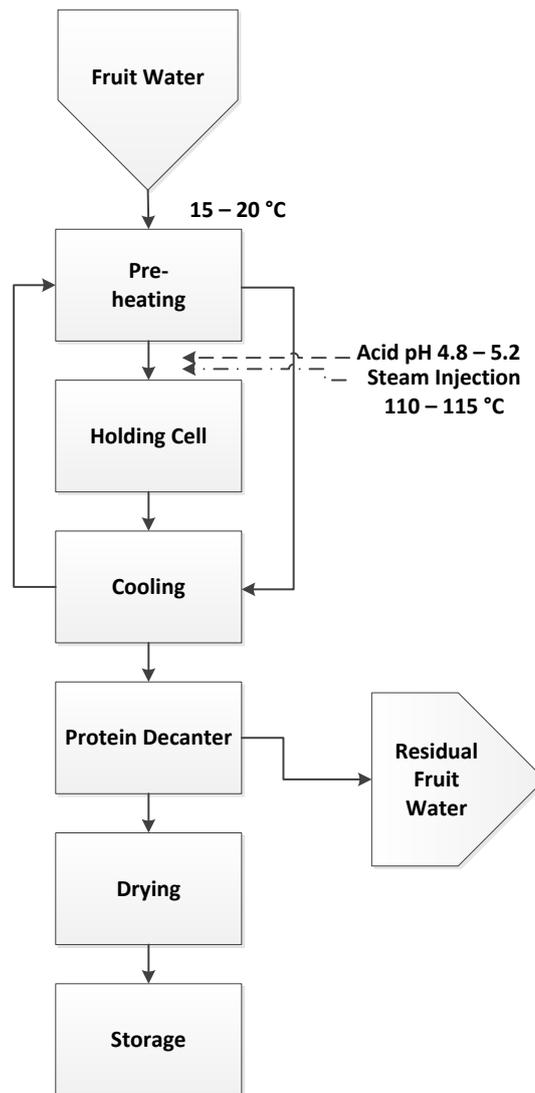
Figure 1: Protein extraction for potato fruit juice [113]

Potential procedures without heat treatment are represented by membrane filtrations e.g. reverse osmosis or ultrafiltration. During reverse osmosis an undesired salty and bitter taste of the proteins can arise and the functionality decreases. The ultrafiltration with a subsequent diafiltration is more promising because proteins with a higher quality can be manufactured and yields up to 50% arise. Unfortunately, these techniques are limited by the occurrence of membrane fouling at large scale processing and the presence of antinutritional factors like protease inhibitors or glycoalkaloids [102, 104, 116, 118]. Additionally, protein extraction of potato fruit juice under non-desaturating conditions was described in literature: the first step is concentrating the protein by disc stack centrifugation, followed by ultrafiltration, diafiltration and optionally freeze-drying [117].

The proteins of potato fruit juice can alternatively be precipitated by ion exchange (e.g. on carboxymethylcellulose) or adsorbed by bentonite [116, 119, 120]. Besides proteins, amino acid fractions can be separated by utilization of ion exchange resin. Moreover, the fruit juice is desalted and protein yields of 21 – 32% can be achieved. Disadvantages of the adsorption procedure are high amounts of protease inhibitors which occur in the protein concentrates. Moreover, the adsorbent has to be removed prior food application [118]. An alternative to heat coagulation is the precipitation at an acidic pH values. Several methods were tested and citric acid as well as ferric chloride was identified as most suitable

leading to soluble protein precipitates [105, 121-123]. Another study examined the influence of various additives on the solubility of proteins from potato fruit juice and figured out that the addition of $FeCl_3$, $ZnCl_2$ and organic solvents (methanol, ethanol, isopropanol) increased the precipitation and resolubility [118].

Modification of extracted proteins is efficiently performed by an enzymatic hydrolysis with proteases to increase the solubility, functional properties and nutritional values [124-126]. Waglay and Karboune [103] examined the proteases Flavourzyme, Alcalase, Papain and Novo Pro-D for hydrolysis of proteins isolated from potato fruit juice and figured out that Alcalase, Flavourzyme and Papain possessed high catalytic activities whereas Novo Pro-D showed a low degree of hydrolysis. Further differences were measured with regard to the end products: Papain generated unique peptides that can be related to protease inhibitor fractions, whereas Flavourzyme mainly produced peptides which arise from protease-inhibitors.

Similar to potato fruit juice, potato processing water is a source of proteins that arises throughout potato processing e.g. during spraying on potatoes to wash the excess starch and fiber off. Protein recovery was achieved by centrifugation, membrane filtration (filter paper 2.5 mm and 0.22 mm PVDF) and ultra-filtration with a 10 kDa PES-membrane [127].

2.7 Purification of pulp

After potato rasping and extraction of starch, the potato pulp accumulates in high amounts – approximately 0.75 tons of pulp arises per ton of purified starch, varying with the used plants and processes applied. Within the European Union, about 140,000 tons of dried potato pulps are generated during starch production annually [128, 129]. The pulp mainly consists of water which amounts up to 90%. Other ingredients include cell debris, intact starch cells and cell aggregates of the potato skin. Chemical analyses showed the presence of starch (37% of dm), cellulose (17% of dm), pectin (17% of dm), hemicellulose (14% of dm), fibers (7% of dm) protein/amino acids and ash (4% of dm respectively) [130, 131]. Untreated pulp can be applied as growth substrate for yeasts in vitamin B_{12} production or as component for other growth substrates in biogas production. The wet or partially dried potato pulp is mainly used as low value cattle feed to avoid decomposition [132, 133]. De-watering is achieved by decanters and results in an increase of the dry matter from 5% to 17 – 18% [134]. Distinctly higher amounts of dry matter (85 – 86%) can be obtained by using centrifugal sieves. An alternative is the application of pressure cloth filters, although this process is restricted by film formation and the limited processing due to batch-wise application [113]. The completely dehydrated pulp can be used in the paper industry to substitute wood fibers [135].

After extraction of nitrogen-containing components, potato pulp can be utilized as fertilizer. By hydrolysis the pulp is converted into suitable substrates for fermentations, e.g. alcohol production. Moreover, enzymatically hydrolyses are applied to modify and utilize potato pulp proteins. Kamnerdpetch, Weiss [124] showed that the endoprotease Alcalase and the exopeptidase Flavourzyme were most suitable while the hydrolysis can be further improved by the combination of both enzymes. Similarly, Waglay and Karboune [136] figured out that commercial available multi-enzymatic systems (e.g. Depol 670L and Ceremix 2XL) were most efficient.

Nutritional applications include the preparation of pectin or pectin-starch mixtures for food industry as described by Abousteit and Kempf [137]. The researchers obtained pectin fractions without starch contamination by hydrolysis at pH 3.0, atmospheric pressure and a temperature below 60 °C for 10 hours. Other studies focused on the processing of pectin fractions with high gelling abilities [138]. Separation of potato pulp into pectins and starch on the one hand, and cellulose and hemicellulose on the other was achieved by diluted sulphuric acid. Further fractionating can be performed by precipitation pectins with

methanol or acetone [139]. The extraction of galactan-rich rhamnogalacturonan I of potato pectic polysaccharides is gaining attention, due to its beneficial health effects. The microwave-assisted alkaline extraction was evaluated as most promising. Therefore, potato cell walls were treated at a solid/liquid ratio of 2.9% (w/v) with 1.5 M KOH at 36.0 W for 2.0 min in the micro wave, yielding 21.6% galactan-rich rhamnogalacturonan I [140].

Recently, potato pulp was evaluated for incorporation into gluten-free biscuits, manufactured with rice flour and potato pulp. The physical and sensory acceptability was very promising [141]. Besides, the pulp was examined on its usability as solid fuel. The analyses of its energetic value, densification for pelletisation and its elemental composition led to a promising evaluation as boiler fuel in comparison to other biomass types [142]. However, as the different treatments require a lot of energy only small amounts of potato pulp are processed for technical purposes and high amounts accumulate as agricultural waste. Therefore, further investigations for an increased used are needed to improve the economically value [130].

3. Valorization of tomato residues

3.1 Fertilizer production from cull tomato and tomato processing residues

After harvesting tomato fruits, huge amounts of biomass residues are left on the field (about 24,000 kg/ha, depending on cultivation conditions), namely tomato harvest stalks (plant residues, plant wastes or residual biomass). These wastes are mainly composed of lignin (19%), hemicellulose (14%), cellulose (50%) and pectin (5%) [143]. In addition, the industrial tomato processing generates residues (cull tomato) constituted by the discards of the production line, such as immature, defective or damaged tomatoes. They are discarded in the packaging houses and also in processing plants. The latter generate culls during washing and inspection. One kilogram of processed tomatoes results in 20 g of culls and 20 g of peel and skin residues [144]. Fresh culled tomatoes contain 14 − 20% crude protein, 4 − 5% ether extract, 22% cellulose and lignin (acid detergent fiber), 40 − 60% non-structural carbohydrates (of which 90 − 95% are soluble sugars) and 5 − 10% pectins [145, 146]. These residues often represent an added cost for manufacturing companies because of the disposal processes. The putrescible nature of cull tomato wastes means that storage durations longer than 6 − 7 days should be avoided [147]. During storage, uncontrolled anaerobic fermentation releases methane that has a strong greenhouse effect and affects the formation of tropospheric ozone [148].

These residues, especially cull tomato, are usually sold at low price for animal feeding. This is partly due to the small sizes of the enterprises and their broad geographic dispersion. Alternatively they are given for free to other companies or used as organic fertilizers [149]. However this land application is not an attractive option due to increasing stringent regulations [150]. Riggi and Avola [149] suggested that an environmentally friendly waste management system, capable of extracting high added-value compounds from the wastes (e.g. lycopene), should be applied. Particularly if combined with subsequent transformation of the remaining wastes using anaerobic processes (methane production) or aerobic procedures (composting) with positive side-effects such as nutrient and energy recovery and mitigation of greenhouse gas release [151].

Although composting is an older technology, it has emerged as a leading treatment technique for several bio-wastes, including tomato plant, cull tomato or even the solid fraction obtained after their anaerobic digestion. It is a simple technology consisting of user-friendly small composting plants equipped with tools already available on a farm. Thereby, undegraded organic biomasses are transformed and stabilized through an aerobic thermophilic bio-oxidation. Due to high temperature and aerobic microbial activities,

composting has the potential to remove pathogens and stabilize organic matter, thereby improving soil amendment properties. The success of composting is determined by several key factors, such as composition of materials, temperature, aeration, water content, pH, and turning. The C/N ratio of raw materials is recommended to be 20 – 30 for composting [152]. Tomato plant stalks and especially cull tomatoes usually contain a high nitrogen concentration, so they should be co-composted with carbon rich and relatively dry bulking agents, in the case of cull tomatoes, to balance the C/N ratio and moisture up to 40 – 60%. Several amendments have been used to adjust the initial C/N ratio of chopped tomato plant or cull such as cattle manure and sawdust [153]; two-phase olive-mill pomace plus poultry manure [154, 155]; almond shells and sewage sludge [156]; pine bark [157, 158]; biochar and chicken manure [159]; wheat straw and separated dairy manures [160]; hen manure and sawdust [161] with successful results. Composting of tomato wastes usually takes 2 – 4 months but advancements in composting technology have reduced its duration and improved the quality of compost by means of adding specific compounds or microbial inoculums [157]. The end product, namely compost, may be used as a fertilizer/soil amendment. The quality of compost produced from tomato wastes can be evaluated by stability and maturity parameters as well as the contents of organic matter, nitrogen, phosphorous, potassium, heavy metals, pathogens and the absence of phytotoxins. Most previous studies showed that compost from tomato wastes can have adequate organic matter, nitrogen, phosphorous, potassium contents for plant growth. Mendoza-Hernandez, Fornes [162] used composts prepared from tomato crop waste and mixed them with peat at different proportions as substrates for cutting rooting that improved rooting, root length and root weight of cuttings. Pane, Celano [163] evaluated the use of tomato-based composts within a tomato cropping system and obtained nutrition and bio-stimulation effects responsible for the increased productive response. It has been also reported that long-term applications of these composts improve the nitrogen status of the soil over the years [164].

A similar approach for treatment of these wastes is vermicomposting, which is a product of organic matter stabilization by microorganisms and worms that has been successfully used as a peat substitute in greenhouse tomato production [165]. There are corroborating reports of increased tomato yield when this product is applied [166, 167]. Fernandez-Gomez, Diaz-Ravina [168] demonstrated that the vermicomposting of tomato-plant waste together with paper-mill sludge at a ratio of 2:1 or 1:1 allows the recycling of both wastes, thereby improving the environmental sustainability of greenhouse tomato crops.

In agriculture practices, the use of bio-waste derived soluble substances at low dose, in place of conventional mineral and organic nitrogen fertilizers, could allow promoting plant growth and crop production at low cost. Simultaneously, the risk of environmental impact is minimized [169]. These compounds are defined as bio-stimulants and include humic substances (HS) among others. HS can increase plant growth or even make a crop less sensitive to stressful conditions by several mechanisms of action: stimulation of microbial activity, increased activity of a number of soil enzymes, increased production of hormones in the soil or growth regulators in plants and stimulation of numerous plant metabolism parameters [170]. Using similar procedures to those for extracting HS from the soil, it is possible to extract organic fractions, defined as humic-like substances (HLS), from compost. HLS obtained from composted organic wastes such as sewage sludge, animal and agricultural residues and household are known to improve plant productivity [171, 172]. The alkaline hydrolysis of a composted mix of urban food and vegetable residues has been also reported to be suitable as bio-stimulants [173]. Various liquid fertilizers containing humic acids have been commercialized for use on grass, horticultural plants or crop production [174]. In spite of their positive effect on the plant growth, their use remains controversial because of heterogeneity [175]. To overcome this, a process has been developed to produce homogeneous and high-value liquid organic fertilizer termed Hidrocompost™ from horticultural plant waste compost [176].

A step forward in formulation of fertilizers is the use of plant-growth promoting bacteria that formulated as bio-inoculants are demonstrably efficient and environmental-friendly alternatives to chemical pesticides and fertilizers [177]. They have been used to stimulate crop production through diverse bio-fertilization mechanisms, such as biological nitrogen fixation, solubilization of insoluble minerals, production of phytohormones and biocontrol processes that include phytopathogen antagonism and plant-induced resistance [178]. The presence of bio-protective microorganisms against plant pathogens and plant growth promoting microorganisms in tomato plant wastes based compost confers it an added value [179]. A further benefit of the interaction between microorganisms and stable organic matter is achieved through biological substrate enrichment. Canellas and Olivares [180] have reviewed basic mechanisms and benefits of the combined application of humic substances and plant growth-promoting bacteria to diverse crop fields. Martinez-Balmori, Olivares [181] demonstrated the use of vermicompost as a microbial carrier and identified the product's ability to preserve inoculated nitrogen-fixing bacteria.

In conclusion, several organic matter waste fluxes from tomato processing industries and extracting processes are suitable for the production of quality fertilizers. Thus, a direct self-supply of organic fertilizers for the improvement of farming productive cycles is provided. Concomitantly, the problem of disposing agricultural biomasses, vegetable feedstock and other wastes might be solved. Composting is one of the treatments of choice for fertilizer preparation because it can be performed using most of the tomato processing wastes as raw materials. However, it should be properly managed to obtain high quality compost. The presence of bio-protective microorganisms against plant pathogens and plant growth promoting microorganisms confers it an added value. In addition, composts can also be used for the extraction of soluble humic substances that have a well-known bio-fertilizer activity.

3.2 Lycopene extraction from tomato skins

Lycopene is the major carotenoid in tomatoes and is responsible for the characteristic red hue [182]. From a chemical point of view lycopene ($C_{40}H_{56}$) is a tetraterpenic hydrocarbon with 13 carbon-carbon double bonds, of which 11 are conjugated occurring in various geometrical isomers. The tomato by-products mainly constituted by tomato skins and seeds represents one of the richest source of lycopene. In fact, at the end of ripening stage, tomato skins can contain up to five times more lycopene than tomato pulp [183]. Due to its high degree of conjugation, lycopene is the most potent natural antioxidant among pigments [184]. As a natural antioxidant it may provide protection against a broad range of epithelial cancers and chronic diseases. According to studies in literature, lycopene may also play a role in reducing the risk of cardiovascular disease [185], osteoporosis, hypertension, male infertility and neurodegenerative diseases [186].
Lycopene's major commercial use is as a coloring agent in the food, nutraceuticals and pharmaceutical industries. Due to its deep red color, lycopene is one of the most popular natural authorized pigments and it has been used in the dyeing of various kinds of food products since many years [187-190]. Compared to standard colors, it shows a good color efficiency [191]. In addition, carotenoids are used as natural antioxidants for the formulation of functional foods or as additives in food systems in order to elongate their shelf life [33, 192]. In fact, processed foods are often fortified with carotenoids such as lycopene to increase nutritive value and/or enhance attractiveness. Furthermore lycopene is widely applied in the cosmetics formulations [193, 194]. The use of lycopene in the enrichment of edible vegetable oils contributing to develop a new functional food has been also been explored [195, 196]. For instance olive oil enriched with carotenoids, in particular lycopene, recovered from tomato seeds and skin was obtained as new functional food naturally enriched in antioxidants [197]. Health benefits of lycopene-enriched olive oils have been attributed to act against several disorders related with oxidative stress [198]. New tomato-

based juices enriched with lycopene and polyphenols also represent an innovative process for functional foods [199].

Many studies in literature reported about lycopene extraction from tomato and tomato waste, presenting a wide variety of different methods of extraction, from the conventional organic solvent extraction to the supercritical fluid extraction. Solvent extraction is the most widely used method for the recovery of carotenoids from plant materials, due to their hydrophobic nature and limited solubility in water. The main solvent extraction techniques applied for the extraction of carotenoids from tomato processing by-products are soxhlet extraction and agitation. Several parameters can influence the yield of extraction and many research studies have highlighted the optimization of these parameters (namely solvent type, solvent to solid-ratio, particle size, temperature, extraction time, extraction steps, particle size and moisture content) can increase the recovery [200]. Among these parameters, solvent type is usually considered as the most important factor. Due to its hydrophobic nature, common organic solvents have been tested for lycopene extraction, including hexane, acetone, ethanol, dichloromethane, ethylene acetate, benzene ethyl ether and petroleum ether and mixtures of polar or polar-non polar solvents in different ratios [201, 202]. However, in order to apply the lycopene extract in food products the solvents used for the extraction have to be non-toxic for human health. But the organic solvents used in most extraction processes have adverse effects on human health (most non-polar solvent are considered toxic) and cannot be completely removed. Therefore research for alternative environmentally friendly solvents is conducted. Among the published literature, two interesting solvents are proposed: ethyl lactate and d-limonene. Ethyl lactate is an environmentally friendly solvent produced from fermentation of carbohydrate feedstocks available from corn and soybean industries. The U.S. Food and Drug Administration have approved its use in food products. Ethyl lactate has a relatively high flashpoint and is colorless, environmentally benign and completely biodegradable into CO_2 and water [203, 204]. Some extraction procedures from tomato processing by-products using this solvent resulted in the highest yield of carotenoids compared to acetone and ethyl acetate [205, 206]. Limonene is the major constituent of essential oil resulting from the citrus fruit skins. D-limonene is extracted from orange peel through a steam distillation and used as a solvent for extracting lycopene from tomato, in comparison with dichloromethane [207]. Even though the final yield of lycopene extraction with d-limonene is lower than with dichloromethane, the procedure can be considered as an interesting alternative to conventional organic solvents.

Ultrasound can be used to aid in extraction, emulsification, homogenization, crystallization, filtration and drying. In fact the mechanical effect of ultrasound provides a greater penetration of solvent into the cellular materials. Thus, it results in the disruption of biological cell walls and facilitate the release of contents [208]. As reported in literature [209], sonication enhanced the extraction yield of lycopene from tomato with minor degradation and isomerization. Furthermore it allowed the application of lower extraction temperatures and a shorter extraction time. However this technique needs in any case a solvent to perform the extraction.

However solvent extraction of lycopene is performed at temperatures higher than room temperature and long heat treatments can cause a degradation of lycopene. Therefore microwave-assisted extraction may provide a solution to this problem. In fact microwave heats extracts within polar components quickly, accelerating the adsorption and desorption of the targeted compounds from matrix. In particular superheating polar cellular components improves migration of lycopene into the extraction solvent, while the short treatment times limit the heat exposure of non-polar components [210]. The extraction occurs as the result of changes in the cell structure caused by electromagnetic waves. By means of microwave it has been possible to evaluate the effect of treatment on lycopene isomers. Finally, microwave and ultrasound can be combined together, as reported in Lianfu and Zelong [211]. They applied ultrasonic and

microwave assisted extraction in a single apparatus to recover lycopene from tomato paste. By this, the extraction yield of lycopene was significantly improved. Microwave assisted extraction has some advantages compared to the conventional extraction techniques, including lower environmental pollution due to reduced consumption of solvent, higher extraction efficiency and a shorter extraction time. On the other hand, some disadvantages occur: additional filtration or centrifugation is necessary to remove solid residues. Furthermore the efficiency of microwaves might be poor when the target compounds or solvents are non-polar or volatile.

Another possibility to improve the conventional extraction is represented by enzyme-assisted extraction. In fact, enzymatic treatment may be used before conventional solvent extraction process, as a pretreatment. Enzyme-assisted extraction is based on the ability of enzymes to degrade cell walls and membranes under mild process conditions, allowing the release of bioactive compounds. This method also offers a more ecological approach. Several studies have investigated the use of enzymes for improving the extraction of lycopene from tomato processing by-products. The most used enzymes were cellulases and pectinases, followed by a solvent extraction with acetone, hexane, petroleum ether, ethyl acetate or mixtures of solvents [212-215]. In all cases, a significant increase of the extraction yield was observed, compared to the untreated samples. Finally, an interesting possibility is presented in a recent paper, where lycopene is extracted by tomato waste skins using a green chemistry protocol devoid of organic solvent [216].

Enzymatic pretreatments exhibit some advantages including reduction in extraction time and solvent consumption, increased yield and quality of product. However, some limitations still exist which are represented by the high costs of enzymes, the inability of enzyme preparations to completely hydrolyze plant cell walls and the difficult industrial feasibility of the conditions requested for the treatment.

The lycopene extraction can always be performed by means of organic solvent, but with the aid of high pressure. The extraction with high pressure is applied by employing temperatures from 50 to 200 °C and pressures from 9 to 15 MPa, which is known as pressurized liquid extraction or accelerated solvent extraction. The high temperatures positively affect the extraction and due to the high pressure applied the solvent maintain in the liquid state at the applied temperature. Under these conditions the liquid solvent is forced into the pores of the matrix and the biocompound solubility is increased. An interesting application is reported by Naviglio, Caruso [187], where a pressurized extraction method by use of the Extractor Naviglio is employed. Through this device lycopene is extracted from industrial tomato by-products at a pressure of 0.7 – 0.9 MPa and using tap water as extracting liquid. In fact lycopene, even if not soluble in water, forms molecular aggregates, which can be recovered by pressure/depressure cycles operating in the extractor device. Another possibility is to use even higher pressure, ranging from 100 to 800 MPa and low temperatures (usually room temperature), which is known as high hydrostatic pressure extraction. This technology has been used successfully for the extraction of many bioactive compounds from plant materials, including carotenoids from tomato processing products. Recently, Strati and Oreopoulou [188] investigated the use of this technique in extracting carotenoids, and especially lycopene, from tomato processing waste using a wide range of organic solvents. The authors found that high hydrostatic pressure extraction led to higher extraction yields compared to conventional solvent extraction process performed at room temperature for 30 minutes. The advantages of using high pressure for extraction processes are shorter processing times, reduced solvent consumption and higher extraction yields. In addition the high hydrostatic pressure extraction presents the advantage to operate at room temperature. While using lower pressure (pressurized liquid extraction), the temperature has to be increased which could affect the functional activity and structure of the bioactive compound.

Finally, supercritical fluid can be employed to perform lycopene extraction. Supercritical fluid extraction (SFE) has been described as an environmentally safe technology. SFE is based on selected properties of

the fluids. The most widely used compound is CO_2, due to its low critical temperature and its low critical pressure. CO_2 represents an attractive alternative to organic solvents because it is non-explosive, non-toxic, inexpensive, able to solubilize lipophilic substances and can be easily removed from the final products. The majority of the research studies in SFE for the recovery of carotenoids have focused on tomato products and industrial tomato by-products. For example Rozzi, Singh [217] demonstrated that lycopene can be extracted with substantial success from industrial tomato by-products with SFE using CO_2 without any other co-solvents. The results of this study indicated that the percentage of lycopene increased with elevated temperature and pressure. Main advantages of this technique are the high selectivity, short extraction times, increased pollution prevention and the use of non-toxic organic solvents [218]. Disadvantages could be represented by its high operating costs, since high pressures have to be applied to maintain the fluid in supercritical state.

3.3 Cutin extraction from tomato skins

With 40 to 85% (w/w), cutin is the main component of the tomato plant cuticle. Tomato cuticle displays a protecting film covering the epidermis of tomato fruits. It consists of lipids, polysaccharides (mainly cellulose and pectin), polypeptides, phenolic compounds and hydrocarbon polymers impregnated with wax. It is synthesized exclusively by the epidermal cells [219]. Thus, the plant cuticle can be considered as polyester waxes complex associates, with a very small hydrophobic nature reactivity, since most of the carboxylic groups present in the membrane are esterified with aliphatic hydroxyl groups of other fatty acids.

Due to the average weight of an isolated cuticle (around 600 µg/cm^2), cutin can be termed as the major lipid plant polymer. Chemically, cutin is defined as a polymeric network of polyhydroxylated C16 and C18 fatty acids which are linked by ester bonds [220-222]. Cutin plays an important role in cuticle as a structural component, as a defense barrier against pathogens [223], as protection against the uncontrolled loss of water together with waxes [222], as well as in transporting substances across plant tissues [224]. Cutin is generally extracted from plant material by using enzymatic treatments, organic solvents or acid hydrolysis. Enzymatic treatments degrade cell walls and membranes of cuticle as they destroy polysaccharides. In most of the studies reported in literature enzymatic treatments act as a pretreatment to degrade the cuticle, prior an extraction with organic solvents. The most used enzymes are cellulase and pectinase, generally employed in acetate or phosphate buffer [225, 226]. These enzymes hydrolyze cell wall components and disrupt the structural integrity of the plant cell wall.

By extraction with organic solvents lipid components of the cuticle are isolated, obtaining a dewaxed cuticle. Generally, the solvents used are chloroform and methanol in the Soxhlet apparatus. The extraction of cutin by using aceton in a Soxhlet apparatus for 24 hours followed by a reflux of the obtained solid material in a solution of propanol was reported and patented [227]. Another organic solvent used to extract cutin from tomato skins is prepared by dissolving potassium hydroxide in methanol. With this method the solid cutin is isolated and then precipitated by acidification [228]. In addition, Luque, Bruque [229] proposed the extraction with diethyl ether of the de-waxed product obtained by saponification to isolate cutin from tomato mature green cuticles.

Finally, another possibility to obtain cutin is by acid hydrolysis. By this means cutin samples were obtained after hydrolysis of dewaxed cuticles in an acid solution (6M HCl) for 12 h at 105 °C to remove polar hydrolysable components. Afterwards, samples were depolymerized in a 3% (w/v) sodium methoxide solution for 18 h at 100 °C [221]. However, a first initial treatment with organic solvent to dewax the cuticle is necessary.

In literature there are some examples of cutin extraction methods combining organic solvent extraction and acid hydrolysis [230, 231]. In some cases, an additional pretreatment of tomato skins is performed,

essentially constituted by a heat treatment with oxalic acid and ammonium oxalate to remove the residual pulp, that can remain attached to the skins [232].

Previous methods which successfully conducted organic solvent-free cutin extractions are very scarcely or missing, in particular by using tomato by-products as raw material. In fact, all methods reported aimed at analyzing the composition of cutin. Whereas no information is available about the use of cutin as raw material for other preparations. Instead, the method patented by SSICA and CTAEX in the previous European FP7 project BIOCOPAC (GA 286446, WO2015/028299 A1), is solvent-free and feasible to industrialization or scale up. This extraction process consists in solubilizing tomato skin in alkaline solution. The skins are mostly (about 78%) soluble in alkaline solution and this method exploits this property. Afterwards, the tomato skins were subjected to a thermal treatment with an alkaline solution (saponification). Subsequently, the raw cutin in solution as sodic resinates, was separated and cleaned of impurities, essentially by filtration and centrifugation. Finally, the solid extract is precipitated by acidification, separated and cleaned of impurities by centrifugation.

A possible application is the production of food microorganisms using tomato wastes. Supplemented tomato wastes have been tested as alternative culture medium for the production of carotenoids by *Rhodotorula glutinis* [233]. They found that higher concentrations of yeast extract negatively affected the formation of biomass but favoured carotenogenesis while higher amounts of glucose in the medium favoured biomass formation. In other sense, valorisation of tomato waste proteins has been studied by Moayedi, Hashemi [234]. It was shown that the proteolytic bacterium *Bacillus subtilis* produced antioxidant and antibacterial hydrolysates during fermentation of the protein fraction of tomato seeds.

4. Valorization of cereal processing residues

4.1 Cellulose extraction from wheat bran and oat husk

Cellulose, the most abundant polysaccharide in nature, has been purified from natural resources and utilized in uncountable applications during thousands of years. Natural cellulose fibers from cotton, flax, hemp, and sisal, have been utilized during millennia for their outstanding properties in textile applications [235, 236]. Furthermore, wood and non-woody plants such as bamboo have been applied extensively for the production of paper and cardboard both for printing and packaging applications [237-239].
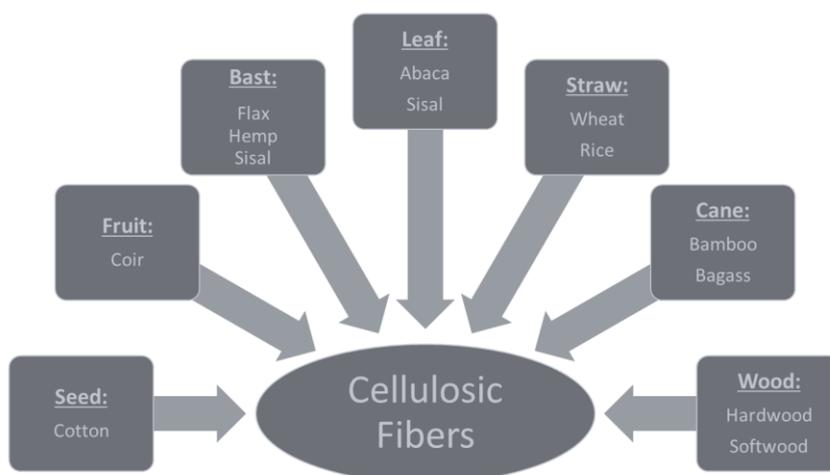

Figure 3: Common natural resources used for the production of cellulosic fibers. Adapted from Akil, Omar [235]

Advantageous features, such as the biodegradability, coupled with low cost, high specific strength and lighter weight than glass, have led to the extensive development of this environmentally friendly bio-based material [216]. In the last two decades, a new family of cellulose-based nanoscale building-blocks has appeared. New technologies have allowed disintegrating cellulose fibers into nanofibers at a reasonable cost [217-219]. These new nanofibers show diameters from 2 to 20 nm, and length in the range of several µm. Due to their immense available surface, compared with micrometric fibers, cellulose nanofibers (CNFs) offer an enormous potential for a wide range of applications, from reinforcement in composite materials to viscosity modifier in suspensions [220]. However, CNFs have been mostly produced from bleached wood pulp, which is used to produce fine paper, and thus has a considerably high price compared to non-renewable materials such as commodity polymers e.g. PP and PE. Therefore, some researchers have focused on the production of CNFs from agricultural residues, not only to decrease their cost, but also to mitigate the environmental impact of agricultural waste, moving towards a bio refinery concept. Recently, an extensive review from Jonoobi, Oladi [221] has covered the different preparation methods for CNFs from various natural resources and residues. Agricultural resources and residues such as wheat straw and soy hulls [222, 223], empty fruit bunches [224], sugar beet pulp [225], potato pulp [226], swede root [227], bagasse [228, 229], rice straw [228], banana rachis [230] and banana peels [231], have been used as a raw material for the production of CNFs. The extraction is conducted by mechanical processes, e.g. high-pressure homogenization, grinding, refining treatments or by acid hydrolyses. By mechanical treatments it is possible to isolate CNFs from cell walls without distinct cellulose degradation [221]. A comparison of three different mechanical processes showed that microfluidization and grinding needed less energy than homogenization. Moreover, the first-mentioned techniques provided higher film toughness [232]. The different isolation methods of CNFs are summarized in Table 2 [221].

Table 2: Mechanical isolation methods of CNFs [240]

Source	Process	Reference
Kenaf (bast) Kenaf (stem)	Grinding and homogenization	Jonoobi, Harun [241], Jonoobi, Harun [242]
Bleached potato pulp	Disintegration in a Waring blender followed by homogenization	Dufresne, Dupeyre [243]
Kraft pulp (Pinus radiata)	Refining, homogenization and grinding	Iwamoto, Nakagaito [244], [245]
Tunicin cellulose, chitosan, collagen	Ultrafine grinder	Taniguchi and Okamura [246]
Dried sugar beet pulp	Disintegration using an Ultra-Turrax mixer followed by homogenization	Leitner, Hinterstoisser [247]
Wheat straw	Cryocrushing, disintegration and homogenization	Alemdar and Sain [248]
Soybean stock	Cryocrushing and passing through a defibrillator	Wang, Sain [249]
Hemp, flax, bleached kraft pulp, rutabaga	Cryocrushing followed by homogenization	Bhatnagar and Sain [250]
Sugar beet pulp	Disintegration in a Waring blender; homogenization	Habibi and Vignon [251]
Bleached kraft pulp	Enzymatic pretreatment, high shear refining	Janardhnan and Sain [252]
Softwood sulfite pulp	Beating in a PFI mill, enzymatic pretreatment, second beating, homogenization	Henriksson and Berglund [253]
Rubber wood	Mechanical pretreatments followed by homogenization	Jonoobi, Khazaeian [254]

Empty fruit bunches	Mechanical pretreatments followed by homogenization	Jonoobi, Khazaeian [254]
Industrial bioresidue (sludge)	Ultrafine grinder	Jonoobi, Mathew [255]
Swede root	Homogenization	Bruce, Hobson [256]
Bagasse and rice straw	Ultrafine grinder followed by homogenizer	Hassan, Mathew [257]
Bleached kraft bamboo	Refining, chemical pretreatments and high-pressure fluidizer	Zhang, Song [258]
Aquatic weed plant water hyacinth	Cryocrushing followed by homogenization	Thiripura Sundari and Ramesh [259]
Prickly pear fruits	Disintegration in a Waring blender followed by homogenization	Habibi, Mahrouz [260]

ITENE previous knowledge has been obtained thanks to an extensive work in looking for new alternative sources for obtaining nanocellulose by valorizing all non-valuable raw materials existing in the nature. For example, in FUNKIFIBRE, a previous research project in the European FP7 framework, oat husk residues from cereal processing were converted into CNFs which were used as a reinforcing agent in the production of bio-composites for packaging applications [261]. To our knowledge, even though there are large numbers of papers in the production of CNFs using agricultural residues, there are no previous publications of CNFs from wheat bran or oat husk. However, some publications have reported the production of CNFs from sesame [262] and rice husks [263]. In the same manner, even though there are several patents related to production of CNFs, which are summarized in Appendix 1 (patent information), none of them includes wheat bran or oat husk as starting material for the production of CNFs. Otherwise, if they are not specific in the source of the plant fiber, they use different production methods than to proposed in AgriMax project.

4.2 Production and extraction of oligosaccharides and phenolic acids from wheat bran

4.2.1 Extraction of biomolecules from bran

Cereals are the most widely cultivated crops worldwide. Cereal grains are consumed universally and are considered to be one of the most important sources of dietary proteins, carbohydrates, vitamins, minerals and fibres for people all over the world. Wheat, together with maize and rice, accounts for about 90% of the world's cereal production, and for about half of the total cereal production within the EU [264, 265]. Based on previous data wheat has a great importance on EU economy and wheat-derived by-products can be considered as a feedstock for biorefinery development. Current worldwide wheat global production is more than 700 Mt/year [264, 265] and about one-fifth of the cultivated wheat total weight is converted into bran (90 to 150 Mt/year) [266, 267]. Currently, it is mainly used as a feed supplement, while the application in the food sector plays only a minor role [268]. However, there is great interest toward innovative strategies for valorising wheat bran through its transformation into added-value biomolecules.

Wheat bran is multi-layered (pericarp, testa, hyaline, aleurone layers and residual starchy endosperm) and consists of different cell types with different chemical compositions. Generally, it comprises approximately 12% water, 13 – 18% proteins, 57% carbohydrates, 4% fats and 1% phenolic acids [269, 270]. Wheat cell wall contains high amounts of oligosaccharides (such as arabinoxylan dietary fibres) and phenolic acids, mainly ferulic acid that acts as a cross-linker binding to sugar residues.

The general composition of wheat bran offers the potential to be used as a substrate in a bio refinery process in order to obtain valuable compounds. Firstly, following the classical route of a biorefinery, bran can be completely disintegrated and separated into fractions of high purity. By this building block chemicals to be used as precursors for higher polymerized compounds can be obtained. Secondly, bran, being a chemically heterogeneous material, contains substances that are valuable *per se*, but need to be separated and purified [269]. To this purpose, two different routes of wheat bran valorisation have been recently carried out aiming at the extraction of carbohydrate and/or non-carbohydrate-based products.

The carbohydrate fraction of wheat bran comprises starch, hemicelluloses and cellulose. While starch can be easily hydrolysed to glucose via enzymatic treatment, hemicelluloses and cellulose need harsher pretreatment steps, including heat treatment, acid and enzymatic hydrolysis. Important oligosaccharides which can be recovered from wheat bran are arabinoxylans and, to a lesser extent, β-D-glucans [269]. Target substances in the non-carbohydrate fraction of wheat bran are ferulic acid and other phenolic acids, followed by vanillin, proteins, amino acids and wheat bran oil. Phenolic compounds in wheat bran mainly consist of phenols containing one aromatic ring (such as hydroxycinnamic acids). More than 90% of the phenolic acids are present in a bound form, and can be released by hydrolysis under either alkaline or acidic conditions. The most abundant phenolic acid in wheat bran is ferulic acid with 0.2 – 15 g/kg. Ferulic acid is mostly linked to cell wall polysaccharides or to lignin via ester and ether bonds and can be released by treatment with strong alkali. Nowadays, the eco-sustainable extraction of this phenol demands a microbiological or enzymatic approach through enzymatic digestion with esterases [269]. This compound shows several beneficial activities for human health (such as antioxidant, anti-cancer, improving vascular function), and thus has a high potential of application in the food, health and cosmetic industry [268-270]. Moreover, ferulic acid isolated from crop by-products can be used as raw material for the production of natural vanillin [271].

The extraction of wheat bran components includes a range of different steps. Fractionation of the raw material allows to simplify its composition, to easily isolate specific high-value components and to a more efficient hydrolysis of fermentable sugars (e.g. for ethanol production) [268, 272, 273]. On the other hand, pretreatment represents one of the most expensive processing steps in wheat bran bio refinery [272] and can affect further exploitation of the recovered compounds (e.g. solvent extractions may limit food application). The most used pretreatments applied are mechanical grinding, thermal processes, ultrasound-assisted extraction, chemical or solvent treatment as well as enzymatic digestion.

Particle size, due to milling process, was found to influence phytochemical extractability. In particular, the recovery of phenolic acids, anthocyanins and carotenoids seems to increase as the particle size distribution decreases [274]. Moreover, extensive ball-milling was found to be the most promising mechanical grinding pretreatment with a strong specificity for the recovery of xylan-based polysaccharides and arabinoxylans [275].

Among thermal treatments, liquid hot water saccharification (especially for lab-scale optimisation) and steam explosion (more applicable to industry) are the most common. Both methods employ similar mechanisms for biomatrix destructuring, with an initial hot water biomass depolymerisation. The most notable difference is the release of pressure following heating performed either gradually (in liquid hot water treatment) or as rapid depressurisation (steam explosion) [273]. Recently, steam explosion-assisted extraction was found to be particularly effective in phenolic acid extraction, with a recovery yield gradually increasing with residence time and temperature [276].

Hydrothermal pretreatment is often chosen because of its relatively simple technological requirements such as the absence of corrosive and hard to recycle chemicals [266]. Generally, hydrothermal processes are performed at 180 – 190°C for 10 – 20 min because harder conditions induce the formation of toxic compounds, such as furfural and 5-hydroxymethyfurfural, generated from hexose and pentose

degradation [266, 272, 273]. Merali, Collins [277] demonstrated that hydrothermal treatment of destarched wheat bran resulted in degradation and depolymerisation of the hemicellulosic arabinoxylans together with some breakdown of cellulosic glucose, and this was associated with a significant reduction in the cross-linking phenolic acids and with a release of ferulic and diferulic acids.

Ultrasonication is a process able to destructurate plant cell walls resulting in the release of the most accessible polysaccharides as well as of the less extractable cell wall components in a shorter time and at lower temperatures. Short ultrasound-assisted extraction was used to isolate hemicellulose components (mainly phenolics-rich heteroxylans) of industrial wheat bran, leading to a sugar yield similar to that of the standard alkaline extraction, and shortening the process by about 60% with a lower NaOH consumption [278]. When aiming at phenolic acid recovery, ultrasonic procedure was found to be more effective than microwave extraction. This difference was attributed to the gelatinization of starch induced by microwave [279].

Classical chemical extractions of oligosaccharides and phenolic acids from wheat bran involve acid (such as sulfuric acid), alkaline (sodium hydroxide) and hydrogen peroxide treatments [275]. Solvent extraction offers the opportunity to partially disintegrate and fractionate biomass, but is less used in wheat bran exploitation. It was demonstrated that different ethanol/water ratios, were more effective in combination with enzymatic treatment [280]. The performance of the ethanol/water-enzyme process was similar to the hydrothermal-enzyme one, whit about 85% of the feedstock dissolved into the liquid phase [266, 280]. Enzymatic digestion of wheat bran can be considered either as a pretreatment, when the aim is to remove interfering molecules for further process steps (such as bioethanol production), or as an extraction technique, when the goal is the recovery of specific compounds (such as phenolic components or oligosaccharides). The use of amylase and/or xylanase for monomeric sugars or oligosaccharides isolation, of protease for peptides and proteins and of cellulase and hemicellulase enzymes, has been largely reported [266, 272, 273, 280]. Feruloyl-esterase was tested for ferulic acid and other phenolic acids release, but due to the extremely complicated structure of the cell wall, a combination with an array of enzymes having different digestion activities (e.g. xylanase), can be more effective [271]. Lasrado and Gudipati [281] proposed sequential enzymatic digestions (α-amylase, glucoamylase, xylanase) for the recovery of a mixture of xylo-oligosaccharides. On the contrary, Hell, Donaldson [275] did not recommend enzymatic treatments as well as fermentative ones for specific oligosaccharide recovery as it is hampered by the coextraction of other cell compounds. In general, the enzymatic treatments seem to be more advantageous against chemical ones as they are more cost and energy effective, more selective, produce a greater range of fractions with different chemical, functional and technological characteristics and also, there is no need for the solvent recovery and purification after the end of the extraction process [268].

Necessarily, the different extraction processes are followed by one or more purification steps, usually based on adsorption and desorption processes with activated charcoal and/or with high specific resins. Another possibility is a compounds isolation based on their solubility in different solvents. However, this is often costly and precarious [269].

Usually, multi-step processes were proposed for wheat bran valorisation, combining different type of treatments. For example, Hromadkova, Paulsen [282] sequentially extracted two different water-soluble arabinoxylan fractions: the first released during enzymatic digestion of starch and protein, the second recovered via NaOH hydrolysis. Wood, Cook [273] recently suggested a multi-step wheat bran bio refinery: sequential amylase, protease and xylanase digestion (leading to starch removal and to the recovery of arabinoxylans, glucose, xylan and arabinan and of proteins) followed by a thermal treatment (liquid hot water or steam explosion) and a cellulose digestion, before the final conversion of fermentable sugars to ethanol.

4.2.2 Valorization of ferulic acid and aromatic compounds as monomers for polymer synthesis

Based on the current state-of-the-art and certain in further future technological improvement, it is clear that wheat bran can be regarded as a mass by-product of enormous versatility, suitable for biorefinery challenge and valorization. In fact, wheat bran can be a source of phenolic and aromatic compounds that can be key intermediates in the manufacture of polymers [283]. Indeed, aromatic compounds offer rigidity, hydrophobicity, resistance against fire and the derived polymers are characterized by good thermomechanical and barrier properties. The attention of this section will be focused towards the preparation of thermoplastic polymers from aromatic phenolic compounds. Among these ferulic acid and vanillic acid are most available and can be used for the production of polyesters. Furthermore, it will be focused towards sustainable and green processes.

The first example of the polymerization of vanillic acid was described in 1955 [284]. Vanillic acid was converted to carboxylate by etherifying the phenolic moiety with ethylene dihalides and subsequently the carboxylate was esterified with ethylene glycol and condensed to linear polyester. The resulting polymer had a glass transition temperature (Tg) of 80 °C and a melting temperature (Tm) of 210 °C. This polymer was studied several times between 1955 and 1974 [285, 286]. Later, in 1981, the same strategy as well as a new one were developed by Kordsachia and coworkers [287] to synthesize vanillic and syringic acid-based polymers. In the new synthetic pathway, the phenolic moiety of vanillic acid was reacted with ethylene oxide, and the self-condensation of the product leads to a polyester with different aromatic substituents. Molar masses, measured by viscometry indicated that the first synthetic pathway provides polyesters exhibiting higher molar mass, in comparison to polyesters produced from the second method. With respect to the first method, the reported polymers showed a Tg of 69 °C and Tm of 212 °C in the case of vanillic acid and a Tg of 58 °C and Tm of 172 °C for syringic acid. From the second method, the polymers showed a Tg of 55 °C and Tm of 254 °C in the case of vanillic acid and a T g of 45 °C and Tm of 73 °C for syringic acid. Interestingly, the polymer produced from vanillic acid exhibits thermal properties similar to polyethylene terephthalate. However, the use of ethylene oxide requires an apparatus suitable for the treatment of toxic and explosive gases. Although the reaction provides complete conversion, the desired hydroxy-acid was only obtained after precipitation with sulfur dioxide, followed by sublimation and crystallization with a mixture of methanol and ethyl acetate. Then, the use of solvents is necessary for the purification step.

In 2010, the synthesis of bio-renewable poly(ethylene terephthalate) mimics, derived from lignin and acetic acid was reported [288]. The reaction starts from vanillin and acetic anhydride and leads to both, a perkin reaction and acetylation of the phenolic group. The resulting compound is hydrogenated and the generated acetyldihydroferulic acid is homo-polymerized. Zinc acetate proved to be the most efficient catalyst and the final material exhibits a molar mass of 17,800 g/mol (degree of polymerization around 100), a melting temperature of 234 °C, a transition temperature of 73 °C and 50% thermal decomposition (Td) at 462 °C. All these values are similar to the corresponding values of PET (Tm = 265 °C, Tg = 67 °C, Td 50% = 470 °C).

Similar, poly(alkylenehydroxybenzoate)s (PAHBs) from three lignin derivatives, vanillin, 4-hydroxybenzoic acid, and syringic acid were synthesized [289], in order to target materials with a wide range of thermomechanical properties. These aromatic aldehydes were oxidized into the corresponding carboxylic acids and the phenol moiety was derivatized with 2-chloroethanol or 3-chloropropan-1-ol. The resulting hydroxyl-acid monomers were homo-polymerized, using antimony oxide as a catalyst, yielding a wide variety of thermomechanical properties as a function of the aromatic substitution. In this series of polymers, the glass transition temperature was tuned between 50 and 70 °C and the melting temperature between 170 and 239 °C. A more sustainable chemical pathway from vanillic acid to polyethylene vanillate

has been recently reported [290]: in particular, etherification reactions of phenolic compounds with a bio-based reagent, ethylene carbonate, instead of chloroethanol, represents an eco-friendly way to improve the reactivity of the phenolic functionality. Then, a final solid state reaction allows reaching relatively high molecular weight (about 5000 g/mol). No purification steps are necessary and solvents are not used. Moreover, properties can be easily tuned by copolymerization.

In the current context of "green" chemistry, 100% bio-based polyesters were synthetized from ferulic acid and vegetable oil derivatives. In particular, a polyester from ferulic acid was produced by polycondensation [291]: first, ferulic acid was transformed into a more reactive monomer. Then, the carboxylic acid was esterified with methanol and the resulting compound was hydrogenated. Hydrogenated methyl ferulate was reacted with two equivalents of ethyl carbonate, yielding an AB monomer. The corresponding polyester was produced by a catalytic homopolymerization, and the final polymer exhibited a molar mass of 5400 g/mol and a semicrystalline feature with a Tg of –27 °C and a Tm of 25 °C. In spite of the presence of an aromatic ring in the monomeric unit, final properties are poor, probably due to the low molecular weight. Amorphous polymers were also synthesized by copolymerization with methyloleate and methylerulate derivatives. The same authors also reported the polycondensation of a vanillin derivative, another phenolic compound derived from biomass and similar to ferulic acid. The reaction strategy employs thiol-ene addition and yield semicristalline polymers [292].

An alternative path toward difunctional monomers for polyesters synthesis and starting from phenolic biomass derivatives is based on the coupling of phenolic substrates. This coupling could occur either on the phenol, yielding dicarbonyl, or on the carbonyl, yielding bisphenol. For instance, a diester was synthesized via the Williamson ether synthesis reaction of two equivalents of methylvanillate and one equivalent of 1,4-dibromobutane [293]. Bisphenols instead, can be obtained via a chemoenzymatic pathway [294]. These building blocks were used for polyester synthesis, for example, Pang, Zhang [293] copolymerized the dicarbonyl derivative with vegetable oil derivatives in order to synthesize fully bio-based semi aromatic polyesters. In order to produce difunctional symmetrical monomers, enzymatic coupling of several phenolic compounds was also investigated [295].

4.2.3 Valorization of aromatic compounds as additives for polymer formulation

Ferulic acid (FA) has gained considerable attention in recent years for its use in preventing oxidative stress. Indeed, many phenolic compounds, including FA, exhibit anti-inflammatory, antimicrobial and anticancer properties. As a photo-protective and antioxidant agent, FA also prevents harmful radiation effects both, as a UV absorber and a free radical scavenger [296-298].

Free FA is a good antioxidant due to its ability to donate hydrogen atoms of phenolic hydroxyl groups in reactions with peroxyl radicals. In this way, stabilized phenoxyl radicals are produced. FA has shown high scavenging activity for hydrogen peroxide, superoxide anions, hydroxyl radicals, and nitrogen dioxide free radicals [296]. The crosslinking properties of FA with both, polysaccharides and proteins suggests that it can be used in the preparation of complex materials to be used in biomedical, pharmaceutical, food, and cosmetic applications [296, 299]. To control the release of FA via diffusion, it has been incorporated into an organic-inorganic nano-hybrid material or has been modified with polymers containing cinnamoyl moieties chemically conjugated as pendant groups to improve photostability [300]. The authors were successfully improving the unstable bioactive compound from decomposition and improving drug loading by chemically incorporating FA into a hydrolytically degradable polyanhydride backbone, enabling controlled FA release.

These characteristics of FA can also be exploited in polymer formulations since during processing and service life polymers are subjected to oxidative degradation due to light and temperature. Nevertheless,

although FA exhibits beneficial properties, it undergoes thermal-, air-, and light-induced decomposition, which reduces its efficacy. In general, the main drawback of the use of extracted natural phenols is their generally limited temperature stability, which causes their degradation during polymer melt processing. Furthermore, natural phenols have often limited solubility in polymers [301].

A way to adapt natural antioxidants to their use in polymers is their derivatization. In fact, by derivatizing hydroxycinnamic compounds, an increase of their activity and thermal stability can be obtained. Another way is their insertion into inorganic host filler in order to avoid diffusion as well as to limit as much as possible their thermal degradation and reactivity with polymer chain.

The derivatization of FA and its use as antioxidant additives are reported by Reano, Cherubin [302] and [303]. They enzymatically synthesized bis- and trisphenols from FA and bio-based diols (butenediols, propanediols and isosorbide) or triols (glycerol). Afterwards, their antioxidant activity at different concentrations and processing methods were investigated in polypropylene (PP) and polybutylene succinate (PBS). In case of PBS, the trisphenols antioxidant was more efficient, while in case of PP the commercial antioxidant Irganox 1010 was better. Indeed, they reported difficulties during melt compounding of PP due to sticking in the feeder and condensation on the extruder equipment. These problems were avoided by processing PBS with solvent casting. However solvent casting is not coherent with green chemistry. Good efficiency of natural extracts was also observed on the thermal resistance and processing under oxygen with PP [304].

Coelho, Hennous [305] developed a strategy for the insertion of FA and other natural antioxidants inside layered double hydroxide. The UV shielding properties were tested when melted inside PBS. They reported that a better UV stability was not fully demonstrated but an enhancement of mechanical properties in the molten state was obtained and less carbon dioxide during photodegradation was formed. On the other hand, crosslinked polymers with antioxidant properties were synthesized inserting FA in a polymer based on methacrylic acid (MAA) and using ethylene glycole dimethacrylate as co-monomer and crosslinker [306]. Co-polymers of FA and methacrylic acid were also obtained in the work of Iemma, Puoci [307] with antioxidant and antifungal properties. The method used was a one-step radical polymerization based on the use of water-soluble redox initiators which allowed us to obtain the copolymer through the direct polymerization of FA and MAA [307].

To our best knowledge, there is no literature focusing on the effects of FA in the agriculture but there are some papers about the effect of incorporation of FA in biodegradable polymers commonly used in the agriculture such as PLA, PBS or starch.

FA has also been effective in increasing the thermal and mechanical properties of PLA. It was reported that introducing bio-mesogenic units could increase the thermal stability and reinforce the elastic properties, while reducing the melting temperature, the degree of crystallinity and the enzymatic degradation rate. The nontoxicity and biocompatibility of degradation indicates promising candidates for medical applications in the area of tissue engineering [308]. Cerruti, Santagata [309] incorporated phenolic compounds derived from wine production residues in starch biopolymers. This natural additive caused a plasticization effect in the obtained extruded films and promoted an earlier disintegration.

According to Kim, Kim [310] and Rizzarelli and Carroccio [311] PBS can undergo three different degradation mechanisms depending on the storage conditions. Like all polyesters, PBS is sensible to hydrolysis by exposure with liquid water or water vapor. In the absence of water, heat, UV light or mechanical stress it can produce primary radicals on the polymer backbone leading to the formation of peroxyl radicals. In the presence of oxygen, the radical–radical coupling of an oxygen molecule with a carbon atom leave a carbon centered free radical. This process can be interrupted by primary antioxidants. Aiming at proposing bio-based antioxidants, the use of natural hindered phenolic

compounds exhibiting antioxidant activity has received increasing interest. Examples are α- tocopherol, lignin, carvacrol, thymol or curcumin.

In the case of skin applications, a high activity or release rate is required. Researchers have been investigated to improve the release rate by increasing the hydrophilicity of the formulation with the aid of incorporating ethylene glycol functionalities in the polymer backbone or using ethylene glycol as linker between two FA molecules, enabling increased polymer hydrophilicity to promote polymer degradation and promote faster FA release. The chemical structures and physical properties of the polymers influence the FA release rates and antioxidant activity (see results in Figure 4, [301]).
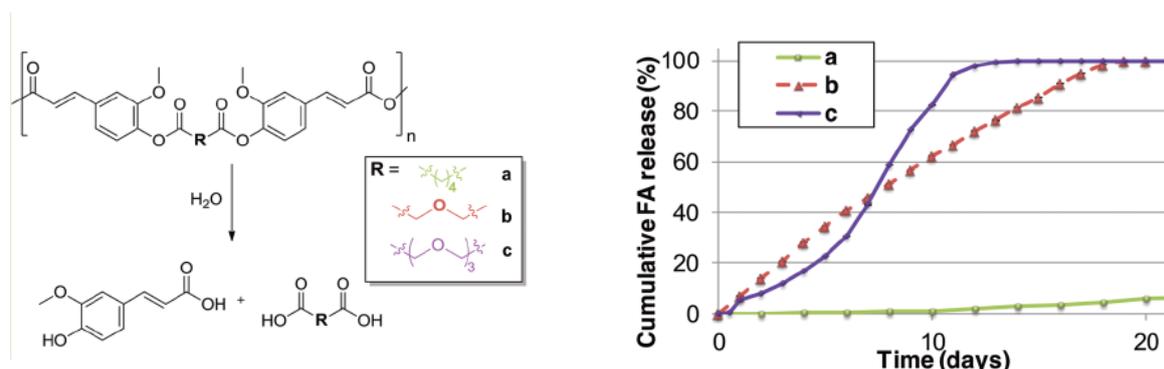
Figure 4: Comparison of release rates between ferulic acid and its derivatives [301]

FA-based poly-anhydride-esters have been found to enable controlled bioactive release and prevent the bioactive functional groups from degradation. As described herein, by incorporating FA into a polymer backbone, the FA retained its antioxidant activity when released via polymer degradation. Further, the FA-based polymer prevented discoloration, indicating a promising FA-based topical formulation [301].

4.3 Production of food microorganisms using cereal processing residues

The production of different bacterial and yeasts strains using wastes from cereal processing have been referenced. Poopathi and Archana [312] investigated the production of *Bacillus thuringiensis* from powdered wheat bran, chickpea husk and corncob and their combinations, and found that corncob supplemented with $MnCl_2$ was as good as Luria-Bertrani medium for its production but 50 times less expensive. To perform liquid fermentation with these by-products, they were boiled and extracted. Wheat straw, barley straw, chili stubble, oats hull and starch glucose were used for solid fermentation of *S. cerevisiae*. Biomass and digestibility of the protein obtained were determined [313]. The production of single cell proteins from *Candida utilis* and *Rhizopus oligosporus* by microbial conversion of wheat bran has been studied. Growth parameters including inoculum size and age, temperature and incubation period were optimized [314] for this process.

The performance of six microorganisms of industrial relevance (*Escherichia coli*, *Corynebacterium glutamicum*, *S. cerevisiae*, *Pichia stipitis*, *Aspergillus niger* and *Trichoderma reesei* were tested for their ability to grow on lignocellulosic biomass hydrolysates obtained from sugar cane bagasse, wheat straw, corn stover and willow wood. Besides, their resistance to growth inhibitors present in these hydrolysates was evaluated [91]. For this, raw materials were previously hydrolysed by enzymatic hydrolysis or by acid hydrolysis using concentrated sulfuric acid. Some growth inhibitors (e.g. furfural, acetate) were present in acid hydrolysed feedstocks. However, all tested microorganisms showed a good growth behaviour on

the pretreated materials. *P. stipitis* and *A. niger* exhibited the overall best performance on renewable feedstocks. Therefore, lignocellulosic hydrolysates from different feedstocks can be used as substrate for industrial fermentations.

5. Valorization of olive residues

5.1 Liquefaction and aroma extraction from olive pomace

The liquefaction and aroma extraction from olive residues are similar to the processes with potato peels (paragraph 2.2 and 2.3). Studies about the liquefaction of olive stones were published by Tejeda-Ricardez, Vaca-Garcia [315]. The liquefaction was performed with phenol (71%wt) and sulfuric acid (6%wt) at 170 °C for 2 h. The products are meant to be used as raw material for phenol-formaldyhe resins. Similar, Briones, Serrano [41] conducted a mild liquefaction of olive stones with polyhydric alcohols to obtain biopolyols. Liquefaction treatment of olive husks were also reported [316-318], whereas information about the liquefaction of olive pomace is rather scarcely [319]. Likewise, reports about the aroma extraction of olive residues are rare due to a more commonly extraction of polyphenols and pectins from olive pomace [320].

5.2 Disintegration of olive pomace and leaves

The disintegration of olive pomace and leaves by steam explosion has been proposed within the AgriMax framework. Steam explosion has been applied for wood already in the thirties of the past century [321]. Nowadays it is still an important technology for treatment of woody biomass with the biofuels development as alternative for the much more intensive torrefaction of biomass, which takes place at higher temperatures and pressures [322]. In general, the biomass is exposed to direct steam for a certain time and pressure ranging from $130 - 220$ °C for 30 seconds to 10 minutes. After a sudden pressure release the steam, which has penetrated within the biomass, expands and a large part of the plant infrastructure is destroyed, making the material more available for enzymatic hydrolysis. In this way enzymatic conversion of cellulose to glucose is improved. This results in high yields of woody biomass to for example bio-based ethanol [323-325]. Some demonstration plants are put into operation but the technology has not yet reached full maturity yet. As such the effects of steam explosion are twofold: the short period of intense temperature and exposure to high pressure steam and water causes reactions to take place, such as hydrolysation of hemicellulose or the formation of furfural or similar substances. These reactions can be enhanced or slowed under addition of chemicals or acid. For example under alkali condition lignin will be dissolved and the conversion rate of hemi-cellulose will be lower. Secondly there is the disruption of the plant fibers of the steam explosion. Both effects can improve the extraction of valuable compounds from biomass. The destruction of plant structure can make certain molecules more available for dissolution by a solvent [323, 326].

Due to the fact that olive crops have to be cut down regularly during cultivation to achieve high yields (olive pruning), huge amounts of residues are generated. Depending on the culture conditions, 1 to 3 tons arise per pruning process. The residues mainly consist of thin branches, leaves and wood, comprising cellulose, hemicellulose, lignin, minerals and extractives. Valuable compounds of the extractives include glucose, phenolics and other antioxidants [325, 327-329]. Steam explosion is considered as an effective pretreatment for obtaining valuable compounds from olive residues, including pomace and leaves [330, 331]. Cara, Ruiz [325] applied steam explosion as a preparatory process for the use of olive residues, mainly olive wood as substrate for enzymatic hydrolysis. Furthermore, it was described that olive pomace treated with steam explosion is a good source of fermentable sugars [332]. Likewise, various phenolic

compounds (e.g, vanillic acid, tyrosol, hydroxytyrosol) can be separated from olive stones and seed husks by steam explosion [333].

Patents literature on pretreatment and olive oil wastes is limited. The different components will probably behave differently in steam explosion: The pulp might have no big benefit from pretreatment. For the olive stones and leaves it may be useful, but probably different optimal conditions apply. Important for the process steps downstream are also the washing and neutralization procedures [323, 326].

5.3 Extraction and purification of phenolic compounds from olive pomace and leaves

Since olive processing residues are rich in bioactive compounds especially phenolic acids, triterpenic acids and flavonoids, their extraction is highly desired and numerous application possibilities exist. By this means olive residues can be valorized. Several methods for the extraction of phenolic compounds are applied, e.g. extraction with organic solvents, ultrasound- or microwave-assisted extraction and high-pressure processes [334-337]. Most commonly, solid/liquid extraction is used for plant materials whereby the extraction yield is dependent on the applied parameters. For example, the addition of water enhanced the polyphenol yield during extraction with ethanol [338-340]. Furthermore, an adjustment of the pH value to an alkaline milieu increased the extraction due to an improved solubility of the phenolic substances [341].

Olive pomace arises during olive oil production with 800 kg/ton olives and approximately 7 millions of tons per year in Europe. It is composed of skin, pulp, stone and olive kernels [342]. Polyphenols of olive pomace are extracted under high pressure and incubation (25 bar, 180 °C for 90 min) with a mixture of ethanol:water (50:50 v/v) and yields in 5.77 mg caffeic acid equivalents/mL, measured by the Folin–Ciocalteu assay [343]. In contrast, the successive extraction of defatted olive pomace with chloroform, chloroform:methanol (9:1) and methanol resulted in 207 – 210 mg oleuropein equivalents/kg (Folin–Ciocalteu colorimetric method). Another procedure was described by Berthet, Angellier-Coussy [342]: the milled olive pomace was mixed in a liquid ratio of 1:15 (w/w) with ethanol:water (70:30) and extracted at 80 °C for 90 min. The main phenolic compounds in olive pomace were oleuropein, ligstroside aglycone, tyrosol, oleuropein aglycone, caffeic and ferulic acid, varying depending on the cultivar [344]. For purification of the phenolic extracts, solid-phase extractions with silica-based C-18 cartridges are used. The phenolic recovery can be raised with this purification step up to 97 – 100% [345]. Furthermore, nanofiltration was described as a promising technology to purify polyphenols from olive mill waste waters [346].

Olive leaves represent about 10% of the harvest weight and contain higher concentrations of antioxidants than the other parts of the plant [347, 348]. Traditionally, polyphenols of olive leaves are extracted by maceration. However, the efficiency is rather low [349]. Therefore, several other techniques were developed, e.g. supercritical fluid extraction, pressurized liquid extraction, derivatized polar extraction, dynamic ultrasound assisted extraction and microwave assisted extraction [350-352]. The best extraction conditions for phenolic compounds of olive leaves were determined by response surface methodology. According to Sifaoui, Chammem [353], an extraction with water at 58 °C, pH 8 for 54 min and a liquid-to-solid ratio of 77:1 were most effective. The best conditions for an alcoholic extraction were published by Mkaouar, Bahloul [354] and are composed of 95.6% ethanol, 55 °C and 40 ml/g dry matter. By applying an ultrasonic-assisted extraction at high temperatures, the polyphenol yield can be further improved [349]. The use of hydroalcoholic solvents, like methanol or ethanol-water mixtures were investigated in detail, due to their ability to extract lipophilic as well as hydrophilic phenolic compounds [336, 355]. The main phenolic substances in olive leaves were analyzed by high performance liquid chromatography

(HPLC) coupled with Photo Diode Array Detection (DAD) and showed six major compounds: oleuropein, verbascoside, luteolin-7-O- glucoside, apigenin-7-O-glucoside, hydroxytyrosol and tyrosol [356-358].

The polyphenols of olive oil chain by-products including olive leaves, olive pomace or olive oil mill wastes have different application potentials in the food market [359-362]. Polyphenols have evidenced antioxidant activity [33-35, 363, 364] and antimicrobial effects with protective effect against pathogenic agents, both gram-positive and gram-negative bacteria, yeast, and molds [365-367]. In addition, flavonoids have been related with enhancements in the antiviral activities [368]. The incorporation of polyphenol extracts such as gallic acid from waste waters of olive oil pomace has also been tested in enriched meat such as pre-cooked beef or pork improving their lipid stability [369]. Moreover, polyphenols could be an interesting ingredient in the design of new beverages for their potential benefits on human health [370, 371]. For instance, Kranz, Braun [372] evaluated fruit smoothies fortified with olive leaf extract containing high amounts of oleuropein and hydroxytyrosol determining that at higher polyphenol levels of 20 mg/100 g, sodium cyclamate and sucrose were able to reduce bitter taste perception.

5.4 Purification of olive fibers

The dietary fiber content of olives varies among the different cultivars, but is in general noticeable with 5 – 20 g/100 g total dietary fibers [373-375]. Almost one third of olive pulp cell walls consist of pectic polysaccharides with an esterification degree of more than 80%. The soluble fraction is mainly composed of polyuronides and arabinans, the neutral fraction of arabinans with arabinose and the acid part homogalacturonans and rhamnogalacturonans [374]. Olive endocarp is mostly lignified and contains high amounts of cellulose and hemicelluloses [376]. As olives are predominantly processed to oil by pressing, the residues of olive oil production are rich in dietary fibers. Olive pomace is composed of 65.3 wt% insoluble fibers and 5.5 wt% soluble fibers. Therefore, insoluble fibers represent the major fraction (approximately 92%) with hemicellulose, cellulose and lignin being most represented [377]. Due to their limited application, only a few refinery processes were described. Valiente, Arrigoni [378] used cellulases, hemicellulases and pectinolytic preparations to saccharify fibers of olive press cake and incorporated them in bakery goods. A prior treatment with chlorite improves the enzymatic hydrolysis [379]. Dufresne, Dupeyre [380] used lignocellulosic flour of ground olive stones for the production of poly-(hydroxybutyrate-co-valerate, PHBV)-based composites and measured a significant reinforcing and a stabilization effect. Another study described the incorporation of olive husk flour into a polypropylene matrix [381]. The researchers observed an improved thermal stability of the composites. The fibers were purified by an extraction with methanol/water (90:10) for 12 h at room temperature to remove starch and waxes. Similar, an extraction of olive pomace with ethanol/water (70:30) for 90 min at 80 °C was applied to remove polyphenols [342]. This aimed at preventing browning reactions due to their oxidation. Afterwards, the fibers were recovered by filtration and purified by an acid-alkaline fusion.

Besides their application as composites, fibers of olive cell wall were extracted from olive mill by-products and are designated for the derivation of microcrystalline or powdered cellulose, gelling agents or fat replacements [331, 375, 382-384]. Pectic material of olive pomace, which could replace fat in confectionary, was obtained by an extraction with nitric acid. Afterwards, the substrate was purified with chelating agents and recovered by an alcoholic precipitation with ethanol [382, 385]. The recovered olive pectin extract possessed a methylation degree of 42% and its rheological properties were comparable to citrus pectin.

The extraction of dietary fibers from olive mill wastewater was conducted by citric acid and ethanol. Subsequently, ethanol was added to precipitate the alcohol insoluble residues. The isolated and concentrated water soluble fraction showed gel forming abilities [383].

5.5 Production of food microorganisms using olive mill wastewaters

Olive mill wastewaters (OMW) is characterized by large variations in its chemical composition mainly depending on olive cultivar, harvesting period and extraction system [386]. The organic fraction of OMW is composed of sugars, poly-phenolic compounds, organic acids and residual oil [387]. Polyphenols could exert antimicrobial or toxic effects against target microorganisms and thus, it is not convenient to be contained in culture media. For this reason, OMW can be submitted to a chemical process in order to decrease its polyphenolic content.

OMW has been investigated as a medium source for the production of single cell proteins and secondary metabolites. Solid fermentation of OMW by different *Pleurotus* species, *S. cerevisiae*, *Kluyveromyces lactis*, *Oidodendron* spp. and *Penicillium* spp. in order to produce microbial biomass and bioremediation has been investigated [388]. Aouidi, Khelifi [389] studied the production of *Geotrichum candidum* biomass, for its use as starter for cheese production using a combination of OMW enriched with cheese whey and found that the combination was a cost effective medium. OMW was also a good source of nutrient for the production of microbial protein from new isolated yeasts, e.g. *Schwanniomyces etchellsiii* M2 and *Candida pararugosa* BM24 [390].

Lipase production by *Candida cylindracea* on a supplemented OMW has been investigated by Brozzoli, Crognale [386]. The production of citric acid by means of OMW fermentation using *Yarrowia lipolytica* strains has been also studied [387]. In this sense, Sarris, Galiotou-Panayotou [387] examined citric acid and biomass production of *Yarrowia lipolytica* on OMWs supplemented with sugar and nitrogen compounds and found efficient growth of different strains when cultivated on glucose-enriched OMWs. Moreover, polyphenols were reduced to 13 – 34% in all fermentations. Similar results were obtained by Papankolaou, Galiotou-Panayotou [391].

Solid wastes from the olive oil processing (waste pomace) have also been studied for the solid state fermentation with the aim to provide a substrate for yeasts [392]. In this study, solid wastes were submitted to an alkaline pretreatment and to a delignification process by *Phanerochaete chryosporium*, *Phlebia radiate*, *Pleurotus ostreatus* or *Dacrymyces stellatus.* Subsequently, a saccharification by *Trichoderma* spp. was performed to provide substrates for *Candida utilis* or *S. cerevisiae.* A combination of these processes increased the level of crude protein in the raw pomace suggesting that it could be used for animal feed.

6. Conclusion

This review summarized the valorization potential and technologies of agricultural and food waste products, especially of tomato, olive, cereals and potatoes. These materials exhibit considerable economic impact due to their high occurrence within the EU. It was demonstrated that several valuable compounds can be extracted by different techniques out of food wastes and by-products. Furthermore, numerous application possibilities were described. Nevertheless, the processes are improvable, e.g. to enhance the extraction yield, to reduce process effort and costs or to develop more application opportunities. Besides, it would be preferable to simplify and generalize the methods to increase the applicability. Therefore, further research and optimization studies on valorization technologies might be necessary.

7. Appendix

7.1 Patent information

Potato						
Topic, nº	**Patent**	**Priority date**	**Applicant**	**Status**	**Abstract**	**Relevance/ Differences vs. AgriMax**
Potato protein purification 1	WO2010139734 (A2) - METHOD FOR SEPARATING PLANT PROTEINS Patent in German	2009	Südchemie	published	The present invention relates to a method for separating plant proteins using a three-layer mineral	The patent explicitly addresses the separation of potato proteins from other fruit juice constituents such as glycoalkaloids and protease inhibitors and thus the provision of a purified patatin fraction. This is relevant for AgriMax.
Potato Protein purification 2	US201113637029. Process for Manufacturing Soluble and Functional Plant Proteins, Products Obtained and Uses	2011	Roquette	Not available	The invention relates to a process for manufacturing soluble and functional plant proteins, characterized in that it comprises at least one functionalizing step that consists of a treatment of 0.01 s to 1 s constituted of a step of heating plant proteins at a temperature of 100 DEG C. to 160 DEG C. and a step of cooling the heated plant proteins. The invention also relates to a process for converting non-functional plant proteins to functional proteins. Another subject of	Highly specific process for the re-functionalization of proteins. Could be applied on denatured pulp protein but in general not of a high relevance

					the invention is a plant protein, characterized in that it has a solubility in water of greater than 50% (with the exception of a potato protein for which the solubility in water is 25%), an emulsifying capacity between 700,000 mPas and 1,200,000 mPas for a sample directly placed at 4 DEG C. for 24 h (with the exception of a potato protein for which the emulsifying capacity for a sample directly placed at 4 DEG C. for 24 h is between 400,000 mPas and 600,000 mPas) and between 500,000 mPas and 1,100,000 mPas for a sample treated at 75 DEG C. then placed at 4 DEG C. for 24 h and an emulsifying capacity between 70% and 95%. A further subject of the invention is the use of said plant protein in the manufacture of food.	
Potato Protein purification 3	JP19900274559. Purification of Potato Juice Patent in Japanese	1990	Morinaga & Co Ltd	published	PURPOSE:To eliminate the offensive odor of potato juice useful as a confectionery improver or food material by treating with e.g. an ion exchange resin a liquor obtained by separating protein from a concentrated juice freed from potato starch and then by carrying out treatment with an enzyme. CONSTITUTION:Firstly, a concentrated juice produced by removing starch from potatoes in the potato starch production process is heated and thermocoagulable protein is recovered. The resulting residual liquor is	Process for treating potato fruit juice after protein removal is of relevance for AgriMax.

					then treated with an ion exchange resin (pref. anion exchange resin) and activated carbon (e.g. woody activated carbon) followed by treatment with transglucosidase, thus accomplishing the objective purification.	
Potato Protein purification 4	WO2008069650. Native Potato Protein Isolates	2006	Cooperatie AVEBE U A	published	The invention relates to a process for native potato protein isolation, to native potato protein isolates, to the use thereof, and to a food product comprising a native potato protein isolate. The invention provides a novel isolation process for obtaining highly pure native potato protein isolates having a glycoalkaloid concentration of less than 150 ppm	Process for flocculating and adsorbing potato protein and thus separating the protein from glycoalkaloids As part of a larger patent family, the process described might be of relevance for AgriMax if the respective protein purities are needed
Potato Protein purification 5	CN102504011. Method for separating and preparing potato protein powder from potato juice	2012	CHINA NAT RES INST OF FOOD & FERMENTATION IND	Published	The invention discloses a method for separating and preparing potato protein powder from potato juice, which comprises pretreating fresh potato juice by defoaming and crude separation, performing membrane separation to obtain trapped liquid, subjecting the trapped liquid to diafiltration desalting, sterilization and drying to obtain potato protein powder, reusing permeate liquid from membrane separation for washing precipitate obtained by pretreatment, mixing liquid obtained by washing the precipitate with fresh potato juice, and	The process described might be of relevance for AgriMax if the respective protein purities are needed

					delivering to a membrane separation system.	
Potato Protein purification 6	CN101845078. Method for extracting protein from wastewater of potato starch	2010	UNIV LANZHOU	Published	Method for extracting protein from wastewater of potato starch, comprising the following steps: standing and precipitating potato starch wastewater, and centrifuging and filtering; adding an acidic reagent to adjust the pH value, centrifuging and filtering to obtain protein, washing, centrifuging and filtering again to obtain washed protein 1; adding an alkali reagent in supernate after centrifugation and extraction of the protein 1, adjusting the pH value to be 8.50, centrifuging and filtering to obtain protein, washing, centrifuging and filtering again to obtain washed protein 2....	As above
Potato Protein purification 7	CN101220078. Method for extracting protein from waste liquor from potato starch process	2008	TONG YU [CN]	Published	The invention relates to a method for extracting protein from potato starch processing waste solutions, comprising the united application of the techniques of filtration, preheating, PH value adjustion, flocculation, condensation/separation, diluteness, drying, etc.	As above
Potato Protein purification 8	WO1997042834A1	1997	Gist-Brocades B.V.	Published	The present invention relates to food compositions which comprise undenatured potato protein as an ingredient, more specifically to food compositions in which all or a portion of the animal protein, milk protein, fat or hydrocolloids is replaced by undenatured	This intention gives interesting information about the application of potato protein which is relevant within AgriMax.

					potato protein and to a process for preparing such undenatured protein.	
Potato peel liquefaction 9	WO/2016/094900A1	2016	CERENA, Departamento de Engenharia Química e Biológica, Torre Sul, Instituto Superior Técnico, Av. Rovisco Pais, Lisboa, Portugal	Available full text	Upcycling potato peel waste - Data of the pre-screening of the acid-catalyzed liquefaction Herein, the data acquired regarding the preliminary and exploratory experiments conducted with potato peel as a biomass source for the direct thermochemical liquefaction is disclosed. The procedure was carried out in a 2-ethylhexanol/DEG solvent mixture at 160 °C in the presence of p-Toluenesulfonic acid. The adopted procedure afforded a bio-oil in high yield (up to 93%) after only 30 min. For longer reaction times, higher amounts of solid residues were obtained leading, consequently, to lower yields. © 2016 The Authors.	To take inputs for the process of liquefaction.
Ethanol production from potato peel 10	United States Patent 8328994	2014	School of Chemical and Biotechnology, SASTRA University, Thanjavur, 613402, Tamilnadu, India	Not avaliable full text, ony abstract.	Ethanol production from corn, potato peel waste and its process development Corn is one of the richest sources for the production of ethanol. This project was carried out to study the optimum conditions for the production of ethanol. The parameters like, pH, Substrate concentration and particle size were optimized using response surface method in the MINITAB 16 software. Both solid and submerged fermentation were studied. Submerged fermentation turned	To take inputs for the process of liquefaction. An attempt was made to produce ethanol from Potato peel waste, however it proved corn as an efficient substrate

					out to be favourable. Yeast fermentation was employed simultaneously with the saccharification process (SSF) for 72 hours. An attempt was made to produce ethanol from Potato peel waste, however it proved corn as an efficient substrate. There was a considerable yield of ethanol of 15.88g/l using pH 5.5, an intermediate particle size of 0.157mm and at a substrate concentration of 10% (W/V). A process development for the entire production was made involving the reactor design and the equipments to be used at an industrial scale.	
Aroma extraction of potato 11	United States Patent Application 20140127390	2013	Department of Applied Chemistry, Faculty of Science and Engineering, Kinki University, Osaka, Japan Nakamura, A. Ono, T., Yagi, N., Miyazawa, M.	Not avaliable full text, ony abstract.	Volatile compounds with characteristic aroma of boiled sweet potato Sweet potato (Ipomoea batatas L.) is a tuberous root crop that is extensively cultivated in the tropical regions. When baked, it has a characteristic odor. To be able to identify the odor-active compounds, aroma extraction dilution analysis (AEDA) was performed with gas chromatography- olfactometry (GC-O) method. The odor activity value was performed in order to determine the relative contribution of each compound to the odor of the sweet potatoes. The result indicated that a total of seventy-five compounds from Ipomoea batatas L. Cv Ayamurasaki, Beniazuma and Simon 1	To take inputs for the process of aroma recovery. The result indicated that a total of seventy-five compounds from Ipomoea batatas and eighteen odor-active compounds were identified

					were identified by GC-mass spectrometry (GC-MS), which accounted for 91.6%, 84.1% and 87.7%, respectively. The main components of volatile oil from Ayamurasaki were hexadecanoic acid (22.4%), phenylacetaldehyde (10.2%), guaiacol (3.9%) and p-vinylguaiacol (3.8%). Eighteen odor-active compounds were identified, including phenylacetaldehyde (floral odor), maltol (sweet odor) and methional (potato odor). Characteristic aroma from two other kinds of sweet potatoes (Beniazuma and Simon 1) were investigated.	
Ethanol production from potato peels 12	United States Patent Application 20100120109	2002	Mann, P., Siewert, S., Totter, J.	Not avaliable full text, only abstract.	Fermenting potato peels and chips into ethanol A study was performed on fermentation of the potato peels and chips into ethanol. The two plants in Idaho which use potato by-products from nearby French fry processing facilities to make fuel, were discussed. The major challenges faced at the ethanol plants were also described. The ethanol plants were designed to handle processing water from the potato processing plants.	To take inputs for the process of liquefaction.
Extraction of phenolic acids from potato peel 13	CN104000935 A	2014	UNIV ZHEJIANG GONGSHANG	Granted	A disclosed method for extracting anti-oxidative phenolic acids from potato peel slag mainly comprises the following steps: (1) crushing; (2) employing a normal-pressure solvent water for extraction	Essentially SLE with novel clean-up step no mention of novel assisted extraction

					washing; (3) employing subcritical water to extract phenolic acids in potato peel slag; (4) employing macroporous adsorption resin for purification; and (5) performing concentrating, refrigeration or spray drying on the eluate, so as to obtain the high-purity anti-oxidative phenolic acid. The above phenolic acids are applicable to industries such as foodstuff ingredients, cosmetic and the like. The method fully utilizes the property characteristics of the water solvent at a subcritical state, helps to change wastes into valuables, has the characteristics of green technology, good product quality, wide adaptability and the like, and accords with requirements on green-foodstuff chemical engineering.	
Method for extracting solanine from potato peels 14	CN101856427B	2010	湖南农业大学	CN Grant	The invention relates to a method for extracting solanine from potato peels. The method comprises the following steps of: safely and innocuously extracting a crude solanine extract from potato peels by using ethanol with the assistance of ultrasonic wave; and separating and purifying the crude solanine extract by using macroporous absorption resin to obtain a potato solanine extract. The method can be used for safely, effectively and industrially producing the potato solanine extract with a purity	Represent prior art, but there is substantial difference between the technologies and the scope of application

					specification of 20-35 percent to realize the high-valued utilization of potato resources and the industrial production of serial products. Moreover, the solanine which is a main active constituent of the potatoes is extracted, separated and purified by adopting a chemical technology of natural products and a modernized production technology of traditional Chinese medicine, which sufficiently embodies a green chemical production concept.	
Method for extracting and detecting alpha-solanine in potato 15	CN102866219B	2012	湖南农业大学	CN Grant	The present invention discloses a method of potato α- solanine extraction and detection, comprising the steps of: (1) α-solanine extract: Fresh potatoes meat with crushed tissue homogenizer homogenized, weighed sample set in a bottle, the extract was added, after sealing, ultrasonicextraction, the extract through the membrane use; extract said volume ratio = 1: 1 concentration of 1% formic acid - water / methanol volume ratio = 1: 1 the mass concentration of 1% hydrochloric acid - water / methanol, mass concentration of 0.5% formic acid - water or mass concentration of 0.5% hydrochloric acid - water; wherein the ultrasonic extraction under ultrasonic frequency 35kHz extractiontime is 5 ~ 15min. (2) LC-MS detection α- solanine: The α- solanine m / z [M + H] + = 868.78 for	Represent prior art, but there is substantial difference between the technologies and the scope of application

					the target ion, selected ion monitoring mode using quantitative, standard control solution injection detecting a concentration (X, ppb) as the abscissa, the peak area (Y) for the vertical axis, the standard curve, the regression equation is calculated in accordance with the content of α- solanine regression equation. This method can be simple, fast and accurate detection of potato α- solanine.	
Method for extracting active ingredient of natural product and uses thereof 16	CN101138686A	2007	沈军	CN Application	The present invention pretreats a solid-phase material of a natural product. A liquid-phase solvent suitable for extracting the solid-phase material is selected base on the characteristics of effective components in the solid-phase material. With a gas-liquid-solid phase processor, the solid-phase material and the liquid-phase solvent are mixed and conveyed in the way of adverse flowing and the solid-phase material is extracted dynamically. Moreover, the physical field, the temperature, the pressure and so on can be added to strengthen the extraction efficiency. Solvent and impurities are removed from a solution extracted from the (saturated) solvent with the effective components by one art or more arts of segregation, purification, concentration, drying and other prior arts, so an extracted material with the effective components is got. The whole production	Represent prior art, but there is substantial difference between the technologies and the scope of application

| | | | | | course forms a production technical system with the dynamic extraction of effective components in the natural product in the way of adverse flowing as the core. The production technical route of the system is raw material arrow material pretreatment arrow he core technology of dynamic extraction in the way of adverse flowing arrow segregation and purification arrow concentration and drying arrow effective components. Compared with a production technical system with intermittent solvent extraction as the core, the present invention can easily realize the technical achievement transformation and the industrial-scale production. CN101138686A | |

Tomato

Topic, nº	Patent	Priority date	Applicant	Status	Abstract	Relevance/ Differences vs. AgriMax
Carotenoid extraction from plants 1	US7572468 B1	2009	The United States Of America As Represented By The Secretary Of Agriculture, United Technologies	published	Methods for extraction of carotenoids from carotenoid-containing plant material using an extraction solvent comprising ethyl lactate. The invention is also directed to products obtained thereby. In the method, a sample of dry, particulate carotenoid-containing plant material is contacted with the ethyl lactate extraction solvent to extract the carotenoids. The method also includes the use of an ethyl	Examined to set–up the lycopene extraction method to applicate for AgriMax.

					lactate-ethanol blend as the extraction solvent. After extraction, the solvent containing the extracted carotenoids is separated from the extracted plant solids and treated to separate the dissolved carotenoids from the extraction solvent and obtain a carotenoid-containing concentrate. The concentrated carotenoid product may be used directly or may be subjected to further treatment. After removal of the dissolved carotenoids, the extraction solvent can be recycled for further use.	
Extraction of lycopene from tomato 2	WO2008055894 A1	2008	Biolyco S.R.L.	published	The invention discloses a process for the extraction of lycopene from tomato by-products characterised in that said extraction is performed by means of a solvent mixture comprising two or more components, wherein one is apolar or moderately polar and has affinity for lycopene and at least one of the other solvents is polar. As example, a first solvent is an apolar solvent, a second solvent is a protic polar solvent, a third optional solvent is an aprotic polar solvent. In particular, said mixture has the following composition: hexane 10%-80%, ethanol 10%-60% and acetone 10%-60%. The use of multicomponent mixtures characterised by high extractive activity,	Examined to set–up the lycopene extraction method to applicate for AgriMax.

					fast extraction kinetics is one of the advantages of the present invention.	
Extraction of bioactive compounds of tomato 3	WO2006111163 A1	2006	Novozymes A/S	published	A method for producing a plant extract comprises incubating a plant material with an enzyme composition comprising a lipolytic enzyme.	In the patent is proposed an enzymatic pre-treatment of tomato skin to improve the extraction of bio-active compounds. This step will be avoided in lycopene extraction method to applicate for AgriMax in order to simplify the process and easily realize the scale-up of the process.
Extraction of lycopene from tomato 4	104610009	2015	JIANGSU YAKEXI FOOD CO., LTD.	published	The invention discloses an extraction method for lycopene. The method comprises the following steps: (1) pretreatment of tomato pomace: a step of drying the tomato pomace and crushing the dried tomato pomace into powder with particle sizes of 60 to 80 meshes for subsequent usage; (2) preparation of an aqueous two-phase system of an ethanol-ammonium sulfate solution: a step of weighing absolute ethyl alcohol and an ammonium sulfate solution with a mass fraction of 40% to 50%, uniformly mixing the two solvents, and carrying out standing for delamination; (3) ultrasonic treatment: a step of adding the treated tomato pomace powder into the aqueous	In the patent an ultrasonic extraction method for lycopene rejected is proposed. This method is interesting for AgriMax project. Other routes for lycopene extraction seem easier to implement in Chiesa's plant.

					two-phase system prepared in the step (2), carrying out uniform mixing under stirring, carrying out standing, and after delamination, placing the obtained mixture in an ultrasonic cell disruptor and carrying out ultrasonic treatment under the conditions that ultrasonic power output is 200 W to 400 W, ultrasonic treatment temperature is 35 to 45 DEG C, and ultrasonic treatment time is 10 to 20 minutes; and (4) filtration and extraction: taking out the ultrasonically-treated solution from the ultrasonic cell disruptor and carrying out standing and vacuum filtering. The extraction method for lycopene provided by the invention uses the aqueous two-phase system and the ultrasonic extraction in combination, so the advantages of the two extraction methods are exploited and the extraction rate of lycopene is greatly improved.	
Extraction of lycopene from tomato 5	US12309905A1	2009	Fu Zhun Precision Industry (Shenzhen) Co Ltd Foxconn Technology Co Ltd	published	Innovative food supplement based on biological lycopene, which is the bulk product, i.e. the total extract, obtained by treating with supercritical carbon dioxide a suitable extraction matrix, made by 50% biological tomato berries and 50% biological dry fruits (almonds, nuts and the like) and/or other components, following a co-extractive technology. Tomato berries are conveniently de-	Even if the treatment with SC-CO$_2$ excludes, in the first analysis, the use of organic solvents, this method for lycopene extraction requests the control of many experimental parameters and not negligible costs.

					hydrated, milled and riddled; the co-extraction matrix (dry fruits, vegetables, others) is conveniently de-hydrated and milled. The obtained total extract is directly used for preparing lycopene based food supplements, without any modification or additivation. With respect to the known commercial food supplement, based on lycopene, such biological lycopene has unique quality features: the total extract is 100% natural; absence of chemical solvents; lycopene concentration in the final natural formula (not artificial); absence dosing problems and contra-indications. In the final product, lycopene is mixed with other natural anti-oxidants, co-extracted from the used vegetables. The boxing up of the bulk product (total extract) is made in soft or hard caps in several shapes and colors or in tablets or in other way (e.g. liquid, others).	There are the affecting factors like matrix type, particle size (drying, grinding and sieving operations are needed), lycopene content, flow rate of SC-CO_2,temperature and pressure on lycopene yield. Furthermore, many studies reporting that if optimum process parameters are employed, pure lycopene may be obtained without using a co-solvent. Moreover, 100% yield of lycopene extraction of tomatoes should not be targeted due to degradation of the product. Other routes for lycopene extraction seem easier to implement in Chiesa's plant.
Extraction of humid substances in compost samples 6	ES2286917B1	2008	Moreno, J.; Suárez-Estrella, F.; López, M.J.; Vargas-García, M. C.	Published	Obtención de un producto líquido rico en sustancias húmicas mediante un procedimiento sencillo, rápido y extrapolable a nivel industrial y cuya aplicación a nivel agrícola sea satisfactoria. La obtención de dicho abono	UAL AgriMax partners are the authors of this patent and it applicable in the project

					se ha llevado a cabo gracias a la optimización del proceso de extracción de las sustancias húmicas presentes en muestras de compost de origen vegetal. Las condiciones óptimas en las que se llevó a cabo dicho proceso implicaron altos valores de pH (> 10) y temperaturas superiores a 100∘C. La aplicación del producto obtenido bajo tales condiciones, a nivel agrícola, ha mostrado aspectos de enorme interés tanto desde el punto de vista del desarrollo vegetal como en relación a las características del suelo o de la microbiota asociada a dicho sustrato.	
Using tomato straws as fertilizer 7	CN103951476 A	2014	HUANG FUZHONG	Not available as full text	The invention relates to a method for preparing a bio-organic fertilizer by adopting tomato straws as a main raw material, wherein tomato stalks with a characteristic of rich resource is adopted as a main raw material, animal manure and pond mud are adopted as auxiliary materials, and a straw decomposition agent is adopted as a fermentation agent to prepare an inexpensive bio-fertilizer. The preparation process comprises: adopting a straw decomposition agent to ferment tomato straws until the straws rot and become into irregular segments, and the rotten straws, animal manure and pond mud are mixed and continuously fermented to obtain the bio-fertilizer.	Similar process will be applied in AgriMax

					According to the present invention, the produced bio-organic fertilizer is rich in organic matters, further contains nitrogen, phosphorus, potassium and other nutrients, is commonly used fertilizer for various crops and various soils, and has effects of product quality improving, yield increase and chemical fertilizer consumption reducing; and a large number of the tomato straws can be converted and utilized in the tomato production place so as to reduce pollutions of burning on atmosphere, soil, water, and environment, extend the industrial chain, achieve multi-level value increase of agricultural resources, increase industrial added value, and increase farmer income.	
Production of humic acid as fertilizer 8	CN103058772 B	2015	INNER MONGOLIA YONGYE BIO TECH CO LTD	Granted	The present invention relates to a method for preparing high activity of humic acid bio-fertilizer, bio-organic fertilizer including humic acid 97-99%, effects capabilities bacteria 0.2-3%, 0.1-0.3% activator, high organic nutrient quality, with good soil conditioning; are stable, lasting fertilizer; balanced comprehensive nutritional products, for a variety of crops containing inorganic nutrients, fertilizer efficiency, promote crop growth, yield and quality and; suppress pathogens have better control effect; improving crop root	Similar process will be applied in AgriMax

					environment, increasing crop nutrient absorption, promote crop root system, enhance crop resistance; after farmers planted using good effect, increase production, it is a production of green, high activity of humic acid bio-fertilizer organic foods	
Production of fertilizers 9	US20110045976 A1	2011	Mario Jorge Villaverde Fernandez Ana Isabel Fernandez Martinez Juan Antonio Casanova Roca Jorge Malo Lopez-Roman Jose Antonio Nicolas Martinez Isidro Blanca Pico Antonio Garcia Gomez Pedro Martinez Ortiz	Granted	The invention relates to a novel biological fertilizer, a method for obtaining same and the use thereof as a plant growth stimulator, said fertilizer comprising a pure culture of strain C3 of Pantie dispersal, a pure culture of strain M3 of Azospirillum brasilense and indole-3 acetic acid, all of which are immobilised in a single solid medium acting as a slow release system. The method includes the following main steps: culture of the microorganisms; immobilisation of the cells, nutrients and other substances in the medium; and a single fluid bed drying step which enables lower temperatures to be used and lower moisture contents to be obtained, thereby providing the fertilizer with greater stability. The action of the fertilizer commences upon contact with the plant.	Similar process will be applied in AgriMax (different microorganism and substrate)
Production of bio-fertilizers of vegetable wastes 10	CN 201210010577	2012	Chinese	Application published	The invention relates to a method for preparing biofertilizer by fermenting waste vegetables, straw and livestock and poultry feces. The fermented biofertilizer	Similar process will be applied in AgriMax (not same treatment neither feedstocks)

| | | | | | is prepared from the following raw materials in parts by weight: 90-110 parts of waste vegetables, 45-55 parts of straw, 18-22 parts of livestock and poultry feces, 6-10 parts of rice bran, 1.7-2.0 parts of urea, and 1.7-2.0 parts of ammonium sulfate. The invention also provides a preparation method of the fermented biofertilizer prepared from waste vegetables, straw and livestock and poultry feces. The preparation method comprises the following steps of: crushing the waste vegetables till particle size is below 10 mm, crushing the straw till particle size is below 10 mm, adding 45-55 parts by weight of straw, 18-22 parts by weight of livestock and poultry feces, 6-10 parts by weight of rice bran, 1.7-2.0 parts by weight of urea, and 1.7-2.0 parts by weight of ammonium sulfate to 90-110 parts by weight of waste vegetables, mixing, adjusting the water content of the mixed material to 50-65%, adding 0.08-0.12% of composite microorganism agent and 0.008-0.010% of composite enzyme based on the weight of the mixed material, sufficiently and uniformly stirring, controlling water content of the fermentation material to be 50-65%, adjusting the pH to 6.2-7.8 with 1% lime water, and carrying out aerobic | |

					fermentation for 10-20 days to obtain the biofertilizer product.	
Production of bio-fertilizers

11 | CN101676243A | 2010 | LIAONING YUANHENG BIOTECHNOLOG | Application published | The invention provides a production process of a biological-organic-inorganic ternary compound fertilizer which is prepared by the following steps: mixing crop stalks, such organic components as livestock manures and active biological agents, regulating the carbon nitrogen ratio from 26 to 35, pH from 5.5-8.2 and moisture from 40% to 65% according to the organic matter contents of the crop stalks and the livestock manures, fermenting the mixture at minus15-75 DEG C for 20-50 days and ensuring the living bacteria count to be 0.03-0.2 billion/g, carrying out turning and oxygenating, fermenting in deep tanks and grinding on the mixture to prepare the biological organic fertilizers, mixing the biological organic fertilizers with the inorganic fertilizers and trace elements and simultaneously adopting the low-temperature drying process after extruding granulation and the biological agent spraying and cooling technology. The method can greatly shorten the decay period, ensure little nutrient loss and little generating capacity of sour gases in the processes of fermentation and decay and complete decay and fermentation, can | Similar process will be applied in AgriMax (not same treatment neither feedstocks) |

					enhance the stress resistance of the crops, ensure obvious disease-resistant effects and high survival rates of specific functional bacteria and has wide application. Through field contrast tests, both the production and income are increased by 10-25% by applying the biological organic fertilize	
Composting of cane sugar press 12	WO2008133488A1	2008	ESTRADA Sergio Rubén TREJO RENDÓN Julieta Salomé VELOZ Morales Minerva Rosas Mendez Ana Itzel Reyes	Application published	This invention comprises improved composting of cane sugar press mud and lignocellulosic materials. The result is a low density humectant substrate (SHBD) for use in agriculture. The process takes place in semi-static biopiles which are homogenized and aerated mechanically. The lignocellulose materials are added in a supplied batch system, in steps and doses which depend on the type of lignocellulosic material and the quality of the required final substrate. Another objective is to provide, within 8 weeks, a material without pathogenic microorganisms nor weeds, with low density (< 0.4 g/ml), high porosity (110%), and high water retention (> 90%), useful as a substrate in horticulture and forestry production in nurseries and greenhouses; or as a humectant and soil-improving agent in agricultural land and eroded soils. Said substrate has better physical, chemical and biological features for plant	Similar process will be applied in AgriMax (not same treatment neither feedstocks)

					nutrition than equivalent substrates uch as peat and coconut fibres.	
Usage of food wastes as fertilizers 13	US9416062B2	2016	Daniel M. Morash Mark LeJeune	Active	This invention relates to processes and systems for converting fresh food waste into nutrient rich hydrolysates and particulate compositions. The invention also relates to the hydrolysates and compositions useful, for example, as fertilizers, feedstock or other nutrient supplements.	Similar process will be applied in AgriMax (not same treatment neither feedstocks)
Production of fertilizers from tomato stalks 14	CN105218178A	2016	UNIV NORTHWEST A&F	Application published	The invention relates to a method for preparing an organic fertilizer from tomato stalks. The method comprises the steps: adopting the tomato stalks, goat manure and edible fungus production waste (mushroom residue) as main raw materials, mixing the tomato stalks and the goat manure according to the weight ratio of 3: 1, adding 0-40% (by weight) of the mushroom residue into the mixture, diluting a biological microbial agent, sprinkling the diluted biological microbial agent into the mixture, adding a proper volume of clean water to the mixture so as to enable the moisture content of compost to reach 55-65%, uniformly stirring the compost, then, putting the stirred compost into a fermentation cask, carrying out regular compost overturning, and basically completing fermentation when compost body temperature and	Similar process will be applied in AgriMax (not same treatment neither feedstocks)

					environmental temperature are fundamentally equal; and drying the fermentation product in air, and crushing the dried fermentation product, thereby obtaining an organic fertilizer finished product. The method has the advantages that the tomato cultivation waste can be changed into the valuable, and the mushroom residue can be fully utilized, so that wasting of resources is reduced.	
Production of humic acid bio-fertilizers 15	CN 201310013346	2013	Chinese	Application published	The invention relates to a preparation method for a high-activity humic acid biofertilizer. The high-activity humic acid biofertilizer comprises 97-99% of humic acid bio-organic fertilizer, 0.2-3% of special functional bacteria, and 0.1-0.3% of activator. The high-activity humic acid biofertilizer has high quality of organic matter nutrient, is excellent in soil conditioning function, has stable effect and long fertilizer efficiency, has balanced and complete nutrient, comprises multiple inorganic components needed by crops, has high fertilizer efficiency and can promote the growth of the crop and improve the yield and quality, has good disease resistance effect, improves the root system environment of the crop, improves the nutrient absorption of the crop, develops the root system of the crop, and enhances the stress resistance	Similar process will be applied in Agrimax (not same treatment neither feedstocks)

| | | | | | of the crop. After the high-activity humic acid biofertilizer is used by a peasant, a good planting effect can be obtained, and the yield and income are increased, so that the high-activity humic acid biofertilizer is used for producing environment-friendly and organic food. | |

Cereals

Topic, nº	Patent	Priority date	Applicant	Status	Abstract	Relevance/ Differences vs. AgriMax
Manufacturing of a novel plant fiber 1	US2013/0005869A1	2010	Oji Holdings Corp Nippon Paper Industries Co Ltd Kyoto University	Published; Granted	The present invention provides a novel cationized microfibrillated plant fiber and a method for manufacturing the same. A cationic microfibrillated plant fiber that is cationically modified with a quaternary-ammonium-group-containing compound and that has an average diameter of 4 to 200 nm.	These CNFs have cationic charge on their surface, while in AgriMax the CNFs produced will be produced using enzymatic treatments which do not modify the charge of the native plant fibers.
Manufacturing plant fibers as molding material 2	US2013/0005866A1	2010	Oji Holdings Corp Nippon Paper Industries Co Ltd Kyoto University	Published: Granted	The present invention relates to anionically modified microfibrillated plant fibers used for obtaining a thermosetting resin molding material having excellent mechanical strength, a method for manufacturing the same, a molding material containing the anionically modified microfibrillated plant fibers and a thermosetting resin, and a method for manufacturing the same. Specifically, the present invention provides a molding material containing anionically modified	These CNFs are anionically modified, while in AgriMax the CNFs produced will be produced using enzymatic treatments which do not modify the charge of the native plant fibres.

					microfibrillated plant fibers that are anionically modified in the presence of a base by a carboxylic acid represented by formula (I): X—(CH2)n—COOH (I), wherein X represents halogen and n is 1 or 2, and/or by a salt thereof, and a thermosetting resin, and the molding material contains the anionically modified microfibrillated plant fibers in an amount of 10 to 900 parts by weight per 100 parts by weight of the thermosetting resin.	
Manufacturing cellulose out of plant pulp 3	US5964983	1995	Generale Sucriere	Published; Expired	A microfibrillated cellulose containing at least around 80% of primary walls and loaded with carboxylic acids, and a method for preparing same, in particular from sugar beet pulp, wherein the pulp is hydrolysed at a moderate temperature of 60-100° C.; at least one extraction of the cellulose material is performed using a base having a concentration of less than 9 wt. %; and the cellulose residue is homogenised by mixing, grinding or any high mechanical shear processing, whereafter the cell suspension is fed through a small-diameter aperture, and the suspension is subjected to a pressure drop of at least 20 MPa and high-speed sheer action followed by a high-speed deceleration impact. The cellulose is remarkable in that a suspension thereof	Uses plant pulp, and more precisely sugar beet pulp, while in AgriMax other types of vegetal tissue i.e. husks and bran will be used

					can easily be recreated after it has been dehydrated.	
Manufacturing cellulose out of chemical pulp 4	US20090221812	2006	STFI Packforsk AB	Published; Granted	A method for treatment of chemical pulp for the manufacturing of microfibrillated cellulose includes the following steps: a) providing a hemicellulose containing pulp, b) refining the pulp in at least one step and treating the pulp with one or more wood degrading enzymes at a relatively low enzyme dosage, and c) homogenizing the pulp thus providing the microfibrillated cellulose. According to a second aspect of the invention a microfibrillated cellulose obtainable by the method according to the first aspect is provided. According to a third aspect of the invention, use of the microfibrillated cellulose according to the second aspect in food products, paper products, composite materials, coatings or in rheology modifiers (e.g. drilling muds) is provided.	Uses chemical pulp as starting material, while in AgriMax plant husks and bran will be used
Manufacturing cellulose out of beaten pulp 5	US6214163	1995	Tokushu Paper Manufacturing Co Ltd	Published; Active	A super microfibrillated cellulose having an arithmetic average fiber length of 0.05 to 0.1 mm, a water retention value of at least 350%, a rate of the number of fibers not longer than 0.25 mm of at least 95% based on the total number of the fibers as calculated by adding up, and an axial ratio of the fibers of at least 50. The super microfibrillated cellulose is produced by passing a slurry of a previously beaten	Uses beaten pulp as starting material, while in AgriMax plant husks and bran will be used

					pulp through a rubbing apparatus having two or more grinders which are arranged so that they can be rub together to microfibrillate the pulp to obtain microfibrillated cellulose and further super microfibrillate the obtained microfibrillated cellulose with a high-pressure homogenizer to obtain the super microfibrillated cellulose. A coated paper produced with a coating material containing the super microfibrillated cellulose, and a tinted paper produced from a paper stock containing the super microfibrillated cellulose as a carrier carrying a dye or pigment are also provided.	
Production of phenolic acids out of rice bran\n\n6	JP2015224237	2014	YANMAR CO LTD UNIV OSAKA PREFECTURE	Application published	PROBLEM TO BE SOLVED: To provide a method for efficiently producing tocopherol, tocotrienol, [gamma]-oryzanol and ferulic acid from rice bran. SOLUTION: Provided is a method for producing a bioactive substance from rice bran in which the bioactive substance being tocopherol, tocotrienol, [gamma]-oryzanol and ferulic acid, and including a process where a mixture including the rice bran, Calcohol, an alkali aqueous solution, an aliphatic hydrocarbon solvent and an acetic acid ester solvent is irradiated with ultraviolet waves to saponify the rice bran.	Chemical-physical method vs enzymatic method (AgriMax)

| Production of ferulic acid by an ultrasonic treatment 7 | CN104928341 | 2015 | QINGDAO JIARUI BIOLOG TECH CO | Application published | The invention discloses a preparation method for ferulic acid combining ultrasonic-assisted enzymolysis and microbial-fermented bran. The bran is used as raw material. The ferulic acid is prepared through the ultrasonic-assisted enzymolysis and a microbiological fermentation method. The extraction efficiency is improved greatly. A detection result indicates that the extraction efficiency of the ferulic acid in the bran reaches over 95% which is obviously higher than a reported technological level at present. The preparation method for ferulic acid combining ultrasonic-assisted enzymolysis and microbial-fermented bran has the advantages that firstly cellulose, lignin and the like in the bran is degraded through the combination of the technologies of compound microbial fermentation, ultrasonic-assisted enzymolysis and two-step alcohol extraction; secondly the ultrasonic-assisted enzymolysis is adopted in the process of starch removing and albumen removing, the enzymolysis time is shortened, and the removal efficiency is improved; thirdly the producing cost of the technology is comparatively low, the drying links with high energy dissipation is few, the absolute ethyl alcohol can be | Procedure similar to the one proposed in AgriMax, with additional ultrasonic treatment and fermentation step. |

					recycled and used, and commercial production is facilitated.	
Extraction of arabinoxylan from cereal grain 8	WO2014047312	2012	CARGILL INC	Application published	The present invention provides a method for the extraction and isolation of soluble arabinoxylan products from cereal grain. Preferably, such soluble arabinoxylan product is any one of soluble arabinoxylan, arabinoxylan-oligosaccharides, xylose, arabinose, ferulic acid and mixtures thereof. Said method comprises partial debranning of whole cereal grains to obtain partially debranned cereal grains followed by roller milling of said partially debranned cereal grains to obtain cereal bran. The method further comprises the mashing of at least part of said cereal bran in water optionally involving the treatment of the mash with any one of an enzyme preparation, an acid, a base, a peroxide or combinations thereof, either simultaneously or sequentially, to solubilize and optionally depolymerize a fraction of the arabinoxylan comprised in said cereal bran. Preferably, said treatment is done with an enzyme preparation containing an endoxylanase. The method further comprises the separation from said mash of a solubilized fraction, which comprises at least part of the solubilized soluble arabinoxylan products.	Procedure similar to the one proposed in AgriMax to extract ferulic acid, with co-extraction of oligosaccharides and ferulic acid. In AgriMax the optimized procedure will aim at obtaining separate streams of ferulic acid and oligosaccharides.

Production of ferulic acid from wheat bran 9	CN104830927	2015	WUXI QUNSHUO GUTANG BIOTECHNOLOGY CO LTD	Application published	The present invention relates to a method for preparing ferulic acid oligosaccharide syrup by using wheat bran, wherein the method comprises raw material pretreatment, primary pulp blending and reaction, separation washing, secondary pulp blending and enzyme reaction, filtration with a membrane, concentration, and other steps. According to the method of the present invention, various components in the wheat bran are effectively separated through the ultrafine crushing and the alkali method protein extraction, and the cyclone washing treatment is used, such that the separation and washing efficiency is substantially improved, the fibers, the starch and the proteins are separated, and the wheat starch and the proteins are recovered, wherein the starch recovery rate is greater than 80%, and the protein recovery rate is greater than 60%; and the high-temperature process is not used, such that the ferulic acid oligosaccharide extraction rate is greater than 25% so as to substantially improve the added value of the deep wheat processing and reduce the production cost.	Co-extraction of oligosaccharides and ferulic acid. In AgriMax the optimized procedure will aim at obtaining separate streams of ferulic acid oligosaccharides.
Production of ferulic acid from corn bran	CN103664580	2013	GANSU INST OF BUSINESS AND TECHNOLOGY	Application published	The invention relates to a preparation method of a ferulic acid from corn bran. The preparation method comprises the	Extraction of ferulic acid from de-proteinated and

| 10 | | | | | following steps: (1) cleaning and drying the corn bran, deactivating enzyme, milling and screening the corn bran to obtain the processed corn bran; (2) adding water in the processed corn bran to be stirred uniformly to obtain slurry; (3) adding high temperature resistant alpha-amylase in the slurry, and performing water bath and vibration to obtain the starch-removed corn bran; (4) cooling the starch-removed corn bran to room temperature, adding compound protease in the corn bran, performing water bath, keeping warm and continuously stirring to obtain the protein-removed corn bran; (5) performing enzyme deactivation, centrifuging and drying to the protein-removed corn bran till constant weight, and obtaining the dried starch-removed protein-removed corn bran; (6) adding a sodium hydroxide solution in the dried starch-removed protein-removed corn bran, performing constant-temperature water bath and centrifuging to obtain a ferulic acid extracting solution; (7) keeping the ferulic acid extracting solution out of the sun and standing, centrifuging, and diluting the extracting solution to 100 mL; (8) concentrating and drying the diluted ferulic acid till constant weight to obtain the ferulic acid coarse powder. The preparation method is simple | de-starched bran with alkali hydrolysis. |

					to operate, low in cost, and high in yield of the ferulic acid.	
Production of ferulic acid from wheat bran 11	CN103642851	2013	UNIV JIANGNAN	Application published	The invention provides a method for preparing ferulic acid from wheat bran by using a two-enzyme method. Wheat bran is subjected to enzymolysis by utilizing the synergistic effect of recombinant ferulic acid esterase and recombinant xylanase from a laboratory, so as to release ferulic acid and obtain a crude ferulic acid extract. The crude ferulic acid extract is purified by using an HPD-300 weal-polarity macroporous resin, and the fraction with the ferulic acid obtained from purification is dried in vacuum so as to obtain a ferulic acid product. By adopting the method, raw materials for extracting and preparing the ferulic acid are cheap and easily available, in the product purity is high, the preparation process is simple, and the method is simple, convenient and feasible in operation, environment-friendly and applicable to industrial expansion production.	Use of non-commercially available recombinant enzymes.
Manufacturing of ferulic acid and arabinoxylan from cereal brans 12	WO0167891	2000	HWANG, JAEKWAN; PARK, BOSUN; YUN, JUNGMI	Application published	The present invention relates to physiologically active materials separated from the cereals and manufacturing method thereof. Physiologically active materials such as ferulic acid and arabinoxylan present in cereal brans were	Bran pre-treatment via extrusion increases the recovery of ferulic acid and arabinoxylan.

					separated by the extrusion process and the subsequent treatment with plant cell wall hydrolyzing enzymes. This combined process of extrusion and enzyme treatments for cereal brans, compared to the individual treatment, significantly increased the separation efficiency of physiologically active materials in cereal brans, ferulic acid and arabinoxylan, which inherently exist as insoluble materials in the cell wall of cereal bran.	
Production of a bio renewable plastic 13	WO2014075057	2012	UNIV FLORIDA	Application published	An embodiment of the invention is directed to a bio renewable thermoplastic, poly(dihydroferulic acid) (PHFA), which is an effective polyethylene terephthalate (PET) mimic. In another embodiment of the invention, a bio renewable thermoplastic copolymer, poly(dihydroferulic acid-co-ferulic acid) is an effective polystyrene mimic. The PHFA and the copolymer can be prepared by the homocondensation of acetyldihydroferulic acid or the copolymerization of acetyldihydroferulic acid with acetylferulic acid, which are monomers that can be synthesized from starling materials isolated from lignin, rice bran, or other biorenewable sources.	The method proposed is not environmental friendly. In AgriMax a green route will be developed.
Incorporation of antioxidants into polymers	WO2014194055	2013	UNIV RUTGERS	Application published	Certain embodiments of the invention provide antioxidant-based diacids and polymers comprising glycol groups as	Chemical binding of the bioactive molecule to the polymer. In AgriMax a

| 14 | | | | | described herein, and methods of use thereof. In certain embodiments the polymers described herein are formulated as microspheres or hydrogels. Described herein is the chemical incorporation of antioxidants, e.g., coumaric acid, ferulic acid, and sinapic acid, into a polymer backbone for use, e.g., in applications for localized release and rapid delivery. As provided, the chemical composition of the linker molecules used (of which hold together two bioactives via ester linkages) may be used to vary the hydrophilicity of the polymer. The bioactive release rate may also be altered for a tunable release delivery system, allowing for increased bioactive release compared to other linkers previously utilized. | different strategy for the incorporation into polymers will be exploited. |

Olive

Topic, nº	Patent	Priority date	Applicant	Status	Abstract	Relevance/ Differences vs. AgriMax
Polyphenol extraction from olive leaves 1	CN104490977 (A)	2014	GUILIN HEYINXIANG NEW MATERIALS CO LTD	published	The invention discloses a method for extracting olive polyphenol from olive leaves. The method comprises the following steps: (1) pulverizing the olive leaves, adding ethanol according to the ratio of the material to liquid being 1g: 10-30 ml, carrying out shaking extraction and separating a supernatant; (2) filtering the	This intention is relevant because similar processes will be conducted within the AgriMax project.

					supernatant with a membrane filtration device to obtain a clarified liquid; and (3) feeding the clarified liquid to a macroporous resin column at a sampling flow rate of 0.4-0.6 BV/h, eluting with water, then eluting with 65-85% (in volume concentration) ethanol, collecting ethanol eluate, concentrating and drying to obtain olive polyphenol. The purity of olive polyphenol prepared by the method is high.	
Polyphenol extraction from olive leaves 2	CN102935101 (A)	2012	HAIERSOFT CORP	published	The invention relates to an extraction method of olive leaf polyphenol. The method comprises the following steps: with water as a solvent, obtaining olive leaf polyphenol crude extract by adopting microwave extraction, then carrying out macroporous resin separation, pressure reduction and concentration, and vacuum freeze dehydration to obtain the olive leaf polyphenol. The method is characterized in that the the microwave power is increased for every other 20-60 s in the microwave extraction process. The method has the beneficial effects that the use amount of the solvent can be reduced, the extraction yield is increased, and the purity is improved.	As above
Polyphenol extraction of olive waste liquor	CN103494862 (A)	2013	UNIV NORTHWEST NORMAL	published	The invention discloses a method for extracting olive polyphenol from olive processing waste liquor, which belongs to the technical field of bio-separation. The	This intention is not relevant because olive liquor is not addressed in AgriMax.

					method takes the olive processing waste liquor as a raw material, can be used for preparing high-quality olive polyphenol by ethanol precipitation and macroporous adsorption resin separation technologies, and also can be used for obtaining a functional feed additive and an olive protein-polysaccharide compound. According to the method, the olive processing waste liquor is comprehensively developed and utilized, a technical support is provided for producing olive polyphenol, and good economic and social effects are achieved.	
Polyphenol extraction from olive by-products 4	GB2415136 (A)	2004	NATRACEUTICAL SA [ES]	published	A process in which olive polyphenol concentrate is obtained from a by-product of olive oil extraction comprising the steps of: a) mixing the by-product with a polar solvent to give a by-product/solvent mixture; b) extracting polyphenols from the by-product/solvent mixture to give an olive polyphenols solution and extracted solids; and c) concentrating the olive polyphenols solution using membrane separation techniques to yield an olive polyphenols concentrate wherein the concentration of polyphenols present is at least 10wt% and wherein the process further includes a defatting step.	This intention is relevant because similar processes will be conducted within the AgriMax project.
Liquefaction of olive residue	United States Patent 8704020	2016	Chemical Engineering Department, Sapienza University of Rome, Italy	published	Biocrude production by hydrothermal liquefaction of olive residue	Take inputs for the process

| 5 | | | | | Hydrothermal liquefaction (HTL) converts biomass into a crude bio-oil by thermally and hydrolytically decomposing the biomacromolecules into smaller compounds. The crude bio-oil, or biocrude, is an energy dense product that can potentially be used as a substitute for petroleum crudes. Liquefaction also produces gases, solids, and water-soluble compounds that can be converted to obtain valuable chemical species or can be used as energy vectors. The process is usually performed in water at 250°C-370°C and under pressures of 4-22 MPa: depending on the adopted pressure and temperature the process can be carried out in sub-critical or super-critical conditions. In the conditions reached in hydrothermal reactors, water changes its properties and acts as a catalyst for the biomass decomposition reactions. One of the main advantages of this process is that the energy expensive biomass-drying step, required in all the thermochemical processes, is not necessary, allowing the use of biomass with high moisture content such as microalgae or olive residue and grape mark. In this work, the feasibility of a hydrothermal process conducted under sub-critical conditions to obtain a bio-oil from the residue of olive oil production is investigated. The experimental tests were | Hot water changes its properties and acts as a catalyst for the biomass decomposition reactions |

Olive oil by-products valorization 6	ISSN: 14387697	2015	Dipartimento di Scienze Agrarie, Alimentari e Ambientali, Università degli Studi di Perugia, Perugia, Italy	published	New approaches to virgin olive oil quality, technology, and by-products valorization. Extra virgin olive oil (EVOO) merchandize quality is based on analytical parameters describing alteration status and assuring genuineness, but qualitative/quantitative composition of those quality markers related to health and sensory aspects such as monounsaturated fatty acids, phenolic compounds as secoiridoid derivatives, and C_5 and C6 volatile compounds are not mentioned. This paper focuses on the new approaches to the definition of EVOO quality that might include also healthy and sensory parameters and on the agronomic and technological factors that most influence their variability. Crushing and malaxation are discussed as critical points of the technological process since their direct involvement on the phenolic release and on the aroma generation. Variables	Take inputs for the process. The rapid reaching of the optimal malaxing temperature seems to improve polyphenols and volatile concentration.

					such as time, temperature, and oxygen level, during malaxation, were analyzed to design new implant systems for the improvement of EVOO quality. Flash thermal conditioning (FTC) of the crushed olive pastes was briefly discussed as a new approach to the technological process. The rapid reaching of the optimal malaxing temperature seems to improve polyphenols and volatile concentration. The paper shows also recent studies on the valorization of the mechanical extraction co-products as stoned pomaces for the animal feeding and vegetation waters phenolic concentrates and extracts for functional foods and ingredients production. This article provides an overview of the Author keynote lecture delivered at the Euro Fed Lipid Congress and focuses on the group's works. © 2015 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.	
Lignocellulosic residues of olive residues 7	WO/2005/017001	2012	University of the Basque Country, Chemical and Environmental Engineering Department, Plaza Europa, 1, 20018, Donostia, San Sebastián, Spain	Not available full text, only abstract	Influence of microwave activation on chemical properties of liquefied lignocellulosic residues The valorization of lignocellulosic biomass has been attracting increasing attention due to the possibility of using it as a renewable, abundant, and cheap source of raw materials for the chemical industry to produce energy, biofuels, chemicals, and biomaterials. The principal structural and	Take inputs for the process Cellulose and lignin were easier to be degraded under microwave activation, the microwave liquefied products might be used as a potential source of chemicals

| | | | | Briones, R., Serrano, L., Sequeiros, A., Labidi, J. | | chemical changes associated with the influence of microwave activation on liquefied products obtained from several lignocellulosic agro-industrial residues were studied, with emphasis on exploring a liquid product with suitable features to be used as ingredient of high added value chemical products. The liquefied products evaluated were produced by solvolysis liquefaction of some lignocellulosic agro-industrial residues (olive stone, corncob, apple pomace, and rapeseed cake). Cellulose and lignin were easier to be degraded under microwave activation, which indicate the higher hydroxyl content in conventional liquefied products and higher carbonyl content in liquefied products activated by microwaves. The liquefied products were complicated organic compounds, which consisted of glycols, acids, ether, and ester compounds. The microwave liquefied products might be used as a potential source of chemicals. This is an abstract of a paper presented at the CHISA 2012 - 20th International Congress of Chemical and Process Engineering and PRES 2012 - 15th Conference PRES (Prague, Czech Republic 8/25-29/2012). | |

| Valorization of lignocellulosic residues of olives 8 | WO/2015/104349A2 | 2012 | Materials + Technology Group, Chemical and Environmental Engineering Department, University of the Basque Country, Plaza Europa 1, 20018, Donostia-San Sebastián, Spain | published | Valorization of some lignocellulosic agro-industrial residues to obtain biopolyols The valorization of renewable and abundant resources (date seed, olive stone, corncob, rapeseed cake and apple pomace) from agro-industrial activities was performed by mild liquefaction using polyhydric alcohols to obtain biopolyols that constitute an attractive choice for polyurethanes and other industrial sectors. RESULTS: The results indicated that liquefaction yields above 90% were obtained for almost all resources (except for rapeseed cake residue) at a minimum ratio of 0.25 mass/liquefying solvent by using weight ratio polyethylene glycol:glycerol:sulphuric acid of 80:20:3, at quite reasonable reaction temperature and time; 160 °C and 60 min, respectively. The values determined for hydroxyl number and viscosity in polyols from date seeds were found to be in the range of those typical of commercial polyols used in polyurethane foam production. On the other hand, the multifunctional liquids from apple pomace, olive stone, corncob and rapeseed cake could be used not only as precursor in polyurethane production but also for replacement of a certain amount of the polyhydroxy alcohol in polyester synthesis. CONCLUSION: The results obtained demonstrated the | Take inputs for the process The multifunctional liquids from apple pomace, olive stone, corncob and rapeseed cake could be used not only as precursor in polyurethane production but also for replacement of a certain amount of the polyhydroxy alcohol in polyester synthesis. |

					viotry of using polyhydric alcohol liquefaction to generate bio-based polyols, thus opening new avenues of exploitation of these by-products. © 2011 Society of Chemical Industry.	
Biorefinery of olive residues 9	SSN: 00019704	2010	Chemical Engineering Department, University of Córdoba, Spain	Not available as full text, only abstract	Biorefinery of agricultural residues by fractionation of their components through hydrothermal and organosolv processes The combined production of the most abundant agricultural residues in Spain (viz. cereal straw, sunflower stalks, vine shoots, cotton stalks, olive, orange and peach tree prunings, and horticultural and related residues) amounts to over 50 million tons per year. Agricultural residues can be valorized by converting their components jointly (combustion, pyrolysis, gasification, liquefaction) or separately (fractionation). The most useful method for exploiting such components separately involves isolating cellulose fibres for papermaking purposes. In recent times, this valorization method has led to the development of the biorefining concept. Biorefining involves the fractionation or separation of the different lignocellu-losic components of agricultural residues with a view to their integral exploitation rather than the mere use of cellulose fibre to obtain paper products. Biorefining replaces the classical pulping methods based on Kraft, sulphite and	Take inputs for the process The hydrothermal treatment provides a liquid phase containing hemicellulose decomposition products [both oligomers and monomers (glucose, xylose, and arabinose)] and a solid phase rich in cellulose and lignin. By contrast, the organosolv process gives a solid fraction (pulp) and a residual liquid fraction containing lignin and other useful substances for various purpose

					soda reagents with a hydrothermal treatment followed by organosolv pulping. The hydrothermal treatment provides a liquid phase containing hemicellulose decomposition products [both oligomers and monomers (glucose, xylose, and arabinose)] and a solid phase rich in cellulose and lignin. By contrast, the organosolv process gives a solid fraction (pulp) and a residual liquid fraction containing lignin and other useful substances for various purposes.	
Fuel analyses and processing of olive residues 10	ISSN: 00908312	2004	Selcuk University, Konya, Turkey Balikesir University, Balikesir, Turkey Selcuk University, Muh. Mim. Faculty, Department of Chemical Engineering, 42031 Konya, Turkey	Not available full text, only abstract	Fuel analyses and thermochemical processing of olive residues In this study, fuel properties, such as proximate analysis, ultimate analysis, higher heating value, and ash composition of three olive residues from olive oil plants (olive cake, olive kernel shell and olive kernel), were determined by analytical methods. Fuel properties for the combustion analysis of the residues can be conveniently grouped into physical, chemical, thermal, and mineral properties. The carbon content of selected samples varies from about 53% to 55%. The hydrogen content of the species varies from 6.5% to 6.9%. Oxygen content ranges from 35.5% to 36.5%, S is less than 0.1% and N ranges from 0.4-0.9%. This study indicates that olive residues could be used as pyrolizable and liquefiable	Take inputs for the process This study indicates that olive residues could be used as pyrolizable and liquefiable materials. The yield of liquefaction increased with increasing temperature of liquefaction. In general, the liquid yields from pyrolysis and catalytic liquefaction processes are higher than those of the other thermochemical methods.

					materials. The yield of liquefaction increased with increasing temperature of liquefaction. In general, the liquid yields from pyrolysis and catalytic liquefaction processes are higher than those of the other thermochemical method	
Valorization of olive residues 11		2003	Lab. de Chimie Agro-Industrielle, Ecole Natl. Sup. des Ing./Arts Chim., INP Toulouse, Toulouse Cedex 04 31077, France Tejeda-Ricardez, J., Vaca-Garcia, C., Borredon, M.E.	Not available as full text, only abstract	Design of a batch solvolytic liquefaction reactor for the valorization of residues from the agricultural foodstuff Olive stone residues (23%wt) were liquefied in phenol (71%wt) in the presence of sulfuric acid (6%wt) as catalyst at 170°C during 2 h. A 500 ml classic reactor under atmospheric conditions was used to establish the characteristics of the new 2001 liquefaction reactor. The liquefied products can be used as raw material for phenol-formaldehyde resins. The batch feeding procedure, the average temperature and the configuration of the reactor largely determined the viscosity and the molecular weight of the liquefied products. These parameters were positively modified by the constantly presence of olive stone moisture and water from depolymerization in the reaction medium. A jacketed cooling wall in the upper half of the 2001 reactor and a heat exchanger were necessary to	Take inputs for the process

					accelerate vapour condensation, and to improve the contact in the reaction mixture. The recovery of liquefied products was also improved by using a closed container with a pressure-equalizing system that avoids the release of phenol vapour to the atmosphere.	
Recover of phenolic compounds from olive

12 | ES 2143939 | 1998 | CONSEJO SUPERIOR INVESTIGACION [ES] + (CONSEJO SUPERIOR DE INVESTIGACIONES CIENTIFICAS) | Published | Spanish patent ES 2143939 discloses the use of a steam explosion and mannitol process to recover the structural phenolic components from the olive pits and the kernel shell. With this process, the materials are treated in a 2 l steam explosion unit at temperatures around 200° C for time periods of 2–4 minutes, then an abrupt decompression occurred and the subsequent unloading of the reactor. The results obtained show that hydroxytyrosol is extracted from the pit in soluble extract concentrations of up to 1% in dry weight of the pit, less quantity than that obtained in the pulp, where this polyphenol is mainly found. In the case of the kernel shells, tyrosol is obtained in concentrations of up to 0.5% in dry weight and it is verified that the addition of acid to the material before the treatment appreciably increases the quantities of phenols detected in the soluble extract. | Seems relevant for AgriMax |

Topic, nº	Patent	Priority date	Applicant	Status	Abstract	Relevance/ Differences vs. AgriMax
Extraction of polyphenols from plant materials 13	US 7109384 B2	2004	Centro De Investigaciones Energeticas, Medioambientales Y Technologicas	Expired	The hydrothermal treatment is based on placing the crude residual plant material in contact with hot water in a closed reactor, comprising the following steps: a) placing the material to be treated in contact with water in a closed reactor, and adjusting the solid/liquid ratio so that it ranges from 1/5 to 1/15 (w/v): b) stirring; c) heating to a temperature between 180 and 240° C., and at a pressure so that the water is maintained in liquid phase; d) constantly stirring the mixture for a time period between 4 and 30 minutes; and e) cooling the reactor to approximately 40° C., unloading the mixture, filtering and recovering the liquid fraction.	Provided data on high temperature extraction of polyphenols

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