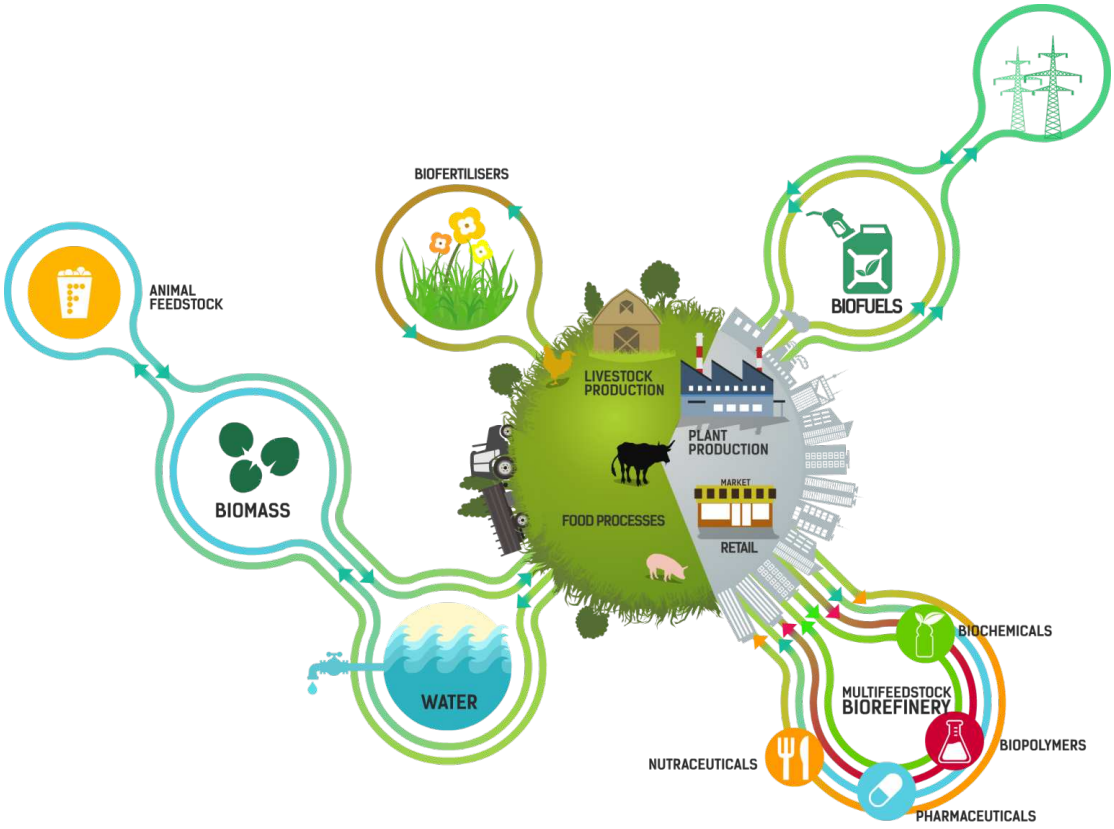
Characterisation of Agricultural Waste Co- and By-Products



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Introduction

The purpose of this study is to provide a database/inventory of the physicochemical characteristics of the main Agricultural Wastes Co- and By-products (AWCB) that are produced in the EU countries. The AWCB will be characterised mainly in terms of energy content, nutritional value, minerals, valuable compounds and water content. In the context of circular economy, aiming to eliminate waste and maximize recycling and reuse of resource (European_Commission, 2014), the physicochemical characteristics of the AWCB produced throughout the agricultural value chain, greatly specify the valorisation processes and methodologies that can be adopted. This study constitutes Deliverable 1.2 of the **Work package 1: Agricultural Waste Value Chain Assessment** of the European Union's Horizon 2020 research and innovation programme "AGROCYCLE" under grant agreement Nº 690142.

General study context

Generation of AWCB during the production, processing and consumption of agricultural commodities is unavoidable. Either referring to non-edible parts of each commodity (e.g. straws, pruning, manure, bones etc.) or to edible parts and quantities that are removed or discarded so as to reassure quality and health appropriateness of the final product/food (e.g. peels, rotten fruits and vegetables, spoiled meat and milk), AWCB are estimated to more than 700 million tons per year in Europe (Pavwelczyk, 2005). Apart from its significant quantities, the physicochemical characteristics of the various AWCB denote that there is immense potential for their reuse/recycle/valorisation through various different processes.

The EU has recently put forward the need for advancement of the European bio-based economy (or bio-economy), that refers to the use of renewable biological resources and its valorisation through conventional or novel processes into new products, materials, energy etc (European_Commission, 2012). In the context of development of European bio-economy, valorisation of AWCB seems of highly importance given that it addresses basic societal challenges, namely: *Ensuring food security* (AWCB, most of the times, cannot be used as human food in its present form); *Managing natural resources sustainability* (valorisation of AWCB increases the portion of agricultural production that is used and not wasted); and *Reducing dependence on non-renewable resources* (AWCB, as well as the commodities that they originate of, are renewable materials that can be used instead of non-renewable resources).

The reuse/recycle of AWCB in a wide range of agricultural as well as other uses is not something new; people have always tried to increase exploitation of the available resources. For example, straw and other plant deriving AWCB have been used for animal fodder or bedding material, manure has been used as organic fertilizer to increase nutrients (e.g. nitrogen and phosphorus), as well as organic content of fields, whereas pruning and forestry residues have been used for energy source mainly for heating. However, both new needs and policies, such as the promotion of bio-economy in Europe, as well as advancements in technologies have put forward either novel and more efficiently processes/techniques for conventional AWCB uses (i.e. as energy, fertilizer etc.) or have resulted in new bio-based products and valorisation practices such as recovery of high-added-value compounds, production of functional materials, novel feeds for chemicals production etc.

In all the aforementioned valorisation practices, the physicochemical properties of the AWCB streams play a decisive role on the valorisation route that will be adopted. For example, AWCB that have high energy content seem more appropriate for energy exploitation, whereas AWCB with increased concentration of nitrogen and phosphorus seem favourable quantitates for organic fertilizers. The physicochemical characteristics may also affect the technologies that can be used; i.e. different technologies will be used for energy exploitation of an AWCB with high and low moisture, or high and low ash content, respectively. Finally, detailed knowledge of AWCB physicochemical properties may result in multiple/interrelated valorisation processes; e.g. recovery of high-added-value bioactive compounds from an AWCB through enzymatic hydrolysis of the lignocellulosic matrix

that encloses the bioactive compound may render this AWCB appropriate for energy exploitation through fermentation for ethanol production or enhanced anaerobic digestion for biogas production.

As already mentioned, recent trends both in R&D and policy fields have resulted in a significant volume of available data on AWCB physicochemical properties and characterisation. However, given that most of these R&D activities are focused/oriented in a specific valorisation process/field (i.e. either for energy, bio-chemicals, organic fertilizers etc.), reported data mainly refer to a specific valorisation field. Taking also into account the fact that AWCB are, by nature, significant versatile in respect to their properties, it is concluded that data from many different sources should be collected and reviewed so as to obtain an accurate characterisation of their physicochemical properties. This characterisation seems necessary for obtaining a broader view concerning their valorisation potential through different options/pathways.

Scope of this report

The main objectives of this report include:

1. Collection of data concerning characterisation of the main AWCB considered in this project in respect to their physicochemical properties;
2. Review of relevant R&D and patent information related to processing/recovery of high-added-value bioactive compounds from AWCB;
3. Set up a relevant database, that could be updated during the entire period of the project, and which will be integrated in the Decision Support System (DSS) that will be developed in the context of "Work package 7: Knowledge platform and training".

As regards the type of AWCB that are considered as part of the report, given the great number of agricultural products/commodities produced in Europe, as well as the many different and versatile AWCB streams produced throughout the whole commodity value chain, some restrictions and assumptions were put forward, that allowed for the on-time completion of the report, without overlooking the overall objectives of this study. These assumptions, together with the catalogue of the commodities and their respective AWCB, as well as the physicochemical properties that were included in the report are summarized in Chapter 2. Next, the collected data are presented in different Chapters, one for each commodity. Each Chapter provides some basic data concerning the commodity in question, followed by Tables where the physicochemical data of its main AWCB streams are summarized, together with some brief comments. Finally, a short overview on the R&D literature and patents for recovery of high-added-value bioactive compounds from these AWCB streams is given in tabular form.

Methodology

Selection of commodities and corresponding AWCB

The economic accounts for agriculture show that the total output of the agricultural industry in the EU28 in 2014 was estimated to EUR 418.5 billion at basic prices. In 2013, the EU28 produced 306 million tonnes of cereals, including rice, 109 million tonnes of sugar beet, approx. 50 million tonnes of potatoes, more than 60 million tonnes of fruits and vegetables and 22.6 million tonnes of grapes. Farms across the EU28, also produced 165 million tonnes of milk and more than 43 million tonnes of meat (at slaughtering) in 2014 (EUROSTAT, 2015a). In Table 2.1, the top 10 commodities, in terms of quantities for all the countries of the EU28 is presented, based on data for the year 2013 (FAO, 2016). It is obvious that most of these commodities are the same in the top 10 list for most of the countries of the EU28. In fact, the following 26 commodities: Milk cow, Wheat, Potatoes, Barley, Sugar beet, Maize, Pigs, Grapes, Tomatoes, Chicken, Oats, Olives, Sunflower seed, Apples, Triticale,

Rye, Cattle, Oranges, Onions, Cabbages, Tangerines, Carrots, Cauliflowers, Rapeseed, Peaches, and Rice, cover more than 94.0% of the top 10 list for all the EU28 countries. Therefore, the study will be focused on the main AWCB stream of the aforementioned 26 commodities. This list is rather wide, containing commodities from all the main agricultural groups, i.e. 4 animal products (milk and meat), 6 cereals including rice, 3 oil seeds, 7 fruits including tomatoes and olives, 4 vegetables, 1 tuber (potato) and 1 root crop (sugar beet); the above list is a good representative of all the main agricultural commodities produced in the EU28.

Table A: Top 10 agricultural commodities in the EU28 countries in terms of quantities.

COUNTRY	COMMODITIES									
Austria	Sugar beet	Milk cow	Maize	Wheat	Barley	Potatoes	Pigs	Apples	Grapes	n.a.
Belgium	Sugar beet	Milk cow	Potatoes	Wheat	Pigs	Chicken	Carrots	Turnips	Pears	Chicory
Bulgaria	Wheat	Maize	Sunflower	Milk cow	Barley	Rapeseed	Grapes	Potatoes	Tomatoes	Chicken
Croatia	Maize	Sugar beet	Wheat	Milk cow	Barley	Grapes	Potatoes	Sunflower seed	Apples	Soybeans
Cyprus	Milk cow	Potatoes	Pigs	Tangerines	Oranges	Milk goat	Grapes	Chicken	Milk sheep	Grapefruit
Czech Republic	Wheat	Sugar beet	Milk cow	Barley	Rapeseed	Maize	Potatoes	Chicken	Triticale	Pigs
Denmark	Milk cow	Wheat	Barley	Sugar beet	Pigs	Potatoes	Rapeseed	Rye	Chicken	Cattle
Estonia	Milk cow	Barley	Wheat	Rapeseed	Potatoes	Oats	Pigs	Peas	Cabbages	Rye
Finland	Milk cow	Barley	Oats	Wheat	Potatoes	Sugar beet	Pigs	Chicken	Cattle	Rapeseed
France	Wheat	Sugar beet	Milk cow	Maize	Barley	Potatoes	Grapes	Rapeseed	Pigs	Triticale
Germany	Milk cow	Wheat	Sugar beet	Barley	Potatoes	Rapeseed	Rye	Pigs	Maize	Triticale
Greece	Maize	Olives	Wheat	Tomatoes	Grapes	Potatoes	Oranges	Milk cow	Milk sheep	Peaches
Hungary	Maize	Wheat	Milk cow	Sunflower	Barley	Sugar beet	Apples	Maize green	Rapeseed	Grapes
Ireland	Milk cow	Barley	Cattle	Wheat	Potatoes	Pigs	Oats	Chicken	Mushrooms	Cabbages
Italy	Milk cow	Grapes	Maize	Wheat	Tomatoes	Olives	Apples	Sugar beet	Oranges	n.a.
Latvia	Wheat	Milk cow	Rapeseed	Barley	Potatoes	Oats	Rye	Cabbages	Pigs	n.a.
Lithuania	Wheat	Milk cow	Sugar beet	Barley	Rapeseed	Triticale	Potatoes	Oats	Pigs	Rye
Luxembourg	Milk cow	Wheat	Barley	Triticale	Potatoes	Rapeseed	Cattle	Grapes	Pigs	Oats
Malta	Milk cow	Wheat	Potatoes	Tomatoes	Onions	Cauliflowers	Broccoli	Pigs	Lettuce	Chicory
Netherlands	Milk cow	Potatoes	Sugar beet	Pigs	Onions	Chicken	Tomatoes	Carrots	Turnips	Cucumbers
Poland	Milk cow	Sugar beet	Wheat	Potatoes	Triticale	Maize	Rye	Apples	Barley	n.a.
Portugal	Milk cow	Tomatoes	Grapes	Olives	Potatoes	Chicken	Apples	Pigs	Oranges	n.a.
Romania	Maize	Wheat	Milk cow	Potatoes	Sunflower	Barley	Cabbages	Sugar beet	Grapes	Tomatoes
Slovakia	Wheat	Sugar beet	Maize	Milk cow	Barley	Rapeseed	Sunflower	Potatoes	Rye	n.a.
Slovenia	Milk cow	Maize	Wheat	Apples	Barley	Grapes	Potatoes	Chicken	Cattle	Pigs
Spain	Olives	Wheat	Grapes	Milk cow	Tomatoes	Pigs	Oranges	Sugar beet	Potatoes	Tangerines
Sweden	Milk cow	Sugar beet	Barley	Wheat	Oats	Potatoes	Rapeseed	Pigs	Rye	n.a.
United	Milk cow	Wheat	Sugar beet	Barley	Potatoes	Rapeseed	Chicken	Oats	Cattle	Pigs

Each one of these commodities result in numerous solid, sludgy or liquid AWCB streams throughout its value chain from harvesting, to processing and final consumption. The number of AWCB streams differ for each commodity, however most of the time there are over 5 main AWCB commodities; for example, throughout the olive value chain there are 7 main AWCB streams, namely: branches and twigs from pruning, rotten and spoiled olives, leaves, pomace, olive mill wastewater, table olive wastewater, and pits. Accordingly, for maize there are 6 main AWCB streams, namely: stalks, leaves, husk, cobs, maize cake, and wasted maize oil. It is obvious that, in the context of this study, it is not possible to collect data for all the AWCB of the aforementioned commodities since the number of different AWCB may exceed 120. Based on the aforementioned, it was decided to narrow down the number of AWCB for each commodity to the main two AWCB, in terms of quantity. In some cases, in order to have data from various different streams (both solid and liquid), a liquid or sludgy AWCB stream was chosen instead of the two main solid AWCB. The list of the AWCB that are considered in this report are summarized in **Error! Reference source not found.**. Onions does not seem to have any ther important AWCB than their peels/skin, so only one AWCB is considered this commodity.

Table B: List of the AWCB considered in this report.

COMMODITY	1ST AWCB	2ND AWCB
Milk cow	Manure	Whey wastewater
Wheat	Straw	Bran
Potatoes	Peels/skin	Potato processing wastewater
Barley	Straw	Bran
Sugar beet	Pulp	Molasses
Maize	Stalks	Cobs
Pigs	Manure	Slaughter wastewater
Grapes	Pomace	Lees
Tomatoes	Peels/skin	Tomato processing wastewater
Chicken	Litter	Slaughter wastewater
Oats	Straw	Bran
Olives	Pomace	Olive mill wastewater
Sunflower seed	Stalks	Cake
Apples	Pomace	Apple processing wastewater
Triticale	Straw	Bran
Rye	Straw	Bran
Cattle	Manure	Slaughter wastewater
Oranges	Pomace	Orange processing wastewater
Onions	Peels/skin	-
Cabbages	Peels/skin	Leaves
Tangerines	Pomace	Tangerine processing wastewater
Carrots	Peels/skin	Carrots processing wastewater
Cauliflowers	Peels/skin	Leaves
Rapeseed	Stalks	Cake
Peaches	Peels/skin	Kernel
Rice	Straw	Husk

Selection of physicochemical properties

There are numberless data concerning physicochemical characterisation of biomass and corresponding AWCB. However, many of these data are not useful due to various problems that arise from the lack of well-established methodology, unsuitable scientific approaches, incomplete data reporting and misunderstandings (Vassilev et al., 2010). Some of these problems include: analytical

and representative problems, lack of generally accepted methodology, terminology and classification systems, uncomplete description of sample collection, storage and processing conditions, and incomplete characterisation of AWCB samples.

Another thing that should be carefully taken into consideration is that there are different ways to express the composition of biomass samples, which are equally used in the scientific literature, however not always explicitly specified. The major ways of expressing the composition of a biomass/AWCB sample are the following:

i. The "as received" composition (ar) includes the moisture content of the biomass, typically at the point of harvesting or delivery. It is the most valid composition to be used in terms of performing combustion calculations, estimating efficiencies, etc. On the other hand, the exact as received composition is obviously affected by the moisture content and all the factors which affect it. Also, the moisture content is the most easily controlled quality parameter of the fuel, being subject to change through drying processes. As a result, the moisture of a sample may vary between the sampling point, the delivery point and the final analysis in the lab. Therefore, although extremely useful for actual applications, the as received composition is not typically a valid indication for comparisons between biomass types.

ii. The "dry basis" composition (db) refers to the composition of the biomass excluding all water content. Obviously, this state can only be applicable for laboratory samples – all other types of drying in "real-life" applications always leave some of the moisture, however low, in the fuel. The dry basis is a good starting point for comparing the properties of different fuel types and is the typical format in which most laboratories report their results. However, it does not take into account variations in the inorganic part of the biomass which may be due to the impact of the supply chain.

iii. The "dry, ash free" basis (commonly abbreviated as "daf") refers to the composition of biomass excluding all water and ash content. The dry, ash free basis is an even more ideal case than the dry basis, since actual separation of the ash from the organic part of biomass is impossible.

In this study all the physicochemical properties are expressed on "dry base", except for the moisture content which is expressed in "as received" base. Literature data expressed in other ways were converted to "dry base", whereas data that did not explicitly state their expressing base were not received into consideration. Conversions between different expression bases are described in the *European Standard EN 15296:2011 "Solid biofuels - Conversion of analytical results from one basis to another".*

The valorisation/reuse of AWCB includes many different processes and ways. For instance, straw can be used as fodder (with or without processing), bedding material, for energy exploitation through direct burning or preferably through various processes like pyrolysis, anaerobic digestion, hydrothermal carbonization etc., as organic fertilizer/soil conditioner to replenish soil organic matter, or for production of insulation panels (ecococon, 2016), or substrate for growing mushrooms (Yang et al., 2013a). It is obvious that different physicochemical characteristics and properties are of interest in each one of the following applications. In order to organize the numerous physicochemical characteristics of the different AWCB, it was decided to group together physicochemical characteristics that refer to one of the five subsequent categories:

i. Energy related properties,
ii. Fodder related properties,
iii. Fertilizer related properties,
iv. Wastewater related properties (only applicable to liquor AWCB), and
v. Bioactive compounds related properties.

The parameters/properties that are included in the aforementioned categories are subsequently summarized.

Energy related properties

The identification and characterisation of a material as potential fuel is the initial and most important step during the investigation and applications of such a fuel. The composition and certain physical properties determine the quality, potential applications and environmental problems related to the fuel. For energy characterisation of fuels the most widely used analysis include: a. energy content, namely high and low heating values; b. proximate analysis, namely fixed carbon, volatile matter, ash yield and moisture; and ultimate analysis, namely carbon, oxygen, hydrogen, nitrogen and sulfur quantitative analysis.

The lower heating value (also known as net calorific value) of a fuel is defined as the amount of heat released by combusting a specified quantity (initially at 25°C) and returning the temperature of the combustion products to 150°C, which assumes the latent heat of vaporization of water in the reaction products is not recovered. The higher heating value (also known gross calorific value or gross energy) of a fuel is defined as the amount of heat released by a specified quantity (initially at 25°C) once it is combusted and the products have returned to a temperature of 25°C, which takes into account the latent heat of vaporization of water in the combustion products. Determination of calorific value can be done based on various analysis standards, e.g. *European Standard EN 14918:2009: "Solid biofuels. Determination of calorific value"*.

Proximate analysis refers to the breakdown of the fuel in volatiles, char or fixed carbon and ash. The proximate analysis is typically given on a dry basis and should be measured in a laboratory employing the relevant European standards (*EN 15148 for volatiles, EN 14775 for the ash content*). The content of fixed carbon, "char", is calculated by subtracting from 100 the weight composition of the other two compounds.

The elemental or ultimate analysis is the second typical way to present the components in the organic part of fuels. Instead of grouping compounds based on the chemical structure or the combustion behavior, the ultimate analysis presents directly the main elements present in the organic part of biomass. The ultimate analysis is also commonly referred to as the CHNS analysis on the basis of the most commonly measured elements. The measurement of the elemental composition for C, H and N is typically performed in laboratory equipment called elemental analyzers. The *EN 15104:2011: "Solid biofuels. Determination of total content of carbon, hydrogen and nitrogen"* instrumental methods standard should be followed for their measurement. For sulphur and chlorine different procedures are described in the relevant standard, which is *EN 15289: "Solid biofuels - Determination of total content of sulfur and chlorine"* (BISYPLAN, 2012).

Fodder related properties

Chemical analysis can provide valuable information about the actual chemical constituents of a biomass sample influencing digestion, and consequently specifying biomass quality as a fodder. Chemical analysis methods cannot give a direct estimate of nutritive value, but based on statistical associations they can predict animal performanc (Cherney, 2000). The first widely used method for analysis of the various macronutrients in feed is the Weende or proximate analysis developed in 1860 by Henneberg and Stohmann in Germany (Henneberg & Stohmann, 1860). Proximate Analysis is a partitioning of fodder compounds into six categories based on the chemical properties of the compounds. The six categories are: moisture, ash, crude protein, crude lipid (or ether extract), crude fibre, and nitrogen-free extracts (digestible carbohydrates). Due to the unsatisfactory principle of crude fiber term, this analysis is replaced with the Van Soest Detergent Fiber analysis.

The concept behind the detergent fiber analysis is that plant cells can be divided into less digestible cell walls, contains hemicellulose, cellulose and lignin, and mostly digestible cell contents, contains starch and sugars. Van Soest separated these two components successfully by use of two detergents: a neutral detergent (NDF) and an acid detergent (ADF) (Soest, 1963; Soest & R.H., 1967). NDF equals Hemicellulose + Cellulose + Lignin, whereas, ADF equals Cellulose + Lignin. Neutral Detergent Fiber is a good indicator of "bulk" fiber and thus feed intake. Acid detergent fiber is a good indicator of digestibility and thus energy intake. These analyses are not standard and there does not exist any European standard regarding these physicochemical properties.

The moisture level is important factor both for storage of biomass samples and for its use for biological processes. The moisture and low volatile materials are removed by heating, and the remaining portion is the dry matter, moisture-free content of the sample. Crude protein measures the nitrogen content of a feedstuff, including both true protein and non-protein nitrogen. It is based on the assumption that protein contains about the same amount of nitrogen (16%). Ether extract is applicable for the determination of crude fat in dried biomass feeds, whereas the ash fraction contains all the mineral elements obtained after oxidizing all organic matter in a weighed sample of the material by incineration.

Despite the fact that these properties have been developed for evaluation of biomass samples as fodder in animals, they can provide valuable data, and thus are also used for the characterisations of biomass samples that are going to be processed through biological processes i.e. fermentation for ethanol production, anaerobic digestion for biogas production or other biological processes for bio-technological production of chemicals, biomolecules, enzymes, single-cell-biomass, etc.

Fertilizer related properties

Organic fertilizers include fertilizers that derive from animal or plant material. Fertilizers should provide the soil with the following three main macronutrients: nitrogen, phosphorus, and potassium, and the three secondary macronutrients: calcium, magnesium and sulfur. Therefore, in order to assess the performance of various AWCB samples as organic fertilizers it is important to analyze their content in the aforementioned elements. Nitrogen is measured through the ultimate analysis of biomass samples, whereas the other minerals are measured in the ash of the biomaterial, after organic matter incineration. Given that the concentration of biomass samples in these minerals is rather low, the unit that it is used to express their concentration is mg/Kg on "dry base".

Wastewater related properties

Many AWCB streams are of liquid of sludgy phase; typical liquid AWCB streams include wastewater produced during processing like whey stream during cheese production, olive mill wastewater, slaughter wastewater etc.; some dilute manure streams could also considered as/liquid/sludgy AWCB. These AWCB can be characterised/analysed through common procedures used in water and wastewater analysis.

Wastewater is characterised in terms of its physical, chemical and biological composition. Physical parameters include Total Solids, Total Suspended Solids, Total Dissolved Solids, Turbidity, Conductivity, Color etc. Common chemical parameters include Total Organic Carbon (TOC), Chemical Oxygen Demand (COD), Biological Oxygen Demand (BOD), Total Nitrogen (TN), Total Phosphorus (TP), Total Kjedlhahl Nitrogen (TKN), pH, Alkalinity, Oil and Grease, as well as analysis of specific ions. Finally, biological characteristics comprise number of Coliform organisms, specific bacteria, toxicity etc. (Tchobanoglous et al., 2003). The number of required properties for accurate characterisation of a liquid AWCB greatly depends on the treatment/valorisation process that has been selected. For example, knowledge of alkalinity levels is highly important in anaerobic process or when nitrification is required, however it is not a critical parameter in aerobic biological oxidation of organic matter.

Nonetheless, there are some properties parameters that are usually determined in all the wastewater analysis. These parameters are subsequently summarized.

i. pH: The hydrogen ion concentration is an important quality parameter of all water/wastewater samples. The hydrogen ion concentration is expressed as the negative log of the hydrogen ion concentration and its concentration range greatly affects mainly biological and chemical treatment processes.

ii. Conductivity (mS/cm): The electrical conductivity of a liquid is its ability to conduct electric current. Given that electric current in water is transported by ions, the conductivity is a surrogate measure of total dissolved solids content. The conductivity also affects biological and chemical processes, and is also an important parameter that determine suitability of water for irrigation.

iii. Total Alkalinity (meq/L): Alkalinity in water samples mainly comprise hydroxide, carbonates and bicarbonates concentration. The alkalinity is a measure of the acid buffering capacity of the sample, i.e. its ability to resist pH changes caused by acids addition.

iv. Total Solids and Total Fixed Solids (mg/L): Total Solids quantifies the concentration of solids materials in a water/wastewater sample. Total Solids are obtained by evaporating the liquid sample to dryness (usually with heating at 105 ^{o}C) and measuring the mass of the residue. Total Fixed Solids refer to inorganic solid material in a water/wastewater sample remaining after incineration of the Total Solids at a temperature of approx. 550 ^{o}C.

v. Total Suspended Solids and Fixed Suspended Solids (mg/L): They refer to the portion of Total Solids and Total Fixed Solids respectively, which is separated through filtration with a filter paper with pore size in the range of 0.45 μm to 2.0 μm.

vi. Total Organic Matter (mg/L): It is a surrogate parameter quantifying the organic carbon present in a liquid sample. The test method uses heating, or chemical oxidation to convert organic material to CO_2, which is then measured with a gas analyser. The TOC is a measure of its organic pollutant characteristics and it can be related with COD values.

vii. Chemical Oxygen Demand (mg/L): The COD test is used to measure the oxygen equivalent of the organic material in a liquid sample that can be oxidized chemically, using dichromate in an acid solution. It is also a surrogate parameter of organic matter and is highly important in aerobic biological processes.

viii. Biological Oxygen Demand (mg/L): The BOD test is the most widely used parameter to quantify the concentration of biodegradable organic matter present in a water/wastewater sample. Despite having serious limitations (e.g. toxic compounds) and rather moderate accuracy, it remains the preferred options for determining the biodegradability of the organic matter present.

ix. Total Nitrogen and Total Kjeldahl Nitrogen (mg/L): Nitrogen in water/wastewater samples may be present in various forms including NH_4^+/NH_3, NO_3^-, NO_2^-, and organic nitrogen. Total Nitrogen measures all the nitrogen species present in water/wastewater sample, whereas Total Kjeldahl Nitrogen measures organic plus ammonium/ammonia nitrogen.

x. Total Phosphorus (mg/L): Likewise, phosphorus in water/wastewater samples can be found in various forms like orthophosphate, polyphosphate and organic phosphorus. Total Phosphorus measures all the aforementioned phosphorus forms through an acid digestion process that converts all phosphorus forms to orthophosphate that can be determined photometrically.

xi. Oil & Grease (mg/L): The concentration of dispersed oil and grease is an important parameter for water quality. Oil and grease in water can cause surface films and shoreline deposits. Oil and Grease in water is commonly determined by extraction into a non-polar, hydrocarbon-free solvent followed by measurement of the infrared absorption spectrum of the extract.

Bioactive compounds related properties

Bioactive compounds are essential and non-essential compounds that occur in nature, mainly in small amounts and have an effect on living organism, including people. Bioactive compounds, comprise many different organic molecules that are mainly secondary metabolites, mainly of plant origin, that are not directly involved in the growth, development or reproduction of an organism, but are required for the survival of the organism in its environment. Secondary metabolites play an important role in plant defence, and many of them can be used as high-added-value chemicals for medicines, flavourings, anti-oxidants etc.

There is no fixed, commonly agreed upon system for classifying secondary metabolites. However, based on their biosynthetic origins, plant secondary metabolites can be divided into three major groups: Flavonoids and allied phenolic and polyphenolic compounds, Terpenoids and Nitrogen-containing alkaloids, and sulphur-containing compounds (Crozier et al., 2007). Given their widely diverse nature, these organic compounds are not quantified through standard analytical techniques, but usually require high-tec chromatographic-based analysis (e.g. GC, HPLC, GC-MS etc.). These compounds, usually, exist in low concentration in biomass samples, and most of the times they are enmeshed/bound to some structural organic biopolymers. Therefore, isolation of such compounds requires an extraction/recovery procedure from the bulk of the biomass material. Despite the low concentration of bioactive compounds, their high bioactivity, complex molecule structure that hinders their chemical synthesis from simple molecules, and their high value/price renders their recovery of highly importance. Typical categories of bioactive compounds found in AWCB include: carotenoids, anthocyanins, betalains, phenolic acids, monoterpenes, isoflavones, flavonols, stilbenes, procyanidins, isothiocyanates, glucosinylates, glycosides, peptides, fatty acids, steroids, alkaloids, terpenes, waxes etc.

CEREALS & OIL SEEDS

1. Wheat

Wheat is a principal food crop in many countries around the world and its production in 2016/17 is forecasted at 744.4 million tons, 9.4 million tons ahead of last year's record. It is a major part of most diets of the EU, US and China populations and ubiquitous grain crop in consequence of its agronomic adaptability, ease of storage, nutritional goodness and the ability of its flour to produce various products. In agriculture, it imparts 13.1% to the value added and 2.8% in the gross domestic product (GDP) (WheatOutlook, 2016).

Wheat milling by-products—such as straw (dry stems and leaves left after the harvest of wheat), bran (outer seed coat of a wheat kernel), shorts (more inward layers of the seed coat that contain some starchy or floury components), and middling (an intermediate fraction that consists of a combination of bran and shorts)—are mostly used as livestock bedding or low-grade animal feed providing minimal return. At present only about 3.2% of the economic return on wheat is from straw (Dunford & Edwards, 2010). However, the better utilization of wheat by-products can also support the medicine, cosmetics, soil fertility, bio charcoal, fuel, livestock bedding and fodder, basket-making and fermentation industry. They can also be a source of an additional income for the farmers. This can be an important motivational factor in promoting an efficient harvesting, collection and management of wheat by-products.

Utilization of wheat by-products in the fermentation industry

Synthetic and expensive substrates are being replaced by agro-industrial by- products for the production of a wide range of value added biotechnological products (Mojsov, 2010). Wheat straw (WS) is an efficient substrate due to its better air circulation, loose study binding ability and efficient penetration by fungal mycelium. It is the cheaper substrate so it is a cost-effective substrate in fermentation industry. Extracellular hydrolytic enzymes are being produced using WS under Submerged Fermentation (SF) as well as Solid-State Fermentation (SSF) systems. A large number of secondary metabolites can also be obtained by fermentation of WS (Yasin et al., 2010).

Utilization of wheat by-products in the pulp industry

Nonwood fibers containing cellulose and hemicellulose have a long history as a raw material in pulp industry (Mrudula & Murugammal, 2011). Straw and grasses are thus being utilized in larger amounts in this industry. WS can be easily pulped and bleached with about 40% yield and producing fine textured study (CWC & Domta_Inc., 1997). Cellulases and hemicelluloses' enzymes have central application for bio bleaching and production of dissolving pulp. The biosynthesis of these enzymes takes place using different cellulosic substrates including wheat bran, wheat straw etc. (Drankhan et al., 2003; Gubitz et al., 1998).

Bioremediation

Bioremediation has the potential to restore contaminated environments at no expense. Treatment of wastewater through safer methods has always been the focus of environmentalists using various microbial and plant species (Javed et al., 2012). However, degradation of heavy metals has been a question mark for human being. WS, an abundantly available source is reported for sorption of heavy metals, i.e. chromium. It is a very cheap and flexible substrate for metal ions. Functional groups like hydrolytic, carboxylic and phenolic groups in the lignin, cellulose and fatty acids are ideal for ion fixation (Dupont et al., 2003).

Soil fertility and organic content

Crops grow by utilizing the minerals from soil. When crops are harvested the mineral contents of the soil are also lost and thus the supplementation of synthetic fertilizers is required. To provide a substitute for that, organic wastes or agricultural wastes can be added to soil to fulfil the demand of crops. WS a major staple crop is harvested on a massive scale every year and the residues are helpful in maintaining the soil fertility if added as such or by mixing with the urea to balance the nitrogen content in the field (T.D. & G.W., 1983).

Medicinal value

WS has been reported to relief from condition of biliousness (Drankhan et al., 2003). It has been suggested that tooth-disorders i.e., Pyorrhea can be prevented and cured using WS. Chewing of wheat grass not only benefits by exercising of teeth and gums but also assists in digestion. It acts as brilliant mouth wash especially for sore throat and pyorrhea as well as it keeps tooth from decay and tooth aches. Moreover, it extracts out toxins from the gums and hence controls bacterial growth (Kumar, 2011). With dermatological context, the ash of WS has been reported to remove skin blemishes. [11]

Making biochar

Charcoal produced by pyrolysis of wood, straw, waste, etc. for capturing and storage of carbon is known as biochar. Growing concern about greenhouse gas emissions make it crucial to find ways of exploring carbon sinks along with the control over its discharge. Biochar is technically considered as most feasible way of creating carbon sink as well as for improving soil structure to enhance the productivity of soils about 2-3 times. The peculiar structure of biochar offers large surface area which is important in improving the soil texture, arability, retention of nutrients and provides surface for growth of beneficial microorganisms. Moreover the water holding capacity of soils is also increased by adding biochar to them, thus helps prevent leaching of valuable nutrients into streams and rivers (Goodall, 2010).

1.1 Wheat straw

Wheat straw (WS) is a by-product, the dry stalk of wheat (Figure 1.1) after the grain and chaff have been removed (Bajpai, 1999; Mrudula & Murugammal, 2011). It consists of around 60% of the crop. One hectare of wheat produces more than 4.8 tons of straw (Saha et al., 2005). The main fractions of WS are nodes, internodes and leaves (Figure 1.1) (Mckean & Jacobs, 1997). It is usually gathered and stored in a straw bale and has many uses.

The chemical analysis of WS is summarized in Table 1.1. WS is primarily composed of carbohydrates (cellulose, hemicellulose, lignin), being also rich in proteins, minerals (calcium and phosphorous), silica, acid detergent fibres and ash. Along with these components, WS is also rich in bioactive compounds and vitamins (Slavin, 2003). However the accurate composition of macro and micronutrients can vary from cultivar to cultivar, (Safdar et al., 2009) stages of plant growth, the nature of soil and fertilizer to be used and climatic conditions (Yasin et al., 2010). The physical content revealed that parts of wheat plant like internodes (68.5%), leaf-sheath (20.3%), leaf-blade (5.5%), nodes and fines (4.2%) and grains and debris (1.5%) show varied mass percentage of WS fractions (Mckean & Jacobs, 1997).

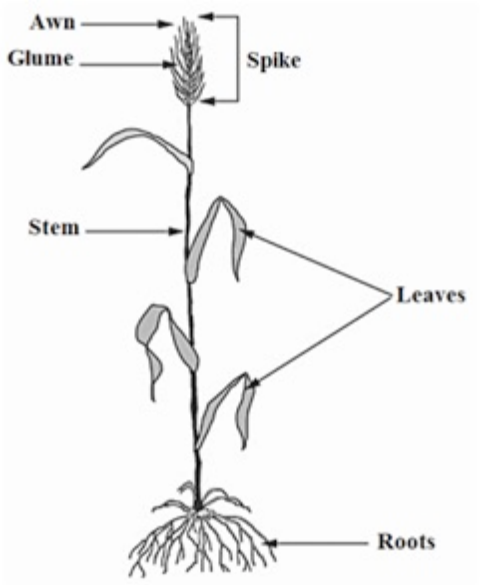

Figure 1.1: Morphology of wheat plant showing spike (head) (ECN, 2016).

Table 1.1: Summary of main physicochemical characteristics of wheat straw (Dunford & Edwards, 2010; ECN, 2016; feedipedia, 2016; Khan & Mubeen, 2012; Pasha et al., 2013).

PARAMETER	VALUE (AVERAGE)
ENERGY	
Higher Heating Value (HHV) (MJ/kg)	16.19-18.95 (17.15)
Lower Heating Value (LHV) (MJ/kg)	15.08-17.06 (16.07)
Metabolizable energy (mcal/kg)	0.304
Fixed Carbon (%wt)^{am}	16.34
Volatile Matter (%wt)^{am}	66.03
Ash (%wt)^{am}	2.8-16.95 (9.56)
Moisture (% wt)^{am}	8.15-10.06 (8.88)
Carbon (%wt)^{db}	38.58-47.79 (42.65)
Oxygen (%wt)^{db}	36.28-42.98 (40.44)
Hydrogen (%wt)^{db}	5.07-5.91 (5.54)
Nitrogen (%wt)^{db}	0.35-1.07 (0.70)
Sulfur (%wt)^{db}	0.13-0.29 (0.19)
FODDER	
Dry matter (%wt)^{am}	89.0-94.0 (91.0)
Crude protein (%wt)^{db}	3.6-4.2 (3.9)
Crude fibre (%wt)^{db}	41.5
Neutral Detergent Fiber (NDF) (%wt)^{db}	77.5
Acid Detergent Fiber (ADF) (%wt)^{db}	50.0-54.0 (52.0)
Lignin (%wt)^{db}	7.2-22.9 (13.2)
Cellulose (%wt)^{db}	33.7-40.0 (37.2)
Hemicellulose (%wt)^{db}	21.0-35.0 (28.0)
Ether extract (%wt)^{db}	1.4
Ash (%wt)^{db}	3.07-18.85 (8.94)
Starch (%wt)^{db}	1.0
Total sugars (%wt)^{db}	1.2
Silica and silicates (%wt)^{db}	4.5-5.5 (5.0)
Gross energy (%wt)^{db}	18.5
FERTILIZER	

PARAMETER	VALUE (AVERAGE)
Nitrogen (g/kg)[db]	3.5-10.7 (6.24)
Phosphorus (g/kg)[db]	0.08-1.01 (0.59)
Potassium (g/kg)[db]	9.75-22.45 (14.86)
Calcium (g/kg)[db]	1.80-8.17 (4.71)
Magnesium (g/kg)[db]	0.44-3.40 (1.49)
Sulfur (g/kg)[db]	1.3-2.9 (1.9)
Manganese (mg/kg)db	15.6-100 (42.5)
Zinc (mg/kg)[db]	8.5-33.8 (19.1)
Copper (mg/kg)[db]	2.4-5.7 (3.9)
Iron (mg/kg)[db]	64.1-219 (155.7)
Nickel (mg/kg)[db]	1.0
Silicon (mg/kg)[db]	30,000-33,982 (31,991)
BIOACTIVE COMPOUNDS	
Policosanols (*Eicosanol, Heneicosanol, Docosanol, Tricosanol, Tetracosanol, Hexacosanol, Heptacosanol, Octacosanol, Triacontanol*) (mg/kg)[db]	137.0-3,000 (1,137.2)
Phytosterols (*stigmasterol, β-sitosterol, stigmastanol*) (mg/kg)[db]	833.9-1,205.9 (1,079.9)
Phenolic compounds (*p-Coumaric acid, Ferulic acid*) (mg/kg)[db]	1,350-2,130 (2,240)
Triterpenoids (mg/kg)[db]	Traces

WS is renewable, usually dispersed, accessible nearby, mouldable, anisotropic, hydroscopic, eco-friendly, multipurpose, nonabrasive, permeable, viscoelastic, recyclable, burnable, and imprudent (Rowell & H. Spelter, 2003). WS contains both lipophilic and hydrophilic compounds which may be released or interfere during pulping and pretreatment of feedstock before hydrolysis of carbohydrate polymers to their monomeric sugars before microbial fermentation (Sun & Sun, 2001; Sun et al., 2003). Lipophilic extracts from WS contains free fatty acids (25.8–48.4%), waxes (9.4–27.0%), sterols (4.1–8.0%), triglycerides (3.3–11.0%), sterol esters (2.6–5.1%), minor amounts of diglycerides (0.3–0.5%), and resin acid (0.5–3.1%) (Sun et al., 2003).

According to Table 3.1, WS holds various bioactive compounds such as policosanols (PC), phytosterols (PS), phenolics, and triterpenoids, having enormous nutraceutical properties like anti-allergenic, anti-artherogenic, anti-inflammatory, anti-microbial, antioxidant, anti-thrombotic, cardio-protective and vasodilatory effects, antiviral, and anticancer. These compounds are protecting against various ailments like hypercholesterolemia, intermittent claudication, benign prostatic hyperplasia and cardiovascular diseases (Table 1.2). Recovery of these high value bioactive compounds during or before bioconversion of wheat straw to ethanol improves the feasibility of the conversion process (Dunford & Edwards, 2010). WS is valuable to build up composite products like sorbents, geotextiles, structural composites, filters, moulded products, non-structural composites, packaging and permutations with other resources (Rogers et al., 2007). In general isolation of health beneficial bioactive compounds such as PS and PC directly from grains, straw, and other natural sources may not be economically feasible because of their low concentrations in the feedstock. However, utilization of by-products concentrated in these compounds could improve the economic viability of PS and PC isolation.

Table 1.2: Functional and nutraceutical effect of bioactive compounds of wheat straw (Berger et al., 2004; Bhattacharyya & Connor, 1974; Elkind, 2006; Guyton & Hall, 1996; Katan et al., 2003; Liu et al., 2007).

BIOACTIVE COMPOUNDS	FUNCTIONAL AND NUTRACEUTICAL ROLE
Policosanol	Intermittent claudication, hypercholesterolemia, promoters of endothelial, function, inhibitors of platelet aggregation and thrombosis
Phytosterol	Coronary heart disease, phytosterolemia, atherosclerosis
Triterpenoids	Benign prostatic hyperplasia
Phenolic acids	Reduce oxidation process

1.2 Wheat bran

Wheat bran (WB) is another major by-product of the dry milling of common wheat (*Triticum aestivum L.*) into flour. WB is suitable for livestock feeding and very palatable to most classes of animals (Fuller, 2004). It is a bulky feed that can be used to lighten dense, heavy feed mixtures. It can be readily incorporated into mashes.

WB consists of the outer layers (cuticle, pericarp and seedcoat) combined with small amounts of starchy endosperm of the wheat kernel. Other wheat processing industries that include a bran removal step may also produce WB as a separate by-product: pasta and semolina production from durum wheat (*Triticum durum Desf.*), starch production and ethanol production (feedipedia, 2016). Good bran should have a fair coating of flour and be in the form of large, dry and non-adherent flakes. It is sold raw or pelleted (Gohl, 1981).

It is important to note that WB is not a product with a universally accepted definition and clear boundaries. Though national regulations may contain mandatory requirements on bran composition, ingredients sold under that name encompass a wide range of wheat by-products. Milling yields variable proportions of flour, depending on the quality of the final product. The extraction rate (flour:grain ratio) goes from 100% for a whole-meal flour to less than 70% for pastry flour. Typical extraction rates range from 75% to 80%, resulting in 20 to 25% wheat offals (Kent & Evers, 1994). WB represents roughly 50% of wheat offals and about 10 to 19% of the kernel, depending on the variety and milling process (Hassan et al., 2008).

In the industrial milling process, after a cleaning step that removes grain impurities, the grains are tempered (soaked to toughen the outer layers and mellow the starchy endosperm in order to facilitate their separation) and then subjected to a series of grinding operations that produce finer and finer flour particles. The first grinding steps yield coarse particles of broken wheat and bran, and the later steps produce other by-products. Milling by-products are traditionally named after their quality (fineness, colour, etc.) and/or the stage of the process at which they arose, with considerable variations between languages, countries, regions, milling processes and even mills. In industrial countries, these products used to be sold separately (coarse bran, fine bran, middlings, second clear, thirds, etc.) but are now mixed together in variable proportions (McDonald, 2002).

Consequently, wheat milling offals form a continuum of products with a decreasing fibre: starch ratio, from the fibrous coarse brans produced by the first grinding steps to starchy feed-grade flours. WB sold for animal feeding are typically mixtures of true coarse brans and finer products from the later grinding stages. In rural and traditional milling, flour is directly separated from bran in a one-step milling and screening. This type of bran has a higher starch content and a higher nutritive value (Piccioni, 1965). The situation is made even more complex by the existence of WB from other wheat species (durum) and wheat processing industries.

The chemical analysis of WB is summarized in Table 1.3. Protein, minerals, oil and fibre are mainly found in the outer layers of the grain, and WB is richer in these nutrients than the whole grain. WB is

relatively rich in protein (14-19% dry matter, sometimes higher) and minerals (4-7% dry matter), notably calcium (0.07-0.2% dry matter) and phosphorus (0.9-1.3% dry matter). Its oil content (3-5% dry matter) is higher than that of the whole grain. The fibre and starch contents are inversely correlated and extremely variable, as they depend on the relative amounts of envelopes, endosperm and other fractions mixed together. However, a product marketed as bran should contain relatively high amounts of fibre:crude fibre 7-14 dry matter, NDF 35-54% dry matter, ADF 9-16% dry matter and low amounts of ADL 2-4% dry matter. WB should also contain about 15-30% dry matter of starch. Fibre is the main constraint for the utilization of WB in animal nutrition, particularly in monogastrics. For that reason, the energy values of WB are always lower than those of the whole grain, in all animal species (feedipedia, 2016).

Table 1.3: Summary of main physicochemical characteristics of wheat bran (ECN, 2016; feedipedia, 2016; Hosseinian & Mazza, 2009).

PARAMETER	VALUE (AVERAGE)
FODDER	
Dry matter (%wt)[am]	87.0
Crude protein (%wt)[db]	17.3
Crude fibre (%wt)[db]	10.4
Neutral Detergent Fiber (NDF) (%wt)[db]	45.2-51.0 (48.8)
Acid Detergent Fiber (ADF) (%wt)[db]	13.4-39.0 (29.6)
Lignin (%wt)[db]	3.0-11.1 (6.0)
Ether extract (%wt)[db]	3.9
Ethanol/Toluene extract (%wt)[db]	10.8
Ash (%wt)[db]	5.6-7.0 (6.3)
Starch (%wt)[db]	23.1
Total sugars (%wt)[db]	7.2
Gross energy (MJ/kg dry matter)	18.9
FERTILIZER	
Nitrogen (g/kg)[db]	27.4-139.2
Phosphorus (g/kg)[db]	11.1
Potassium (g/kg)[db]	13.7
Calcium (g/kg)[db]	1.4
Magnesium (g/kg)[db]	4.5
Zinc (mg/kg)[db]	89.0
Copper (mg/kg)[db]	13.0
Iron (mg/kg)[db]	155.0
BIOACTIVE COMPOUNDS	
Tanins (eq. tannic acid) (g/kg)[db]	1.3
Pectin (%wt)[db]	6.0
Phenolics, free (mg/100g)	13.7 ± 1.1
Phenolics, bound (mg/100g)	439.9 ± 10.3
Proanthocyanidins (mg/100g)	509.4 ± 0.7
Amino acids	
Alanine (% protein)	4.6
Arginine (% protein)	6.8
Asparctic acid (% protein)	7.0
Cystine (% protein)	2.1
Glutamic acid (% protein)	1.9
Glycine (% protein)	5.1
Histidine (% protein)	2.7
Isoleucine (% protein)	3.2

PARAMETER	VALUE (AVERAGE)
Leucine (% protein)	6.0
Lysine (% protein)	4.0
Methionine (% protein)	1.5
Phenylalanine (% protein)	3.9
Proline (% protein)	6.3
Serine (% protein)	4.3
Threonine (% protein)	3.2
Tryptophan (% protein)	1.4
Tyrosine (% protein)	2.7
Valine (% protein)	4.6

am: as measured; db: dry base

1.3 Patent review on the recovery of bioactive compounds from wheat by-products

Table 1.4 summarizes the results of the patent research on methods developed for the efficient recovery/extraction/isolation of bioactive compounds from wheat straw and wheat bran. It is noted that the results of this research do not include the separation and/or valorisation of carbohydrates/lignocellulosic biomass (cellulose, hemicellulose, lignin) for the production of biofuels, and the synthesis of bio-herbicides and/or bio-fertilizers. Following the objectives of WP1, the patent research has been focused on the isolation/extraction of high-added value phenolics, proteins, anti-oxidants, etc.

Table 1.4: Summary of patents on the recovery of bioactive compounds from wheat by-products.

Patent No	Issue Date	Title	Type of AWCB	Recovered high added compound
CA 2618734A1 CN 101283092A EP 1752533A1 EP 1913136A1 EP 1913136B1 US 7981650 US 20090181431 WO 2007019949A1	22/2/2007	Fusion proteins between plant cell-wall degrading enzymes, and their uses	Maize and wheat brans	Ferulic acid (4-hydroxy-3-methoxy-cinnamic acid)
CN 104689598A CA 2836200A1 CA 2836200C EP 2881155A1 US 9084948 US 20150157958	10/6/2015	Pressurized low polarity water extraction apparatus and methods of use	Vegetable materials and straw, including wheat straw, barley straw, rye straw, oat straw, brassica straw, flax broken shoulder, sorghum, switchgrass, sugar cane	Polyphenols
CN 1366025A	28/8/2002	Process for extracting phytic acid from rice husk (bran)	Rice husk, rice bran, wheat bran, corn	Phytic acid
CN 1393434A	29/1/2003	Process for extracting inositol from rice bran (wheat bran)	Rice husk, Wheat bran, Rice bran	Inositol
CA 2401699 A1 DE 60023187D1 EP 1259631A1	7/9/2001	Manufacture and purification of mycophenolic acid	Wheat bran, rice bran, rice husk	Mycophenolic acid

Patent No	Issue Date	Title	Type of AWCB	Recovered high added compound
EP 1259631B1 US 6927047 WO 2001064931A1				
US 5736384A	7/4/1998	Thermostable xylanase	Xylan and xylan-containing oat spelts bran, wheat bran, pulp, bagasse, corn fiber, agricultural wastes such as rice straw and plant fiber	Xylanase XP1
CN 101311274A	26/11/2008	Process for enhancing extraction rate of ferulaic acid form plant stalks by steam explosion pretreatment	Plant straw including corn stalks, wheat straw, rice straw and the like	Ferulic acid
JP 2004520058A	8/7/2004	Fractionation method of bran cereal	Bran, for example wheat, barley, rye, triticale, and oats or rice cereal grains of the seed coat	Germ rich fractions, endosperm rich fraction and aleurone-rich fractions, glucose, soluble hemicellulose, soluble oligosaccharides
CN 104224939A	2014	Extraction method of flavones in bitter buckwheat straws	Wheat straw	Flavones

2. Barley

Barley (*Hordeum vulgare L.*) is the fourth most widespread cereal in the world, with a total acreage of about 50 million hectares and a total grain production of about 150 million tons, of which about 40% in the EU, 20% in Eastern Europe, 10% in Northern America, the remainder mainly in temperate regions of the other continents (Fortunati et al., 2016a). There are thousands of cultivated barley landraces and hundreds of cultivars. Cultivars can be classified according to several factors: the number of rows of grains (2-row and 6-row), compactness of spikes, hull adherence (hulled or naked barley), presence or size of awns (awned, awnletted or awnless varieties), growth habit (winter or spring barley) and color (white, blue or black kernels (CFIA, 2005). End-use may also be a way to classify barley (OECD, 2004). Further classification of barley hull depends on its grain composition, being classified into normal, waxy or high amylose starch type, high β-glucan, high lysine and proanthocyanidin-free (Baik & Ullrich, 2008). The average yield for barley grain is 2.7 t/ha but there are large differences between countries, from yields as high as 8.39 t/ha in Belgium to yields as low as 0.6 t/ha in Morocco and 0.2 t/ha in Lesotho (FAO, 2016).

A longitudinal structure of barley grain is presented in Fig. 4. The structure of barley grain is very similar to other cereal crops (wheat or oat). The barley grain is one-seeded which is called the caryopsis. Hull of the grain, which is composed of epidermis, fiber and parenchyma, constitutes about 10- 13% of the barley weight (Yadav & Hicks, 2015). The hull covers the caryopsis, which includes the different layers of the grain known as bran, endosperm, and germ. These layers are made up of sub-layers, which are highlighted in Figure 2.1. The total weight of the barley grain kernel ranges from 32-40 mg. The endosperm is the main part of the grain and is mainly composed of granular starch embedded in protein matrix.

Barley kernel is composed of hull (10-13% of kernel weight), bran (~14% of kernel weight), endosperm (~83% of kernel weight) and germ (~2.5% of kernel weight) as shown in Fig 4. The endosperm is the most important component of barley kernel, consisting of 70-77% carbohydrates, 12-16% protein, along with less than 2% of vitamins (niacin, thiamine, etc.) and minerals (selenium, iron, magnesium, zinc, phosphorous and copper). In addition, the germ, which includes the embryo contains high quantity of protein (12-20%), followed by an appreciable amount of lipids (1.5-5%), B-complex vitamins and trace minerals (<2.5%). The bran is mainly composed of approximately 3% of protein, with 3-5% trace minerals (iron, zinc, manganese, etc.), B-vitamins (3-6%) and about 4.5-15% non-starch carbohydrates, which provides the dietary fiber (USDA, 2016). Barley bran is composed of hull, pericarp, testa, and the aleurone layer (Chakraverty et al., 2003).

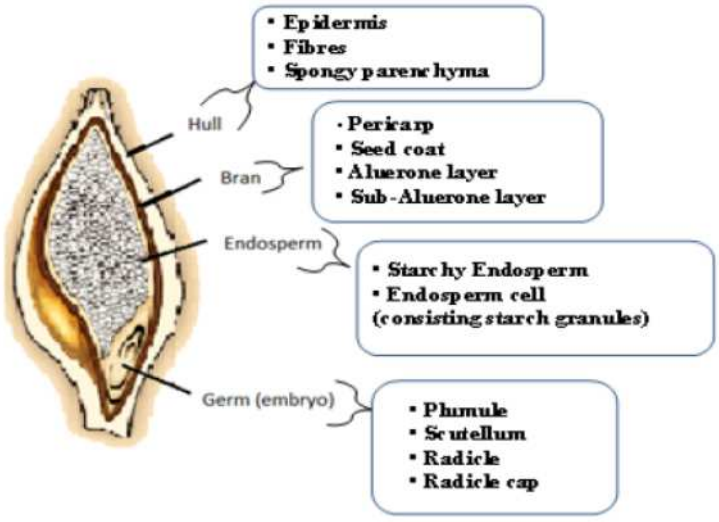

Figure 2.1: Longitudinal structure of barley grain with sub-layers (Hoover & Vasanthan, 2009).

Barley grain has three major uses: livestock feed, raw material for alcohol and starch production, and food (Akar et al., 2003; Fortunati et al., 2016a; Monfort et al., 2005; OECD, 2004).

- Barley is of utmost importance for livestock feeding, which accounts for about 85% of barley production. Six-row barleys, which have higher protein content, are a valuable feed ingredient. Two-row barleys contain more starch and less protein and are thus preferred for brewing (barley with more than 11.5% protein causes beer cloudiness).
- Barley grain is used for the production of alcohol (beer, whisky and ethanol), non-alcoholic beverages (barley tea, breakfast beverages).
- Food products include starch flour, flakes and pearled barley and it is a staple food in several countries including Morocco, India, China and Ethiopia.
- The by-products of barley grain processing are used as feed: brewer's grains, brewer's yeast, malt culms (barley sprouts and rootlets), barley distillers and solubles, hulls, bran and barley feed (the by-product of pearl barley production).
- Barley straw (the leftover stems after the barley grains are harvested) is an abundant biomass in the regions producing barley for malting, feeds, and fuel ethanol.
- Barley hulls (husks) are potential by-products of barley ethanol production.
- Barley forage can be fed to livestock as pasture, hay or silage.
- Barley straw is also used as fodder for ruminants and as bedding material.

Barley is a hard grain that should be crushed or ground, otherwise it will pass undigested through the alimentary tract. Feed efficiency improves with the removal of hulls, grinding, or the breaking of the bran layer. Common processes include rolling (dry or steam rolling), flaking, grinding, and pelleting (OSU, 2006). Ground barley can be shifted into a finer fraction containing less than 3% fibre and a coarser one containing about 11% fibre. The finer fraction is more suitable for pigs and poultry than whole ground barley (Göhl, 1982b). Dry-rolled and ground barley contains considerable dust that may reduce intake and adversely affect performance and health in cattle (Mathison, 1996).

Whereas in animal feed barley husks are eaten and digested, in brewing they represent a by-product. Both straw and husk have been proposed as thermal-electric power sources (Singh, 2015) or as components for bio-based materials (Bowyer & Stockmann, 2001) with several recognized properties

as, for example, thermal insulation (Palumbo et al., 2015). In alternative, since they contain relevant amounts of cellulose (Adapa et al., 2009), they have been proposed for cellulose extraction (Sun et al., 2005b; Sun et al., 2005a) or isolation of cellulose nanocrystals by acid hydrolysis (Espino et al., 2014).

The chemical analysis of barley straw is summarized in **Error! Reference source not found.**. Barley straw, i.e. the crop residues remaining in the field after grain harvest, has a very high C/N ratio, which limits its contribution to soil humus restoration and can even cause temporary N deficiency to the following crop (Wessén & Berg, 1986). The protein and NDF content of untreated straws ranges from 2 to 6%, and 80 to 86%, respectively (Haddad, 2000; McCartney et al., 2006). Values for hay are intermediate between those of the straw and the fresh forage (Chermiti, 1997).

Table 2.1: Summary of main physicochemical characteristics of barley straw (ECN, 2016; feedipedia, 2016; Fortunati et al., 2016a; Yadav & Hicks, 2015).

PHYSICOCHEMICAL PROPERTIES	VALUE (AVERAGE)
ENERGY	
Higher Heating Value (HHV) (MJ/kg)	14.62-16.53 (15.58)
Lower Heating Value (LHV) (MJ/kg)	13.32-15.14 (14.23)
Fixed Carbon (%wt)[am]	4.84-15.94 (10.39)
Volatile Matter (%wt)[am]	67.33-78.48 (72.91)
Ash (%wt)[am]	5.20-9.78 (7.49)
Moisture (% wt)[am]	3.80-11.53 (9.18)
Carbon (%wt)[db]	37.05-40.20 (41.63)
Oxygen (%wt)[db]	36.75-46.33 (41.54)
Hydrogen (%wt)[db]	5.55-5.70 (5.63)
Nitrogen (%wt)[db]	0.56-0.60 (0.58)
Sulfur (%wt)[db]	0.01-0.08 (0.05)
FODDER	
Dry matter (%wt)[am]	90.9-93.2 (92.1)
Crude protein (%wt)[db]	3.8
Crude fibre (%wt)[db]	40.5
Neutral Detergent Fiber (NDF) (%wt)[db]	71.4-90.0 (80.8)
Acid Detergent Fiber (ADF) (%wt)[db]	48.3-48.7 (48.5)
Cellulose (%wt)[db]	56.2
Hemicellulose (%wt)[db]	7.0
Lignin (%wt)[db]	6.5-23.0 (12.9)
Ether extract (%wt)[db]	1.4-4.6 (3.0)
Ash (%wt)[db]	2.2-11.1 (8.6)
Lipids (%wt)[db]	2.0
Starch (%wt)[db]	0.0-2.4 (1.2)
Gross energy (MJ/kg dry matter)	18.2
FERTILIZER	
Nitrogen (g/kg)[db]	5.6-6.08 (5.89)
Phosphorus (g/kg)[db]	0.646-1.863 (1.17)
Potassium (g/kg)[db]	12.188-14.4 (13.29)
Calcium (g/kg)[db]	1.88-4.60 (3.24)
Magnesium (g/kg)[db]	0.766-1.734 (1.23)
Sulfur (g/kg)[db]	0.334
Manganese (mg/kg)[db]	28.0-30.24 (29.12)
Zinc (mg/kg)[db]	15.0
Copper (mg/kg)[db]	10.0-14.07 (12.04)
Iron (mg/kg)[db]	69.97-2829 (1025.3)

PHYSICOCHEMICAL PROPERTIES	VALUE (AVERAGE)
BIOACTIVE COMPOUNDS	
Tannins (e.g. tannic acid) (g/kg)[db]	3.6
Tannins condensed (e.g. catechin) (g/kg)[db]	0.2
Proetein (g/kg)[db]	2.0-26 (14.0)

The chemical analysis of **barley hulls** is summarized in Table 2.2. Barley grain has variable hull content that usually ranges from 7 to 25% on the dry matter basis. The average hull content in most barley varieties is 13% (Evers et al., 1999). There have been many factors reported, which affects the barley hull content in the different barley grains, such as variety, environment, agronomic practices and grain size. In general, Briggs (1998) and Olkku et al. reported that barley hull is an extremely fibrous material and is mainly composed of hemicellulose, cellulose, lignin, ash and protein (Table 2.2) (Briggs, 1998; Olkku et al., 2005). Thus, barley hull can be utilized as a biomass as it has a high content of lignocellulosic material. Grove et al. and Moore and Jung reported that variation in the content of the fiber is due to different barley hull varieties and different agronomic practices (Grove et al., 2003; Moore & Jung, 2001). Due to the contribution of the barley hull to the total fiber content in the barley grain, it becomes difficult for humans, and other monogastric animals, such as rats, pigs, and poultry to digest the fibrous hull due to fewer amounts of fibrolytic enzymes.

Table 2.2: Summary of main physicochemical characteristics of barley hulls (feedipedia, 2016; Olkku et al., 2005; Yadav & Hicks, 2015).

PHYSICOCHEMICAL PROPERTIES	VALUE (AVERAGE)
FODDER	
Dry matter (%wt)[am]	90.8
Neutral Detergent Fiber (NDF) (%wt)[db]	74.9
Cellulose (%wt)[db]	26.5-45.7 (33.67)
Hemicellulose (%wt)[db]	22.4-33.7 (29.5)
Lignin (%wt)[db]	7.2-22.9 (14.93)
Ash (%wt)[db]	4.6-6.0 (5.2)
Lipids (%wt)[db]	3.5
Starch (%wt)[db]	10.3

Ash, mainly silica (SiO_2), is also found in barley hull (5.1%) and in barley grain (1.5% in the peeled grain) (Kulp, 2000; Olkku et al., 2005). The high amount of silica in the hull contributes to its strength, rigidity and integrity. Thus, the plant growth and grain development is improved resist abiotic (e.g. dry soil) and biotic (e.g. diseases) (Liang et al., 2003). Barley hull is a great source of phenolics (Hernanz et al., 2001; Höije et al., 2005). Lignin is considered a typical complex phenolic compound which restricts the digestion of the plant cell wall by animals. Also, free phenolic acids, such as ferulic acid and p-coumaric acid, are present in the barely hull (Slafer et al., 2002). The presence of these free phenolic acids defends barley grain from micro-organism attack due to their antioxidative properties and antibacterial functions.

Barley hull can be further utilized as a source for fermentable sugars for the production of biofuel (e.g. ethanol production). Moreover, phenolic acids are also mainly concentrated in the hull portion of the barley grain (Hernanz et al., 2001; Nordkvist et al., 1984). Hao and Beta showed that 1 kg of barley hull contains 10.71 g total phenolics as measured according to the ferulic acid equivalent (Hao & Beta, 2012). In addition, (Waldron et al., 1996), and (Bunzel et al., 2004) reported that ferulic acid and p-coumaric acid are associated with the cell wall constituents as they are ester-linked to them,

especially with the arabinoxylans and lignin. Garrote et al. (2008) quantified total phenolics as 33-36mg/g of barley hull (Garrote et al., 2008). Earlier studies by Garrote et al. (2004) showed that non-isothermal treatment of barley hull in aqueous media degraded the hemicellulose fraction and selectively released sugar oligomers, monosaccharides, sugar degradation products (such as furfural, hydroxymethyl furfural, acetic acid) and phenolic compounds (Garrote et al., 2004). The presence of high amounts of ferulic acid (43%) and p-coumaric acid (9%) in Brewer's spent barley grain, mainly formed by barley hull, were also reported by Bartolomé et al (Bartolomé et al., 1997; Bartolomé et al., 2003).

From decades, it is known that p-coumaric acid (trans-4-hydroxycinnamic acid) is the dominant phenolic in barley hull, forming linkages with lignin (Higuchi et al., 1967). Chemically, p-coumaric acid and ferulic acid (Figure 2.2) consist of a phenolic nucleus and an extended side chain, which readily generates stable phenoxyl radical that can scavange free radicals and prevent oxidative stress (Graf, 1992). The interest towards these phenolic acids is due to their strong free radical scavenging capacity and chemoprotective effects (Mussatto et al., 2007). Abdel-Wahab (2003) suggested the use of p-coumaric acid for cancer due to its protection against doxorubicin-induced oxidative stress (Abdel-Wahab et al., 2003). Biological effects, which include inhibition of LDL oxidation (Zang et al., 2000), reduction to oxidative damage in DNA (Guglielmi et al., 2003) and platelet aggredation inhibition (Luceri et al., 2007) were reported for the p-coumaric acid.

Ferulic acid, on the other hand, can be absorbed, metabolized and distributed and then excreted as a derivative of phenyl propionic acid, hydrocrylic acid and glycine conjugates (Srinivasan et al., 2007). Ferulic acid also proved to be beneficial in prevention of problems linked to oxidative stress which includes cancer (Chang et al., 2006), inflammatory diseases (Murakami et al., 2002), and Alzheimer's diseases (Jin et al., 2005). In China, sodium ferulate (a salt of ferulic acid) has been used against cardiovascular and cerebrovascular diseases (Wang & Ou-Yang, 2005). Due to the antioxidant activity, free scavenging activity, chelation of active metal ions and modulation of gene expression, phenolics show pharmacological effects (Soobrattee et al., 2005). Therefore, research to establish an effective extraction process to obtain these compounds with high purity has been carried out for a long time.

Figure 2.2: Chemical structure of: (a) p-coumaric acid, and (b) ferulic acid.

Both barley hulls and straw contain valuable arabinoxylans (AX) and other useful carbohydrate and non-carbohydrate components. In barley, AX constitutes about 70% of aleurone walls (Bacic & Stone, 1981), 20% of starchy endosperm walls (Balance & Manners, 1978) and 20–30% of vegetative tissues' walls (Kokubo et al., 1989). Barley hulls contain about 30% hemicellulose in which arabinoxylan is the main polymer (MacGregor & Fincher, 1993).

Barley hull can also be utilized as a substrate for the cultivation of mushrooms and actinobacteria, and as a source of value-added products, such as ferulic acid, p-coumaric acid, xylose and arabinose (Mussatto et al., 2006; Mussatto et al., 2007). Barley hull is considered the most abundant source of hemicellulose polymer, known as xylan. Xylan can be further hydrolysed into xylose and arabinose (Figure 2.3) and then fermented to produce xylitol (a low caloric sweetener with anticarcinogenic properties). Xylitol can be used as a substitute of sugar for diabetic patients (Cruz et al., 2007; Parajó et al., 2004). However, due to low digestibility of barley hull, its utilization as a feed supplement is

limited. The combustion of barley hull is also difficult and not practical due to its high ash content, which lead to the deposition of minerals in the boilers (Cruz et al., 2007). Additionally, the transportation of barley hull to the disposal areas may be very expensive due to its low density (Mahmudi et al., 2005; Searcy et al., 2007). Due to these problems, the current interest of barley hull remains for the use in the saccharification and fermentation processes.

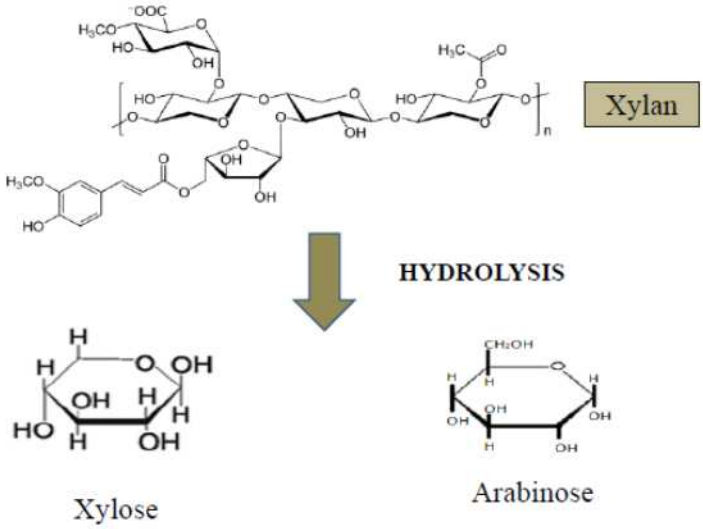

Figure 2.3: Hydrolysis of xylan to xylose and arabinose.

3. Maize

Maize, cultivated in 148 million hectares globally, is one of the most important crop on global level; the EU is the third most important area of maize production after the USA and China. Approximately, 26 million hectares of maize are cultivated each year in the EU; the total estimated value of all the downstream maize products is more than 32 billion euro (ESA, 2016). It is an annual cereal crop belonging to the grass family of Gramineae. Maize, apart from its uses as food and fodder, can be processed into a variety of food and industrial products, including starch, sweeteners, corn oil, beverages, glue, industrial alcohol, and fuel ethanol; the former use in the USA accounts approximately 40% of the total USA maize production (Ranum et al., 2014).

The main AWCB associated with maize production is the maize stover that refers to the above ground biomass except the grain, and comprises mainly the stalks, leaves, husk and cobs of maize plants left in the field after harvesting. Pordesimo et al. (2004) have reported that the total above ground, dry biomass is distributed to approx. 46% grain, 28% stalks, 11% leaves, 8% cobs and 7% husk (Pordesimo et al., 2004). Shinners and Binversie, (2007) concluded that at the time corresponding to mechanical grain harvest approximately 15%, 8%, 21%, and 56% of the total stover dry mass resided in the cob, husk, leaf, and stalk fractions respectively (Shinners & Binversie, 2007). Therefore, considering an average maize production of 78.2 million tons for 2014 in the EU28 (FAO, 2014), the quantities of maize AWCB throughout the EU28 countries can be estimated to 47.6 million tons of stalks, 18.7 million tons of leaves, 13.6 million tons of cobs and 11.9 million tons of husk.

The current uses of maize stover include its use as fuel, litter for animals, soil conditioner, and as fodder for ruminants, despite their relatively low nutritive value. It has been reported that when maize stover are given as fodder to cattle, they choose to eat the most palatable and nutritious plant parts first. This is a strong evidence that the different parts of the maize stover have significant differences in their physicochemical characteristics and should not be regarded as one AWCB (Lardy, 2016). Given that maize stover is mainly consisted from lignocellulosic biomass, it can be used as feed for lignocellulosic ethanol (2nd generation biofuel). In fact, there are already ethanol plants using maize stover as feed in the USA (DuPontCornStoverTeam, 2016), where maize based ethanol is an important market sector. Maize cobs are also characterised by their high absorbency and abrasiveness, making them as ideal biomass-based materials for various industrial applications such as absorbing chemicals and oils, cleaning up industrial or environmental spills, and to blast and polish many materials such as jewellery etc. However, currently maize stover is mainly left in the field, plowed and incorporated in the soil (Jansen, 2012).

Given that the maize stover comprise structural different plant parts (i.e. stalks, cobs, leaves etc.), data for the characterisation of maize AWCB were collected separately for the different parts of maize stover. Focus was placed for maize stalks and maize cobs which comprise an important part of maize AWCB.

3.1 Maize Stalks

Maize stalks refer to dry stalks left in the field after maize harvesting (Figure 3.1).

Figure 3.1: Photo of dry maize stalks left in the field after harvesting.

Concerning energy characteristics, maize stalks can be considered a fuel with rather moderate energy density, ranging between 17.2 and 18.5 MJ/kg of HHV. The moisture level is low, normally between 10 - 15% wt^{db} and the ash content is also moderate, ranging between 2.30 - 13.6% wt^{db}. In respect to other solid fuels (i.e. coal, peat, lignite), it has higher oxygen content and lower sulfur content (Vassilev et al., 2010). Concerning use of maize stalks as fodder for ruminants, maize stalks are generally considered a low quality fodder. Despite its rather low content of lignin (10.7 ± 6.38% wt^{db}), it also has poor protein content, usually less than 5% wtdb. Therefore, various methods have been proposed, including fermentation with fungi and yeasts (Darwish et al., 2012), ensilage (Qingxiang, 2002), alkali treatment (Johnston, 2012), to increase protein content and/or digestibility of maize stalks. Maize stalks can be also used as soil conditioner; maize stalks are important to replenish organic matter in the field after harvesting, control soil erosion and provide some nutrients (mainly N and P) that can be used by the plants in the next harvesting period (Johnson et al., 2004). The nitrogen content of maize stover lies between 5.60 - 14.7 mg/kg^{db}, the phosphorus content is around 1 mg/kg^{db}, whereas potassium is also present ranging between 1.02 - 15.0 mg/kg^{db}. Concerning bioactive compounds, maize stalks, given that they are rich in cell wall materials (i.e. NDF > 82. % wt^{db}), are also rather rich in hydroxycinnamic acids, namely ferulic and p-coumaric acids. These acids are principal components governing cell wall integrity, shape, and defense against pathogenic ingress. As bifunctional molecules with carboxylic and phenolic bonding sites, it is believed that ferulic acid is laid down in ester linkages to primary cell wall polysaccharides and provides ether linkage initiation sites for lignin (Sun et al., 2001). Alkaline treatments dissolve lignin by cleavage of ester linkages in lignin–polysaccharide complexes, thus releasing phenolic acids. FA and p-CA are of great importance either as antioxidants, i.e. in food preservation because of their ability to inhibit fatty acid peroxidation, as feedstocks for the high-added value vanillin bio-production, one of the main flavorings and aroma compounds (Torre et al., 2008), or as potent anti-inflammantory and anti-cancer substances (Nagasaka et al., 2007).

Table 3.1: Summary of main physicochemical characteristics of maize stalks (Banchorndhevakul, 2002; Cardoen et al., 2015; Cherney et al., 1989; Darwish et al., 2012; Demirbaş, 1997; Fu et al., 2011; Ioannidou et al., 2009; Jenkins & Ebeling, 1985b; Mullen et al., 2010; Shuangning et al., 2005; Sun et al., 2001; Wang et al., 2013).

PHYSICOCHEMICAL PROPERTIES	AVERAGE	SD	MIN	MAX	N° SAMPLES
ENERGY					
Higher Heating Value (HHV) (MJ/kg)	18.0	0.48	17.2	18.5	6
Lower Heating Value (LHV) (MJ/kg)	16.5	n.a.	n.a.	n.a.	1
Fixed Carbon (%wt)^{db}	17.4	2.50	13.2	19.3	5
Volatile Matter (%wt)^{db}	77.7	2.45	75.2	80.8	5
Ash (%wt)^{db}	5.71	3.41	2.30	13.6	8
Moisture (% wt)^{am}	17.5	18.5	5.70	50.0	5
Carbon (%wt)^{db}	45.2	1.61	43.7	46.9	6
Oxygen (%wt)^{db}	43.6	3.59	40.1	49.8	6
Hydrogen (%wt)db	5.70	0.51	4.99	6.40	6
Nitrogen (%wt)^{db}	0.79	0.33	0.56	1.47	7
Sulfur (%wt)^{db}	0.07	0.10	0.01	0.22	4
FODDER					
Dry matter (%wt)^{am}	79.55	20.0	50.0	93.6	4
Crude protein (%wt)^{db}	4.96	2.06	3.50	9.18	7
Crude fiber (%wt)^{db}	42.2	n.a.	n.a.	n.a.	1
Neutral Detergent Fiber (NDF) (%wt)^{db}	82.9	7.94	75.7	96.3	5
Acid Detergent Fiber (ADF) (%wt)^{db}	40.7	4.16	35.0	45.1	6
Lignin (%wt)^{db}	10.7	6.38	2.80	18.7	5
Ether extract (%wt)^{db}	0.52	n.a.	n.a.	n.a.	1
Ash (%wt)^{db}	5.68	4.04	2.30	13.6	6
Gross energy (%wt)^{db}	17.9	0.50	17.2	18.3	4
FERTILIZER					
Nitrogen (g/kg)^{db}	7.94	3.29	5.60	14.7	7
Phosphorus (g/kg)^{db}	1.11	0.75	0.37	2.15	4
Potassium (g/kg)^{db}	6.10	6.12	1.02	15.0	4
Calcium (g/kg)^{db}	2.74	1.75	0.80	4.18	3
Magnesium (g/kg)^{db}	2.54	1.27	1.38	3.90	3
Sulfur (g/kg)^{db}	0.70	1.01	0.10	2.20	4
BIOACTIVE COMPOUNDS					
Ferulic Acid (g/kg)^{db}	6.76	1.31	5.24	7.53	3
p-Coumaric Acid (g/kg)^{db}	18.1	9.76	10.5	29.1	3

3.2 Maize Cobs

Maize cobs refer to the central fibrous rachis of the female inflorescence (i.e. the maize ear), after grain removal (Figure 3.2).

Figure 3.2: Photo of maize cobs left after grain removal.

Concerning energy characteristics, maize cobs can be considered a fuel with rather moderate energy density, ranging between 17.0 and 18.9 MJ/kg of HHV; these values are more or less close to the HHV of maize stalks. The moisture level is low, normally between 7 - 18% wt^{db}, which is a little bit more wide to other data found in the literature (4.7 - 12.8 (feedipedia, 2016); and 9.2 - 11.5 (Kanengoni et al., 2015)). In respect to other solid fuels (i.e. coal, peat, lignite) has higher oxygen content and lower sulfur content (Vassilev et al., 2010), just as the maize stalks. Maize cobs are a feed ingredient of low nutritive value, roughly similar to straw or a poor hay. Maize cobs contain little protein, ranging between 0.88 - 9.81% wt^{db}, and are mostly composed of fibre with NDF content higher than 68% wt^{db}. However, the lignin content (10.2 ± 5.95% wt^{db}) is relatively low for such a fibrous product, thus maize cobs are widely used as energy source in ruminant feed, given also their wide availability in large quantities. Compared to available data from the literature crude protein is at the same level with Heuze et al. (2016) (feedipedia, 2016) (i.e. 1.9 - 8.8% wt^{db}) and higher than these reported from Jansen and Lubberstedt (2011) (Jansen & Lübberstedt, 2012) (i.e. 0.75 - 5.63% wt^{db}). Furthermore, data on ash content are generally lower compared to that of Heuze et al. (2016), who reported 1.3 - 7.3% wt^{db} ash content, compared to 1.00 - 3.48% wt^{db} in this report. Maize cobs, just like maize stalks, can be also used as soil amendments (Awotoye et al., 2014); maize cobs have approximately the same composition, albeit a little bit lower, concerning N, P and mineral nutrients to maize stalks. Nitrogen content of maize cobs is 5.38 ± 3.90 mg/kg^{db}, compared to 7.94 ± 3.29 mg/kg^{db} of maize stalks, phosphorus content in the range 0.01 - 1.11 mg/kg^{db}, compared to 0.37 - 2.15 mg/kg^{db} of maize stalks, and potassium content approx. 7.04 ± 2.96 mg/kg^{db}, compared to 6.10 ± 6.12 mg/kg^{db} of maize stalks. Pointer et al. (2014) (Pointner, 2014) reported nitrogen values of maize cobs to 6.80 ± 1.50 mg/kg^{db}, whereas Jansen and Lubberstedt (2011) (Jansen & Lübberstedt, 2012) reported potassium content of maize cobs between 5.15 and 8.72 mg/kg^{db}. Concerning bioactive compounds, maize cobs also have rather high concentrations of hydroxycinnamic acids; ferulic acid and p-coumaric concentrations in maize cobs have been reported to 13.9 and 25.7 mg/kg^{db}, respectively. Compared to maize stalks, the maize cobs have higher concentrations of these two phenolic acids. Therefore, maize cobs are considered an important source for obtaining these phenolic acids together with rice husk and wheat bran (Leffingwell & Leffingwell, 2015).

Table 3.2: Summary of main physicochemical characteristics of maize cobs (Antal et al., 2000; Brunner et al., 2011; Demirbaş, 1997; feedipedia, 2016; Ioannidou et al., 2009; Jansen & Lübberstedt, 2012; Jenkins & Ebeling, 1985b; Kanengoni et al., 2015; Kitani & Hall, 1989; Lu et al., 2006; Lyer et al., 2002; Mullen et al., 2010; Nangole et al., 1983; Pointner, 2014; Torre et al., 2008; Vassilev et al., 2013).

PHYSICOCHEMICAL PROPERTIES	AVERAGE	SD	MIN	MAX	N° SAMPLES
ENERGY					
Higher Heating Value (HHV) (MJ/kg)	18.2	0.71	17.0	18.9	6
Lower Heating Value (LHV) (MJ/kg)	15.9	2.47	14.1	17.6	2
Fixed Carbon (%wt)[db]	15.9	3.09	12.5	18.5	3
Volatile Matter (%wt)[db]	82.6	3.42	80.1	86.5	3
Ash (%wt)[db]	2.67	2.48	1.00	8.10	7
Moisture (% wt)[am]	12.4	5.01	7.60	17.6	3
Carbon (%wt)[db]	46.3	2.16	41.4	48.8	10
Oxygen (%wt)[db]	45.2	3.83	38.1	51.3	9
Hydrogen (%wt)[db]	5.88	0.24	5.38	6.23	10
Nitrogen (%wt)[db]	0.54	0.39	0.14	1.57	10
Sulfur (%wt)[db]	0.07	0.07	0.01	0.18	7
FODDER					
Dry matter (%wt)[am]	87.6	5.01	82.4	92.4	3
Crude protein (%wt)[db]	3.36	2.44	0.88	9.81	10
Crude fiber (%wt)[db]	45.7	n.a.	n.a.	n.a.	1
Neutral Detergent Fiber (NDF) (%wt)[db]	77.1	14.7	67.8	99.0	4
Acid Detergent Fiber (ADF) (%wt)[db]	38.7	9.39	25.2	47.0	4
Lignin (%wt)[db]	10.2	5.95	3.00	16.3	5
Ether extract (%wt)[db]	1.23	n.a.	n.a.	n.a.	1
Ash (%wt)[db]	2.02	1.00	1.00	3.48	6
Gross energy (%wt)[db]	18.1	0.90	17.0	18.9	4
FERTILIZER					
Nitrogen (g/kg)[db]	5.38	3.90	1.40	15.7	10
Phosphorus (g/kg)[db]	0.48	0.47	0.01	1.11	4
Potassium (g/kg)[db]	7.04	2.96	4.82	10.4	3
Calcium (g/kg)[db]	1.24	0.89	0.23	1.90	3
Magnesium (g/kg)[db]	0.42	0.19	0.20	0.55	3
Sulfur (g/kg)[db]	0.66	0.68	0.10	1.80	7
BIOACTIVE COMPOUNDS					
Ferulic Acid (g/kg)[db]	13.9	n.a.	n.a.	n.a.	1
p-Coumaric Acid (g/kg)[db]	25.7	n.a.	n.a.	n.a.	1

3.3 Maize AWCB bioactive compounds patent and literature review

Hydroxycinnamic acids, particularly ferulic acid and p-coumaric acid, occur widely in cell walls of graminaceous plants such as wheat straw and maize stems (Sun et al., 2001). These cinnamic acids act in the cross-linking of plant cell walls and are precursors of a variety of compounds that play an important role in plant defence responses]. Ferulic acid and p-coumaric acid are very abundant, representing together up to 1.5% by weight of cereal cell walls. There is great interest in the potential of ferulic acid and related compounds either as antioxidants, i.e. in food preservation

because of their ability to inhibit fatty acid peroxidation or as feedstocks for the high-added value vanillin production (Torre et al., 2008).

The following short review of relevant patents comprise patents that are focused on extraction of ferulic acid and p-coumaric acid lignocellulosic matrices. Despite the fact that all the lignocellulosic biomass pre-treatment technologies for cellulose and hemicellulose decomposition would, inevitably, result in the extraction/release of hydroxycinnamic acids, these patents/technologies have not been included because their main focus is on cellulose and hemicellulose decomposition and moreover they do not provide quantitative data on the recovered quantities of ferulic acid and p-coumaric acid.

The short review of the relative patents, as well as R&D litereature (Argillier et al., 1996; Sun et al., 2001; Torre et al., 2008; Wang et al., 2013) shows that chemical and enzymatic treatments of agro-industrial wastes, including maize AWCB, can be used to obtain ferulic acid and p-coumaric acid in soluble form that can be later purified through either membrane-based or conventional recrystallization methods to solid ferulic acid and p-coumaric acid. Chemical treatments, including mild alkaline treatments with NaOH, or $Ca(OH)_2$, at ambient or elevated temperatures (100 - 150 ^{o}C), alone or combined with acid hydrolysis or a second step mild alkaline hydrolysis have been reported to remove significant quantities of ferulic acid and p-coumaric acid. Enzymatic treatments include use of ferulic acid esterase, alone or combined with other enzymes, in concentration of approx. 0.05 - 1.0%, mild temperatures (25 - 52 ^{o}C) and pH values ranging between 3.0 and 8.0.

Patent No	US 4038481 A
Issue Date	24/05/1976
Title	**Method for treatment of corn hulls**
Abstract	Corn hulls are subjected to a treatment to obtain three fractions therefrom comprising a cellulosic fraction, a hemicellulose fraction and a noncarbohydrate fraction. The noncarbohydrate fraction is characterized as being an organic solvent extract comprising at least about 15 percent of the dry weight of the corn hulls and containing above about 10 percent by weight ferulic acid.
Type of AWCB	*Maize hulls, maize cobs*
Recovered high added compound	Ferulic acid (4-hydroxy-3-methoxy-cinnamic acid)
Details	A method for treating corn hulls to obtain a cellulose fraction, a hemicellulose fraction and a noncarbohydrate fraction comprising treating corn hulls with a sufficient amount of alkali to hydrolyze the corn hulls to affect liberation of the hemicellulose fraction so that it may be solubilized in water and to solubilize the noncarbohydrate fraction, recovering a hemicellulose fraction, an organic solvent extract of the noncarbohydrate fraction and an insoluble residue comprising the cellulose fraction.

Patent No	WO2014106189 A2
Issue Date	31/12/2012
Title	**Methods of making vanillin via microbial fermentation utilizing ferulic acid provided by a modified caffeic acid 3-o-methyltransferase**
Description/Abstract	This disclosure provides a method of making vanillin including expressing 4- hydroxyphenylacetate 3-hyrdroxylase, caffeic acid 3-O-methyltransferase, methionine synthase, feruloyl-CoA synthetase, and enoyl-CoA hydratase/aldolase in a mixture, feeding p-coumaric acid to the mixture, and collecting vanillin. It further includes an enzyme, such as caffeic acid 3-O-methyltransferase, that facilitates the increased conversion of caffeic acid to ferulic acid, wherein the enzyme has been modified at a residue that allows for increased methylation of ferulic acid, and a method of using the enzyme in the making of ferulic acid followed by vanillin.
Type of AWCB	*Maize cobs*
Recovered high added compound	Ferulic acid (4-hydroxy-3-methoxy-cinnamic acid), p-Coumaric acid ((E)-3-(4-hydroxyphenyl)-2-propenoic acid)
Details/methodology applied	In one aspect, the subject technology relates to the extraction of hydroxy cinnamic acids from plant materials. Among plant materials, maize cob was found to contain abundant hydroxycinnamic acids in its cell wall with release of 2.8% (w/w) p- coumaric acid and 1.6% (w/w) ferulic acid after digestion with sodium hydroxide solution. The released hydroxycinnamic acids were isolated with resin absorption technology (e.g., Wuxi Kangzhen).

Patent No	CN101823955 A
Issue Date	29/10/2009
Title	**Method for extracting ferulic acid from maize peels**
Description/Abstract	The invention provides a method for extracting ferulic acid from maize peels, which belongs to the field of comprehensive utilization of accessory products in the starch industry. In the method, high-temperature water boiling, acid treatment and ultrasonic extraction are added, and the method comprises the following steps of: high temperature water boiling, acid treatment, centrifugal drying, ultrasonic extraction and pH value adjustment. The extracted ferulic acid has higher yield and purity. The method has the advantages of removing starch and partial soluble impurities from the maize peels, degrading xylan, removing partial hemicelluloses and impurities, shortening reacting time, and ensuring that the reaction is performed more completely.
Type of AWCB	*Maize peels*
Recovered high added compound	Ferulic acid (4-hydroxy-3-methoxy-cinnamic acid)
Details/methodology applied	A method of extracting ferulic acid from corn bran, which is characterized by the addition of a high temperature boiling, acid treatment and ultrasonic extraction conditions, the extraction process is as follows: (1) high temperature boiled: the hot boiled corn bran 2-6 hours temperature settings 110-130 ^{o}C, corn bran dry matter and water quality ratio 1:7-1:10; (2) an acid treatment: After the above centrifugal corn bran, dried at 40-60 ^{o}C to a moisture content of 1% The following, then acid treatment with 0.1-0.5% after drying corn bran 2-4h, temperature setting 100-110 ^{o}C, corn bran mass ratio of the dry matter and acid 1:7-1:10; (3) centrifugal drying: The corn bran acid treatment after centrifugation, washed with pure water, and dried at 30-60 ^{o}C to a moisture content below 1%; (4) ultrasonic extraction: Configuration 1% NaOH and 80% ethanol blend ethanol hydroxide soda solution, sodium hydroxide solution by ethanol and corn bran dry weight 1:5-1:10 extracted in ultrasonic extraction machine cycle of 0.5 to 2.0 hours to extract ferulic acid, controlled extraction temperature 70-90 ^{o}C, reaction process plus a small amount of sodium bisulfite to improve extraction efficiency ferulic acid; (5) adjusting the pH: The ferulic acid extract was concentrated under vacuum to dry matter content of 40-60%, adjusted to pH 1.0 to 3.0 with hydrochloric acid, and 1-4 times the volume of ethyl acetate extract, taken ester phase, ethyl acetate was distilled off by vacuum distillation, and the resulting product is ferulic acid.

Patent No	CN102381960 A
Issue Date	31/08/2011
Title	**Method for extracting ferulic acid, p-coumaric acid and pentosan from corn husks**
Description/Abstract	The invention discloses a method for extracting ferulic acid, p-coumaric acid and pentosan from corn husks, which belongs to the technical field of chemical industry. The method includes firstly, soaking corn husks into alkali solution, filtering and extracting p-coumaric acid after filtrate is neutralized to meet pH = 3-4 and concentrated, secondly, soaking the corn husks filtered from the first step into alkali solution, filtering and extracting ferulic acid by ethyl acetate after the filtrate is neutralized to meet pH = 3-4 and vacuum concentration is completed, thirdly, merging aqueous phase after the extraction of ethyl acetate in the step one and the step two, fourthly, desalinizing and condensing by means of nanofiltration, and fifthly, collecting pentosan by means of centrifugal settling after precipitated pentosan is dissolved out. The method for extracting ferulic acid, p-coumaric acid and pentosan from corn husks is short in production cycle and lower in solvent consumption, and thereby production efficiency can be further improved for enterprises.
Type of AWCB	*Maize husk*
Recovered high added compound	Ferulic acid (4-hydroxy-3-methoxy-cinnamic acid), p-Coumaric acid ((E)-3-(4-hydroxyphenyl)-2-propenoic acid)
Details/methodology applied	An extract from corn bran ferulic acid, p - coumaric acid and methods of pentosan, characterized by comprising the following steps: (1) at room temperature with 0.5 5-1 0% of lye. Soak corn husks and stirred, filtered, and the filtrate was neutralized to pH = 3-4 and extracted with ethyl acetate was concentrated under vacuum to p-coumaric acid, water extraction phase after backup; adding a high boiling petroleum ethyl acetate phase was concentrated in vaccum, p - coumaric acid precipitate was collected by filtration and dried, and 5% to 30% diluted alcohol crystallization to obtain high purity - coumaric acid; (2) at room temperature with 1.5-3.0% of lye soaking Step 1 filtered out of corn bran and stirred, filtered, and the filtrate was neutralized to pH = 3-4 and extracted with ethyl acetate and concentrated in vaccum ferulic acid, after extraction of the aqueous phase reserve; ethyl acetate phase was concentrated in vaccum to join high (3) consolidation steps 1 and 2 ethyl acetate; boiling petroleum ether, ferulic acid precipitation; the precipitate was collected by filtration and dried, water or dilute 5% -20% alcohol by crystallization of high purity ferulic acid The aqueous phase was concentrated and desalted by nanofiltration, after adding 95% alcohol and then further concentrated in vaccum, pentosan precipitated, collected by centrifugal sedimentation.

Patent No	CN103319328 B
Issue Date	23/05/2013
Title	**Preparation method for ferulic acid**
Description/Abstract	The present invention discloses a method for preparing ferulic acid, it belongs to the realm isolated from plants extracts. The present invention ferulic acid preparation method comprises the following steps: mixing the fibrous material with a low concentration of the alkaline aqueous solution of alcohol extract obtained alkaline solution containing ferulic acid solution, followed by ultrafiltration to remove soluble macromolecular impurities, then nanofiltration UF permeate was concentrated, and the concentrate was acidified low standing crystallization or organic solvent extraction to obtain ferulic acid products. The present invention utilizes the agriculture and food processing solid waste as raw material to produce can be used in food, pharmaceutical and cosmetic industry productivity features antioxidant ferulic acid, a major economic and social significance.
Type of AWCB	*Maize cobs*
Recovered high added compound	Ferulic acid (4-hydroxy-3-methoxy-cinnamic acid)
Details/methodology applied	A process for preparing ferulic acid, comprising the following process conditions and steps: pretreatment (1) fibrous raw material: The cellulosic material is dried and pulverized; (2) a base polyol A was treated release Wei Acid: The by step (I) pretreated cellulosic material with an alkali solution of alcohol water mixture by solid-liquid ratio Ikg: After 10~15L mixed extraction recovery of ethanol distillation, after filtration and centrifugation to remove the residue, an aqueous solution macromolecules by ultrafiltration to remove impurities, obtained through the liquid reserve; and (3) of ferulic acid to obtain: After step (2) is transmitted through the liquid nanofiltration, the nanofiltration concentrate was acidified by low temperature crystallization or organic After distilling off the organic solvent extraction solvent, to obtain high purity ferulic acid; step (2) in the ultrafiltration with MWCO ultrafiltration membrane is 1000~20000; step (3) above Nanofiltration nanofiltration MWCO membrane is 100~500, nanofiltration pressure 0.1~0.45MPa, a temperature of 15 ~45 ° C.

Patent No	CN1425773 A
Issue Date	27/12/2002
Title	**Process for preparing oligosaccharide and trans-ferulic acid**
Description/Abstract	The present invention discloses a preparation process of oligosaccharide and trans-ferulaic acid. Wheat bran, rice bran, bagasse, bean skin and other plant leftover with high polysaccharide content as material is reacted by polysaccharide hydrolase and feruaic acid esterase to produce oligosaccharide and trans-ferulaic acid. The present invention has wide material source, high extraction rate andlow production cost. The production process has mild condition; uses no acid, alkali and other chemical matter; and has no change in the natural property of the product and no environmental pollution.
Type of AWCB	*Maize cobs, maize stalks*
Recovered high added compound	Ferulic acid (4-hydroxy-3-methoxy-cinnamic acid)
Details/methodology applied	A method for preparing oligosaccharides and trans-ferulic acid to plant cell wall material of industrial waste as a raw material, wherein: polysaccharide hydrolysis enzyme ferulic acid esterase and synergy, of pretreated feedstock conduct hydrolysis, enzymatic hydrolyzate containing oligosaccharides obtained and trans ferulic acid.

4. Oats

Avena sativa L., or the common oat, is a popular cereal grain that has been eaten for at least 3,000 years. Oats are a major cereal grain worldwide and the 6th cereal grain after maize, rice, wheat, barley and sorghum. They used to be more important than they are today: world production was 50 million tons in the early 1960s, while in 2012 worldwide production was less than half, 21 million tons. Once a predominant grain for cattle and horses, oats became marginalized and oat production steadily decreased during the second part of the 20th century, due to their replacement with higher energy cereals such as barley and maize, to increased mechanization and subsequent disappearance of draught horses, and to increased specialization in agriculture requiring less crop rotation and more chemical usage (Blair, 2011). Oats remain competitive in cold northern areas (for example Russia, Canada, Northern USA, Scandinavia) where there are fewer alternative crops (Rines et al., 2006). The dual purpose feed and fodder uses of the oat crop makes it valuable in certain areas, such as the highlands of tropical Africa, Australia and the USA. In these cases, the crop is cut during the first stages of growth for fodder and then allowed to grow until the grain is ready for harvesting (Suttie & Reynolds, 2004). Oat forage is used for grazing, hay and silage, and the straw is used as animal bedding. Due to the presence of hulls, oat grains contain more fibre than other cereals and their nutritional value for livestock tends to be lower. Naked oats have a better energy density and nutritional value. [220] In addition to their use as a livestock feed, oats are commonly used for food, such as breakfast cereals, porridge, hard cakes or used a thickening agent in cooking, but they are unsuitable for bread-making. Oats are gluten-free and used in diets for people with gluten-related disorders. Oats are also popular for their emollient properties in cosmetics (Goujon-Henry et al., 2008).

Oats tend to be used in their country of origin, and the main producing countries are also the main consumers. In 2009, international trade accounted for only 15% of production (FAO, 2016). This may be due partly to the bulky nature of oats and their relatively low value compared to other energy and protein sources. Oats are often fed on-farm and do not enter the commercial market or appear in national statistics. In many countries, the oat crop is not intended for grain but for forage (Hoffman, 1995).

The preparation of oats for human consumption is more laborious than for wheat because oats must be milled to remove the glumes before any further processing can be carried out (Suttie & Reynolds, 2004). Oat milling yields several **by-products**:

- Oat screenings result from the cleaning of raw oats before processing.
- Oat hulls (lemma) are obtained by the mechanical separation (rotating drum) of the hulls from the kernels prior to milling. Oats may be steamed or roasted before that step to facilitate separation. The hulls are removed by air aspiration and the groats, which are the edible huskless grains, are ready for further processing (Bühler_Group, 2007). Oat hulls include small fragments of endosperm and represent up to 25% of the weight of the grain (Thompson et al., 2000).
- Oat mill feed, also called oat dust, is obtained after the transformation of groats into oatmeal. Groats are kiln-dried, sized and cut, producing fines that are mixed with the screenings and the hulls obtained previously. The final ground product, called oat mill feed, is usually intended for animal feeding (Bühler_Group, 2007).
- Oat bran is a by-product of oat flour production. It is used as a health food for human consumption due to its hypoglycemic and hypocholesterolemic effects and high content of B vitamins (Butt et al., 2008).

It is important to note that oat hulls and oat bran are completely different products: oat hulls are a high fibre, low protein and low energy feed while oat bran is a low fibre, high protein and high energy food ingredient. However, the name oat bran is sometimes used as a generic term for more or less fibrous oat by-products, which may be a source of confusion.

Oat hulls, oat mill feed and other oat by-products do not have universally accepted definitions and clear boundaries. Some national official regulations contain mandatory requirements on their composition, but ingredients sold under those names often encompass a wide range of by-products ranging from pure hulls to mixtures of hulls, screenings, and residual endosperm particles.

Due to their high fibre content, oat hulls and oat mill feed are mostly valuable for ruminant and rabbit feeding. They can be used in concentrate pellets (Winfield et al., 2007). Oat hulls can replace sawdust as an alternative bedding material for dairy cattle (Shane et al., 2010). Oat hulls are also a potential raw material for bioethanol production (Perruzza, 2010). Oat hulls mixed with excreta can be used to produce biogas and their methane yield is comparable to that obtained with straw (Kusch et al., 2011).

4.1 Oat straw

Oat straw, is the green, unripe part of the plant, both leaves and stems, and is sold as Avena sativa, green oats or wild oat extract. One can find it in some health food stores and on the Internet as a powder, juice, tincture or as a tea. The nutritive properties of oats and oat straw are not very different, except that oat straw is lower in calories and higher in Vitamin A (carotenes) and Vitamin C, than the grain alone. Oat straw is one of the best anti-osteoporosis herbs – the others are alfalfa, horsetail, nettles and red clover blossoms. Oats is rich in calcium and vitamins needed for building bones. Consistent use of oats and oat straw in the diet reduces cholesterol and improves circulatory function, helps to stabilize blood sugar levels, brings about noticeable improvement in coordination, bone density, balance, memory, sensitivity to pleasant stimuli, clarity of thinking and overall calmness and centeredness.

The chemical analysis of **oat straw** is summarized in Table 4.1. Silicon dioxide occurs in the leaves and in the straw in soluble form as esters of silicic acid with polyphenols, monosaccharides and oligosaccharides. Oat straw contains a high content of iron, manganese, zinc, chromium, magnesium, potassium, phosphorus, niacin and a variety of other nutrients (Blumenthal et al., 1998) and saponins, alkaloids such as avenine, trigoneline, sterols, flavanoids, and calcium (Hoffmann, 1998).

Table 4.1: Summary of main physicochemical characteristics of oat straw (ECN, 2016; feedipedia, 2016).

PARAMETER	VALUE (AVERAGE)
ENERGY	
Higher Heating Value (HHV) (MJ/kg)	18.09
Lower Heating Value (LHV) (MJ/kg)	17.01
Fixed Carbon (%wt)^{am}	12.48
Volatile Matter (%wt)^{am}	73.9
Ash (%wt)^{am}	5.42
Moisture (% wt)^{am}	8.2-10.4 (9.3)
Carbon (%wt)^{db}	46.3-47.6 (47.0)
Oxygen (%wt)^{db}	38.7-43.5 (41.1)
Hydrogen (%wt)^{db}	4.9-5.8 (5.35)
Nitrogen (%wt)^{db}	0.50-0.69 (0.63)
Sulfur (%wt)^{db}	0.08-0.11 (0.095)

PARAMETER	VALUE (AVERAGE)
FODDER	
Dry matter (%wt)[am]	89.6
Crude protein (%wt)[db]	3.6
Crude fibre (%wt)[db]	39.8
Neutral Detergent Fiber (NDF) (%wt)[db]	76.0-77.4 (76.7)
Acid Detergent Fiber (ADF) (%wt)[db]	40.3-44.6 (42.5)
Lignin (%wt)[db]	6.6-15.4 (11.0)
Ether extract (%wt)[db]	1.5
Ether extract (HCl hydrolysis) (%wt)[db]	2.1
Ash (%wt)[db]	2.60-7.82 (5.90)
Gross energy (MJ/kg dry matter)	18.0
FERTILIZER	
Nitrogen (g/kg)[db]	5.0-6.9 (6.14)
Phosphorus (g/kg)[db]	0.01-1.32 (0.78)
Potassium (g/kg)[db]	0.22-29.96 (13.96)
Calcium (g/kg)[db]	0.03-4.21 (2.65)
Magnesium (g/kg)[db]	0.02-1.32 (0.81)
Sulfur (g/kg)[db]	0.97.1.10 (1.04)
Silica (g/kg)[db]	8.66
Manganese (mg/kg)[db]	0.3-33.0 (16.65)
Zinc (mg/kg)[db]	20.0
Copper (mg/kg)[db]	0.1-5.0 (2.6)
Iron (mg/kg)[db]	2.2-747.0 (270)

4.2 Oat bran

Oat bran is defined as the by-product produced by grinding clean oat groats (the oat seed with the hull removed) or rolled oats and separating the resulting oat flour by sieving, bolting, and/or other suitable means into fractions. Specifically, bran corresponds to what would be the outer layers of grain and more specifically the pericarp, with its three sub-layers: exocarp, mesocarp and endocarp (rich in fiber and minerals), testa (rich in vitamins and enzymes) and the aleurone layer (rich in proteins and fats).

The chemical analysis of **oat bran** is summarized in Table 4.2. Oat bran contains a high amount of proteins, little fat, but much more than wheat bran, hence its higher caloric value. Oat bran is rich in carbohydrate energy source, and in vitamins of group B. The importance of this vitamin in the processing of fats, proteins and carbohydrates into energy is vital. Vitamin B plays an important role in nervous system health and the production of hormones, enzymes, or proteins, and strengthening the immune system. Nevertheless, except in thiamin, the wheat bran surpasses to the oat bran.

Table 4.2: Summary of main physicochemical characteristics of oat bran (botanical-online, 2016; ECN, 2016; feedipedia, 2016; Hosseinian & Mazza, 2009; Miller et al., 2007).

PARAMETER	VALUE (AVERAGE)
ENERGY	
Higher Heating Value (HHV) (MJ/kg)	19.07
Lower Heating Value (LHV) (MJ/kg)	17.74
Moisture (% wt)[am]	6.55

PARAMETER	VALUE (AVERAGE)
Carbon (%wt)[db]	47.0
Hydrogen (%wt)[db]	6.1
Nitrogen (%wt)[db]	1.06
Sulfur (%wt)[db]	1.1
FODDER	
Crude protein (%wt)[db]	15.7-17.3 (16.5)
Ash (%wt)[db]	1.9-2.2 (2.1)
Gross energy (MJ/kg dry matter)	10.3
FERTILIZER	
Nitrogen (g/kg)[db]	10.6
Phosphorus (g/kg)[db]	7.34
Potassium (g/kg)[db]	5.6
Calcium (g/kg)[db]	0.58
Magnesium (g/kg)[db]	2.35
Sulfur (g/kg)[db]	1.1
Manganese (mg/kg)[db]	56.3
Zinc (mg/kg)[db]	31.1
Copper (mg/kg)[db]	4.03
Iron (mg/kg)[db]	54.1
BIOACTIVE COMPOUNDS	
Phenolics, free (mg/100g)	2.8 ± 0.2
Phenolics, bound (mg/100g)	85.1 ± 4.3
Proanthocyanidins (mg/100g)	148.0 ± 0.2
β-glucan (total)	6.2-10.8
Vitamin B1 (Thiamin) (mg/100g)	1.17
Vitamin B2 (Riboflavin) (mg/100g)	0.22
Vitamin B3 (Niacina) (mg/100g)	0.934
Vitamin B6 (Piridoxina) (mg/100g)	0.166
Vitamin E	1.71
Folic acid	0.052

5. Sunflower seed

Sunflower belongs to the genus *Helianthus* of the Compositae family. The genus Helianthus was named using the Greek helios meaning sun, and anthos, flower. The inflorescence of the plants of this family are heads in which the fertile flowers are aggregated and bordered by rays, the corollas of sterile flowers. The genus *Helianthus* includes 67 annual and perennial species. The cultivated sunflower is an annual plant with the scientific name of *Heliantbus annuus*. It is an erect, unbranched, coarse annual, with a distinctive large, golden head, the seeds of which are often eaten and are commonly crushed for oil production.

The stem can grow as high as 3 m and the flower head can reach 30 cm in diameter with large seeds. The term 'sunflower' is also used to refer to all plants of the genus *Helianthus*, many of which are perennial plants. What is usually called the flower is actually a head (formally composite flower) of numerous florets (small flowers) crowded together. The outer florets are the sterile ray florets and can be yellow, maroon, orange, or other colours. The florets inside the circular head are called disc florets, which mature into what are traditionally called 'sunflower seeds', but are actually the fruit (an achene) of the plant. The inedible husk is the wall of the fruit and the true seed lies within the kernel (Bassam, 2010).

Sunflower is one of the most important oilseed crops. It is known, that extracts obtained from sunflower seeds and oils exhibit antioxidant capacity (Cevallos-Casals & Cisneros-Zevallos, 2010; Szydłowska-Czerniak et al., 2008). Moreover, sunflower meal is used primarily in ruminant feed, but its nutritional, sensory and functional properties also make it a protein and antioxidant compounds source of interest as a human food. Also, sunflower shells contain phenolic antioxidants (De Leonardis et al., 2005; Szydłowska-Czerniak et al., 2011; Weisz et al., 2009).

The use of sunflower agricultural residues as raw material for different applications has been proposed although there are relatively little reports based on them. Sunflower heads contain pectins and a strong smelling essential oil; whole stalks can find use in paper pulp production, while low density materials can be obtained from ground stalk pith (Marechal & Rigal, 1999). Sunflower hull seeds have been used as raw material for ethanol production by Pichia stipitis with 0.32 g/g ethanol yield from a hydrolysate obtained at 90^{o}C with 0.7 M H_2SO_4 (Telli-Okur & Eken-Saraçoğlu, 2008). Concerning stalks, enzymatic hydrolysis of autoclave pretreated material resulted in 57.8% maximum yield (Sharma et al., 2002b). Subsequent fermentation produced a high ethanol yield of 0.44 g/g ethanol (Sharma et al., 2002a). Caparrós et al. used hydrothermal pre-treatment with sunflower stalks (Caparrós et al., 2008). The liquid fraction issued from pre-treatment was examined for oligomers and monosaccharide composition, while the pretreated solid was used for paper production (Díaz et al., 2011).

It is estimated that 90% of the world's sunflower seed production is crushed for oil extraction. The non-seed part of the heads is also an important biomass source that is almost equal to the seed production. In addition, if dehulling is practised prior to the oil-extraction process, a significant quantity of hulls is produced. In oil-producing hybrids about 25% of the achene weight is the hull, which is composed of equal proportions of lignin, pentosans and cellulosic material, representing 82 – 86% of the total weight. These materials also have a high heating value. The gross heating value is about 17MJ/kg of dry matter (Bassam, 2010).

Heliantbus annuus has an excellent adaptability, and the growth cycle is only about 100 days. These characteristics of *Heliantbus annuus* suggest that it can be used as a good potential energy source and should be further studied as a good biofuel feedstock candidate (Yan et al., 2013).

Figure 5.1: Sunflower head (left photo) and sunflower husks (right photo) (feedipedia, 2016).

5.1 Sunflower stalks

Sunflowers have been considered as one of the major sustainable lignocellulosic materials used not only to extract oils but also for production of biofuels as an alternative to fossil fuels (Fortunati et al., 2016b). Sunflowers are renewable and are cultivated in large quantities around the world; while sunflower seeds represent the fourth source of oil in the world, heads, stalks and leaves remain unutilized after harvesting (Ruiz et al., 2008).

These residues are not eco-friendly because after harvesting they are typically burnt under not well-controlled conditions, causing a negative environmental impact. Every year, the volume of sunflower residues produced in the world represents a huge environmental impact with 3-7 tn of dry matter/ha (Díaz et al., 2011). It has been estimated that each hectare of sunflower culture can produced 3–7 tons of dry biomass, including heads (10%) and stalks (Marechal & Rigal, 1999). So, this low cost, renewable and useless biomass can be considered a huge energy source.

For these reasons, the attention of the scientific community is now oriented to the revalorization of wastes after sunflower harvesting. Currently the most common use of residual stalks is for bioethanol production. However, sunflower residues could be used also as precursors for the extraction of cellulose based materials. Cellulosenanocrystals (CNC) and cellulose nanofibrils (CNF) constitute the two main families of nanosized cellulose. The former is extracted from fibres after a complete dissolution of the non-crystalline fractions, while the latter results from the application of high shearing forces of disintegration leading to a high degree of fibrillation, which yields highly interconnected fibrils. Some different methods are known for the extraction of nanosized cellulosic materials, such as chemical, enzymatic, mechanical treatments, etc. (Fortunati et al., 2016b).

Sunflower stalks of this annual crop consist of two parts, including an inner non-cellulosic pith and an outer woody ring of lingocellulosic fibers. Taking into account the stalk/seed weight ratio of about 2.3, the wall/pith ratio of about 9:1 and wooden wall density of 0.44 g/cm^3, large amounts of residual stalks are available annually which could be used to obtain valuable products (such as bioethanol production after pretreatment and saccharification process and paper pulp production), rather than being burnt as often occurs nowadays (Kim et al., 2016; Rudi et al., 2016).

The main physicochemical characteristics of sunflower stalks are summarized in Table 5.1.

Table 5.1: Summary of main physicochemical characteristics of sunflower stalks (Akpinar et al., 2009; CN103601596A, 2014; Demirbas, 2003; Díaz et al., 2011; ECN, 2016; Erzengin & Küçük, 1998; feedipedia, 2016; Ghugare et al., 2014; Jiménez & López, 1993; Karnjanakom et al., 2015; Kearl, 1979; Plis & Wilk, 2011; Riva et al., 2013; Ruiz et al., 2008; Sharma et al., 2002b; Yan et al., 2013).

PHYSICOCHEMICAL PROPERTIES	AVERAGE	SD	MIN	MAX	N° Samples
ENERGY					
Higher Heating Value (HHV) (MJ/kg)	18.7	3.34	15.9	26.0	9
Lower Heating Value (LHV) (MJ/kg)	17.7	3.29	15.2	24.4	8
Fixed Carbon (%wt)^{db}	8.7	6.59	1.2	14.4	4
Volatile Matter (%wt)^{db}	81.0	6.03	72.7	85.9	4
Ash (%wt)^{db}	7.9	3.64	3.0	13.2	18
Moisture (% wt)^{am}	9.1	5.82	2.3	18.0	5
Carbon (%wt)^{db}	46.0	7.07	35.1	60.3	10
Oxygen (%wt)^{db}	37.6	5.39	26.8	47.5	10
Hydrogen (%wt)^{db}	5.4	0.74	4.8	7.1	10
Nitrogen (%wt)^{db}	1.2	0.69	0.3	2.6	11
Sulfur (%wt)^{db}	0.1	0.07	0.0	0.2	8
FODDER					
Dry matter (%wt)^{am}	88.9	5.08	82.0	94.0	4
Crude protein (%wt)^{db}	7.3	4.49	1.5	16.3	12
Crude fiber (%wt)^{db}	48.8	n.a.	48.8	48.8	1
Neutral Detergent Fiber (NDF) (%wt)^{db}	71.7	16.82	43.2	89.5	6
Acid Detergent Fiber (ADF) (%wt)^{db}	37.2	10.17	22.1	51.0	6
Lignin (%wt)^{db}	16.1	5.85	7.3	26.5	7
Ether extract (%wt)^{db}	1.0	0.79	0.5	2.0	3
Ash (%wt)^{db}	7.9	3.64	3.0	13.2	18
Gross energy (MJ/Kg)	18.8	3.57	15.9	26.0	8
FERTILIZER					
Nitrogen (g/kg)^{db}	11.1	5.53	3.1	20.0	10
Phosphorus (g/kg)^{db}	0.9	0.73	0.1	2.3	7
Potassium (g/kg)^{db}	27.5	22.50	8.0	67.8	7
Calcium (g/kg)^{db}	8.1	4.80	1.6	13.7	7
Magnesium (g/kg)^{db}	1.1	0.27	0.9	1.5	6
Sulfur (g/kg)^{db}	1.2	0.79	0.1	2.5	8

5.2 Sunflower husks

Sunflowers are mainly cultivated for their seeds which are used as a source of oil or as a condiment. When used as a condiment the hulls are discarded, while the whole kernel is eaten. On the other hand, in the oil industry, the sunflower is partially dehulled, prepressed then solvent extracted or completely dehulled, then solvent extracted to obtain the sunflower oil. Sunflower hulls are considered an agro-industrial by-product. Sunflower hulls may be utilized in animal feed, as bedding to animals, for growing yeast and burning in fire places. Mostly sunflower hulls are ground and sold as roughage for livestock (Taha et al., 2012).

The chemical composition of sunflower hulls ranges from 8.53-9.80% moisture, 4.33-6.14% protein, 1.65-2.20% oil, 1.35- 1.68% ash and 18.82-20.05% crude fiber. At the same time, Cancalon (1971) reported that sunflower hulls contain 5.1% lipids, 4% protein and carbohydrate which is mainly made up of cellulose and reducing sugars (25.7%) (Cancalon, 1971). The nutrient composition of sunflower hulls was also reported to be 5% crude protein, 3.9% oil, 44.0% crude fiber, 0.8 Mcal/lb digestible energy, 3% non-soluble carbohyhydrate (Taha et al., 2012).

Sunflower seed shells have been extensively studied regarding their major chemical components of sunflower seed shells such as: lipids, proteins, carbohydrates along with oil, moisture content and even for their average length, width and thickness (Cancalon, 1971; Perez et al., 2007). Furthermore, a few researchers have emphasized in quantitative analyses of total phenolic compounds (TPC) and individual phenolic acids in sunflower shell extracts (De Leonardis et al., 2005; Weisz et al., 2009). Although, 94.6–99.3% of total phenolics are located in sunflower kernels, still shells contain from 0.7% to 5.4% of these compounds, hence they can be sort of source of natural antioxidants (Pedrosa et al., 2000; Szydłowska-Czerniak et al., 2011).

The main physicochemical characteristics of sunflower husks are summarized in Table 5.2.

Table 5.2: Summary of main physicochemical characteristics of sunflower husks (Antal et al., 2000; Antal Jr et al., 2007; Behgar et al., 2009; Demirbas, 2006; feedipedia, 2016; García et al., 1999; Ginenne & Lebas, 2002; ILRI, 2011; Jones et al., 2015; Magasiner & de Kock, 1987; Pawlowski et al., 2013; Radovanovic et al., 2000; Riva et al., 2013; Stauton & Le Valley, 2006; Taha et al., 2012; Werther et al., 2000; Zabaniotou et al., 2008b).

PHYSICOCHEMICAL PROPERTIES	AVERAGE	SD	MIN	MAX	N° Samples
ENERGY					
Higher Heating Value (HHV) (MJ/kg)	20.1	1.48	17.9	22.3	8
Lower Heating Value (LHV) (MJ/kg)	18.9	1.25	17.4	20.8	6
Fixed Carbon (%wt)^{db}	21.6	4.52	14.2	29.0	9
Volatile Matter (%wt)^{db}	72.6	4.04	66.5	76.2	9
Ash (%wt)^{db}	3.7	2.25	1.6	10.3	17
Moisture (% wt)^{am}	6.8	3.36	0.7	11.9	12
Carbon (%wt)^{db}	49.3	3.87	38.1	54.4	13
Oxygen (%wt)^{db}	39.7	3.92	32.9	46.4	13
Hydrogen (%wt)^{db}	5.9	0.58	4.9	7.3	13
Nitrogen (%wt)^{db}	1.0	0.60	0.3	2.4	18
Sulfur (%wt)^{db}	0.1	0.07	0.1	0.2	9
FODDER					
Dry matter (%wt)^{am}	93.3	3.34	88.2	99.3	13
Crude protein (%wt)^{db}	6.5	3.76	2.1	15.1	18
Crude fiber (%wt)^{db}	44.9	14.61	25.0	58.8	4
Neutral Detergent Fiber (NDF) (%wt)^{db}	74.8	11.12	57.8	88.2	5
Acid Detergent Fiber (ADF) (%wt)^{db}	58.7	8.90	45.4	68.5	6
Lignin (%wt)^{db}	22.1	3.38	18.0	27.0	5
Ether extract (%wt)^{db}	4.9	3.94	1.5	10.5	5
Ash (%wt)^{db}	3.7	2.25	1.6	10.3	17
Gross energy (MJ/Kg)	20.1	1.48	17.9	22.3	8

PHYSICOCHEMICAL PROPERTIES	AVERAGE	SD	MIN	MAX	N° Samples
FERTILIZER					
Nitrogen (g/kg)[db]	10.4	6.01	3.3	24.2	18
Phosphorus (g/kg)[db]	0.6	0.41	0.2	1.3	6
Potassium (g/kg)[db]	9.7	5.45	1.1	15.4	9
Calcium (g/kg)[db]	6.7	7.19	1.3	23.6	8
Magnesium (g/kg)[db]	2.7	1.04	1.0	3.9	7
Sulfur (g/kg)[db]	1.3	0.74	0.5	2.4	9

5.3 Sunflower AWCB bioactive compounds patent and literature review

There is a small number of patents regarding the utilization of sunflower by-products for the recovery of high added value compounds. A summary of these patents is presented in the following tables.

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Patent No	CN 1208630 A
Issue Date	24/02/1999
Title	Traditional Chinese medicine series used for anticancer and method for preparing same
Description/Abstract	The present invention relates to a new anticarcinogen series by using sunflower stalk core extract as anticancer effective component and its production method. Said method uses sunflower stalk core as row material and adopts the procedures of crushing, decoction, extraction, filtering, concentration or drying to make the above-mentioned raw material into oral liquor and compound preparation series. Besides, said invention also adopts the chemical synthesis and other preparation process to obtain the invented anticarcinogen microecological oral liquor series and gene medicinal preparation series. Said invention has no toxic side effect, and possesses obvious therapeutic efficacy for carcinoma of stomach, intestinal and other carcinosis.
Type of AWCB	Sunflower stalks
Recovered high added compound	Anticancer agent

Patent No	WO 1991011169 A1, CA2074485A1, DE69100591D1, DE69100591T2, EP0512040A1, EP0512040B1
Issue Date	08/08/1991
Title	Cosmetic compositions containing an essence of sunflower oil cake (helianthus annuus)
Description/Abstract	A cosmetic composition for countering the harmful effects on the skin of chronic exposure to the sun, characterized in that it contains, as an active principle, an essence of sunflower oil cake (Helianthus annuus) which can be useful in inhibiting the photochemical reactions which cause actinic skin aging.
Type of AWCB	Sunflower stalks
Recovered high added compound	Cosmetic composition for countering the harmful effects on the skin of chronic exposure to the sun

Patent No	US 3985815 A, USB519446
Issue Date	12/10/1976
Title	Aqueous crystallization of xylitol
Description/Abstract	A process for obtaining crystalline xylitol substantially free of xylose from a mixture of xylose and xylitol by providing an aqueous solution of about 50 to 75 weight percent xylitol, no more than about 5 weight percent xylose and about 20 to 45 weight percent water and fractionally crystallizing xylitol from the aqueous solution to provide crystalline xylitol containing no more than about 0.10 weight percent xylose.
Type of AWCB	Sunflower hulls
Recovered high added compound	Xylitol

6. Triticale

Triticale (*Triticosecale Wittmack*) is a hybrid crop developed by crossing wheat (*Triticum sp.*) and rye (*Secale sp.*) (Salmon et al., 2001). Modern triticales AC Ultima) are mostly hexaploid which originated from Triticum turgidum subsp. durum rye (Secale cereale) cross. It is understood that this hybridisation between the two species resulted to a crop that possesses a combined advantage of the high yield potential of wheat, and the disease and environmental tolerance of rye. Animal studies have shown the digestibility of triticale to be generally higher than barley and relatively equal to rye (Chrenková et al., 2012). The poor bread making quality of rye and the digestibility problems of barley in cattle increase the need for exploring other avenues of grain sources such as triticale. This is also supported by the nutritional value of triticale which is close to that of wheat and rye (Chapman et al., 2005; Chrenková et al., 2012; Salmon et al., 2001).

Triticale is also rich in phenolics and dietary fibres consisting of both soluble and insoluble fibres (Chrenková et al., 2012; Hosseinian & Mazza, 2009). Although triticale is an excellent candidate for animal feed due to high protein, amino acid, polysaccharide and B vitamin content, it has yet to be well-recognized for human food applications (Hansen, 2010). The insufficient demand for its significant utilization in food products can be attributed to the limited research data available on the characterisation of triticale composites, particularly in triticale by-products such as triticale bran and straw. That is why the overall food market for triticale has remained very small (AGROCYCLE Deliverable 1.1).

Triticale harvesting is accompanied by a high production of straw, which is of direct interest to livestock farmers. For a yield equivalent to wheat or barley, it produces a 30% larger volume of straw, but triticale straw is a little harder than that from wheat (innovationsreport, 2004). That is why triticale straw is used in animal systems along with wheat straw; however, it is not considered to have as high a feeding quality as barley or oat straw. This is likely because of the higher fibre content and lower energy content and protein (Salmon et al., 2001). Detailed physicochemical characterisation of triticale by-products (straw, bran) is rather limited in literature. Fibre and nutrients data were found in FEEDIPEDIA (feedipedia, 2016) only for triticale straw (Table 6.1), while the content of bioactive compounds in triticale bran and straw was only recently assayed by Hosseinian and his co-workers (Agil & Hosseinian, 2014).

Table 6.1: Summary of main physicochemical characteristics of triticale straw (feedipedia, 2016).

PARAMETER	VALUE (AVERAGE)
FODDER	
Dry matter (%wt)^{am}	92.5
Crude protein (%wt)^{db}	3.2
Crude fibre (%wt)^{db}	39.2
Neutral Detergent Fiber (NDF) (%wt)^{db}	75.1
Acid Detergent Fiber (ADF) (%wt)^{db}	47.5
Ether extract (%wt)^{db}	2.2
Ash (%wt)^{db}	5.4
Gross energy (%wt)^{db}	18.7
FERTILIZER	
Nitrogen (g/kg)^{db}	5.12
Phosphorus (g/kg)^{db}	0.3
Potassium (g/kg)^{db}	12.0
Calcium (g/kg)^{db}	2.7

PARAMETER	VALUE (AVERAGE)
Magnesium (g/kg)[db]	0.7

In a recent study by Hosseinian and Mazza the distribution of phenolic acids (free and bound), proanthocyanidins, and lignans in Canadian triticale by-products (defatted triticale bran and straw) was determined (Hosseinian & Mazza, 2009). For comparison, wheat, rye and oat brans as well as triticale flakes and leaves were also assayed.

Most phenolic acids were present in the bound form (89–98%), and released under alkaline extraction conditions (Table 6.2). The antioxidant activity (measured using the oxygen radical absorbance capacity, ORAC) for bound phenolics were 4–5 times higher than the value for free phenolics. Also the phenolics content of triticale straw and wheat bran in the bound forms was significantly higher ($P < 0.05$) than other samples, and thus they showed higher antioxidant activities (Table 6.3). Phenolics such as ferulic acid exhibit strong antioxidant activity (Andreasen et al., 2001; Seeram & Nair, 2002; Zhao & Moghadasian, 2008). Previous studies have shown that the content of bound phenolics is higher than the free phenolics in cereal grains and thus, they have a considerably higher antioxidant capacity than the free phenolics (Beta et al., 2005; Liyana-Pathirana & Shahidi, 2006). The study of Hasseinian and Mazza indicated that bound phenolics are major contributor to the antioxidant activity of triticale and other grain by-products. In addition, a strong correlation existed between the content of phenolics and antioxidant activity. There is a growing interest in products with high antioxidant activities that may reduce the risk of certain diseases. Thus, phenolics from triticale and its by-products have potential to act as natural antioxidants in vivo and provide health benefits upon consumption.

Table 6.2: Free and bound phenolics contents (mg/100g), and antioxidant activities (ORAC, µmol Trolox equivalents/g) in defatted triticale bran, flakes, straw, and leaves, and in wheat, rye, and oat bran (Mean values ± standard deviations, n = 3) (Hosseinian & Mazza, 2009).

SAMPLES	FREE	ORAC (FREE)	BOUND	ORAC (BOUND)
Triticale bran	9.9 ± 1.2	25.4 ± 1.4	270.7 ± 3.2	128.6 ± 5.2
Triticale flakes	1.7 ± 0.2	13.4 ± 0.9	85.8 ± 1.6	35.9 ± 2.3
Triticale straw	3.1 ± 0.4	51.7 ± 1.6	356.1 ± 0.7	220.0 ± 9.4
Triticale leaves	3.7 ± 0.1	48.2 ± 0.8	219.9 ± 13.5	202.5 ± 7.2
Wheat bran	13.7 ± 1.1	66.5 ± 2.2	439.9 ± 10.3	226.6 ± 4.4
Rye bran	12.3 ± 0.9	63.8 ± 1.7	253.4 ± 9.2	180.6 ± 9.6
Oat bran	2.8 ± 0.2	16.9 ± 1.1	85.1 ± 4.3	73.3 ± 3.7

The content of phenolic acids ranged from 65.2 to 252.5 mg/100 g in samples in which ferulic acid predominanted. Other major phenolics extracted were vanillic, p-coumaric, m-coumaric, and vanillin. Gallic, p-hydroxybenzoic, chlorogenic, syringic, and hydroxy-cinnamic acids were present at much lower levels (Table 6.3).

Triticale straw was found to be a rich source of proanthocyanidins, containing 862.5 mg/100 g (catechin equivalents) of tissue (Table 6.4). On the other hand, triticale flakes contained the lowest amount (115.6 mg/100 g) of proanthocyanidins. It has been reported that proanthocyanidins are localized in the outer layer of seed coat, with the endosperm being much lower in these compounds (McCallum & Walker, 1990; Naczk & Shahidi, 2006). This explains why the content of proanthocyanidins in triticale flakes was lower than triticale bran. The total proanthocyanidins levels in triticale bran and straw were 2.5 and 7.5 times higher than triticale flakes (Table 6.4). These

findings are consistent with the results on the contents of phenolic acids (Table 6.2), indicating a positive correlation between phenolic acids content and proanthocyanidins in grain by-products samples. The total proanthocyanidins level in triticale bran was more similar to that of rye bran than that of wheat bran.

Table 6.3: Bound phenolics distribution (mg/100g) in triticale bran, flakes, straw, and leaves, and in wheat bran, rye bran, and oat bran (Mean values ± standard deviations, n = 3) (Hosseinian & Mazza, 2009).

BOUND PHENOLICS	TRITICALE				WHEAT BRAN	RYE BRAN	OAT BRAN
	Bran	Flakes	Straw	Leaves			
Gallic	0.5 ± 0.1	0.5 ± 0.2	0.8 ± 0.6	0.2 ± 0.5	ND	ND	ND
p-OH benzoic	ND	0.1 ± 0.3	1.8 ± 0.5	ND	0.2 ± 0.7	0.1 ± 0.4	6.2 ± 0.2
Chlorogenic	0.2 ± 0.2	ND	1.1 ± 0.2	1.4 ± 0.4	0.7 ± 0.5	0.3 ± 0.2	0.4 ± 0.5
Syringic	1.8 ± 0.4	ND	ND	1.3 ± 0.2	ND	ND	ND
Vanillic	1.5 ± 1.2	1.6 ± 0.6	15.0 ± 0.8	6.1 ± 0.3	2.4 ± 0.5	1.5 ± 0.1	1.4 ± 0.3
p-Coumaric	11.9 ± 0.6	6.7 ± 0.7	16.3 ± 1.3	58.9 ± 0.5	8.9 ± 0.4	12.2 ± 1.1	1.1 ± 0.8
Ferulic	97.1 ± 1.3	53.9 ± 0.3	192.9 ± 0.8	27.3 ± 1.1	159.8 ± 0.4	121.2 ± 1.4	40.5 ± 0.3
m-Coumaric	2.6 ± 0.4	0.4 ± 0.1	8.4 ± 0.1	2.9 ± 0.4	5.5 ± 0.9	2.4 ± 0.1	1.3 ± 0.2
OH-cinnamic	ND	ND	ND	ND	0.8 ± 0.3	0.4 ± 0.1	1.5 ± 0.6
Vanillin	21.7 ± 0.5	13.0 ± 0.2	16.2 ± 0.3	7.9 ± 0.2	43.9 ± 0.2	50.0 ± 1.5	12.8 ± 1.9
Total (known)	137.3 ± 0.6	76.2 ± 0.4	252.5 ± 0.5	106.0 ± 0.5	222.2 ± 0.4	188.1 ± 0.5	65.2 ± 0.5
Total (unknown)	133.4 ± 2.9	9.6 ± 0.6	103.6 ± 3.6	113.9 ± 2.5	217.7 ± 2.1	65.3 ± 1.8	19.9 ± 0.8
Total (all), HPLC [a]	270.7 ± 1.7	85.8 ± 0.5	356.1 ± 2.1	219.9 ± 1.5	439.9 ± 1.3	253.4 ± 1.2	85.1 ± 0.7
Total, Folin–Ciocalteu [b]	284.9 ± 0.4	89.6 ± 0.7	365.3 ± 1.2	226.6 ± 0.5	442.7 ± 0.8	257.3 ± 0.9	94.2 ± 0.5

[a] Results of HPLC/DAD analyses with a reversed-phase Zorbax SB-C18 column;
[b] total phenolic content of the extracts was also determined as described by Fazzari et al. (2008) with minor modifications (Fazzari et al., 2008).

Triticale straw contained 0.27 mg/100 g of lignin secoisolariciresinol diglucoside (SDG), whereas the bran had only 0.01 mg/100 g. The oxygen radical absorbance capacity (ORAC, µM Trolox equivalents/g defatted material) showed that antioxidant activity of bound phenolics was higher than those of free phenolics. The results of this report proved that triticale by-products have the potential for use as nutraceuticals and/or functional food ingredients.

Table 6.4: Proanthocyanidins content (mg/100g) of triticale bran, flakes, straw, and leaves, and in wheat bran, rye bran and oat bran (Mean values ± standard deviations, n = 3) (Hosseinian & Mazza, 2009).

SAMPLE	ETHYL ACETATE EXTRACT	WATER EXTRACT	WATER EXTRACT	TOTAL CONTENT
	Ethanol fraction	Methanol fraction	Acetone fraction	
Triticale bran	22.8 ± 0.2	171.4 ± 0.7	71.2 ± 0.3	265.4 ± 0.4
Triticale flakes	17.0 ± 0.1	62.5 ± 0.3	36.1 ± 0.2	115.6 ± 0.2
Triticale straw	411.5 ± 1.5	229.3 ± 0.9	221.7 ± 0.9	862.5 ± 1.1
Triticale leaves	487.3 ± 1.7	195.9 ± 0.8	163.5 ± 0.6	846.7 ± 1.0
Wheat bran	43.4 ± 0.3	319.7 ± 1.2	146.3 ± 0.6	509.4 ± 0.7
Rye bran	11.5 ± 0.1	170.1 ± 0.7	29.9 ± 0.1	212.0 ± 0.3
Oat bran	13.3 ± 0.1	116.9 ± 0.4	17.8 ± 0.1	148.0 ± 0.2

7. Rye

Rye (*Secale cereale L.*) is a winter-hardy annual or biennial grass. It is mostly grown for its grain, particularly in Europe and North America, in areas where climate and soil are unfavorable for other cereals, or as a winter crop where temperatures are too low for winter wheat. Rye is the only cereal grain other than wheat to have the necessary properties for bread making (Fuller, 2004). While a minor cereal grain (less than 1% of total cereal grain crop) (FAO, 2016), rye remains an important bread grain in Northern and Eastern Europe, where rye flour may contribute more than 30% of the total flour used for bread making (Dendy & Dobraszczyk, 2001). In its main areas of production, such as Poland, rye grain is also used for feed, and more than 40% of the world production was used for animal feeding in 2016 (FAO, 2016). Non-food part of rye is agro waste which is about 15–20% of rye (Duke, 2000; Smith, 1995).

Rye looks like wheat but is longer and more slender and varies in color from yellowish brown to grayish green. It is generally available in its whole or cracked grain form or as flour or flakes that look similar to old-fashioned oats. The main components of rye grain are the same as in other cereals: starch 57-66%, DF 15-17% and protein 7-13% (Nilsson et al., 1997a). Because it is difficult to separate the germ and bran from the endosperm of rye, rye flour usually retains a large quantity of nutrients, in contrast to refined wheat flour. In addition to the grain itself, several rye by-products are occasionally used in animal feeding, notably rye bran, which is the by-product of rye millling, and rye distillers' grains, the by-products of whisky and ethanol production (Fuller, 2004). Rye is also a valuable fodder (for pasture, hay or silage) and cover crop during winter. When it is used as cover crop in double cropping systems (a warm season crop followed by rye as late fall crop), harvesting rye forage during spring provides supplementary income to farmers who usually grow maize grain and vegetables (Kelley & Mutch, 2011).

7.1 Rye straw

According to statistical data of the European Union, in 2013 about 10 million tons of rye from 2.5 million hectares have been collected. It is estimated that from 1 ton of rye 0.5-2 tons of straw can be obtained (depending on the soil type or variety). This gives from 5 to 20 million tons of rye straw, of which 40% is potentially used for non-agricultural purposes (EUROSTAT, 2015a). These materials contain sugars polymerized to cellulose and hemicellulose that can be liberated by hydrolysis and subsequently fermented by microorganisms to form different chemicals (Baek & Kwon, 2007; Park & Kim, 2012). Therefore polymers from the plant biomass are considered as useful resources convertible to not only pulp and foodstuff but also energy resources such as alcohol, methane and chemical raw materials like furfural and organic acids (Domanski et al., 2016). The chemical analysis of **rye straw** is summarized in Table 7.1.

Table 7.1: Summary of main physicochemical characteristics of rye straw (ECN, 2016).

PARAMETER	VALUE (AVERAGE)
ENERGY	
Higher Heating Value (HHV) (MJ/kg)	18.79
Lower Heating Value (LHV) (MJ/kg)	17.63
Carbon (%wt)^{db}	47.49
Oxygen (%wt)^{db}	41.73
Hydrogen (%wt)^{db}	5.29
Nitrogen (%wt)^{db}	0.46
Sulfur (%wt)^{db}	0.06
FODDER	

PARAMETER	VALUE (AVERAGE)
Neutral Detergent Fiber (NDF) (%wt)[db]	80.4-89.0 (84.7)
Acid Detergent Fiber (ADF) (%wt)[db]	38.0-43.3 (40.7)
Lignin (%wt)[db]	17.0-17.6 (17.3)
Ash (%wt)[db]	1.2-4.57 (3.0)
FERTILIZER	
Nitrogen (g/kg)[db]	4.6
Phosphorus (g/kg)[db]	0.966
Potassium (g/kg)[db]	9.70-10.96 (10.33)
Calcium (g/kg)[db]	2.70-3.17 (2.93)
Magnesium (g/kg)[db]	0.515
Sulfur (g/kg)[db]	0.766
Silica (g/kg)[db]	3.50-4.95 (4.23)
Copper (mg/kg)[db]	2.3
Iron (mg/kg)[db]	70.38

7.2 Rye bran

Rye bran consists of the outer parts of the grain, and depending on the milling process, the bran fraction recovery accounts for approximately 10-20% of the entire rye grain. Rye and wheat grains behave differently during milling (Weipert, 1997). In comparison with cereals and other flour-milling industry by-products, rye bran has lower energetic value, higher fibre content and also more minerals (Table 7.2). They have worse dietetic qualities than wheat ones. Their usage is restricted in feed for older categories of fattening cattle, in lower level for milking cows sometimes.

Table 7.2: Summary of main physicochemical characteristics of rye bran (feedipedia, 2016; Hosseinian & Mazza, 2009).

PARAMETER	VALUE (AVERAGE)
FODDER	
Dry matter (%wt)[am]	88.0
Crude protein (%wt)[db]	16.9
Crude fibre (%wt)[db]	6.3
Neutral Detergent Fiber (NDF) (%wt)[db]	29.0
Acid Detergent Fiber (ADF) (%wt)[db]	8.3
Lignin (%wt)[db]	2.0
Ether extract (%wt)[db]	2.3
Ash (%wt)[db]	5.2
Starch (%wt)[db]	28.4
Total sugars (%wt)[db]	7.5
Gross energy (MJ/kg dry matter)	18.5
FERTILIZER	
Nitrogen (g/kg)[db]	27.04
Phosphorus (g/kg)[db]	8.9
Calcium (g/kg)[db]	1.3
BIOACTIVE COMPOUNDS	
Phenolics, free (mg/100g)	12.3±0.9
Phenolics, bound (mg/100g)	253.4±9.2
Proanthocyanidins (mg/100g)	212.0 ±0.3

Rye bran is rich in dietary fibre (DF) (Table 7.3), the non-digestible part of plant food, which is important for human well-being since many of the health effects are mediated by the microbial fermentation of DF carbohydrates in the large intestine. The DF content of the whole rye grain is 13-17 g /100 g and that of rye bran is 35-49 g /100g (Bach Knudsen et al., 1997; Graham et al., 1988; Nilsson et al., 1997a). Endosperm, on the other hand, is rich in starch. The main DF components of rye bran, as also in whole rye, are arabinoxylan, cellulose, β-glucan lignin, and also, according to the suggested new definition (Anonymous, 2001), fructan. In rye bran, the DF components form the rigid mainly insoluble structure of plant cell walls. Some of the polysaccharides are, however, also found as soluble components, and there is no sharp distinction between the soluble and insoluble fractions. Depending on the processing and extraction conditions, some of the "insoluble" DF complex can be extracted.

Table 7.3: Dietary fibre contents of rye and wheat (g/100 g).

DIETARY FIBRE CONTENT	REFERENCE
wheat: 12 g/100 g rye: 15 g/100 g	(Graham et al., 1988)
rye bran: 38 g/100 g rye flour: 8.4 g/100 g	(Nilsson et al., 1996)
whole-grain rye: 16 g/100 g rye bran: 41 g/100 g	(Nilsson et al., 1997a)
rye grain (7 varieties): 15-17 g/100 g	(Nilsson et al., 1997b)
rye: 17 g/100 g rye bran: 35 g/100 g	(Härkönen et al., 1997)
whole-grain rye 17 g/100 g rye bran: 49 g/100 g wheat: 14 g/100 g wheat bran: 45 g/100 g wheat flour: 3.5 g/100 g	(Bach Knudsen et al., 1997)
whole rye: 15 g/100 g pericarp/testa: 73 g/100 g aleurone: 28 g/100 g endosperm: 6.5 g/100 g	(Glitsø & Bach Knudsen, 1999)
rye grain (4 varieties): 13-16 g/100 g	(Nilsson et al., 2000)
rye whole meal: 19 g/100 g	(Boskov Hansen et al., 2002)

In the work of Karppinen the total content of non-digestible carbohydrates (DF + fructan) of processed rye-bran samples was as follows: 51 g/100 g for extruded rye bran, 42 g/100 g for xylanase-treated rye bran, and 47 g/100 g for the insoluble rye-bran residue (Table 7.3) (Karppinen, 2003). Fructan was clearly concentrated in the rye-bran extract; its content was 22 g/100 g and its recovery was as high as 64%. The starch content in the rye bran extract was only 6.5 g/100 g, while it was 20-24 g/100 g in the other rye-bran samples (Table 7.4).

Table 7.4: Components of the processed rye-bran samples (g/100 g dry weight) (Karppinen, 2003).

	RYE BRAN			
	Extruded	Extruded, Xylanase treated	Extract	Insoluble residue
Dietary fibre*	44	35	12	44
*Soluble dietary fibre**	4.5	2.9	12	1.5
*Insoluble dietary fibre**	39	32	0	43
Pentosan	20	20	16	20
β-Glucan	4.2	4.5	5.7	4.3
Fructan	7.1	6.7	22	3.0
Starch	20	20	6.5	24
Protein	16	16	14	17
Fat	4.4	5.3	2.6	6.4
Ash	6.5	6.4	13	5.2

*According to Asp et al. (Asp et al., 1983).

The highest content of plant lignans was in rye-bran extract (9 mg/100 g) and in the case of other substrates the content was 4-6 mg/100 g (Table 7.5). In all substrates, the main part of these plant lignans comprised syringaresinol (63-68% of the total lignans), of which, however, only a small part was convertible to enterodiol and enterolactone (Heinonen et al., 2001). The isolariciresinol content of rye-bran substrates was also high (12-19% of the total plant lignans), but has not been shown to be converted at all to enterodiol or enterolactone (Heinonen et al., 2001). The remainder of the plant lignans analysed in this study consisted of secoisolariciresinol, matairesinol, lariciresinol and pinoresinol, which are precursors of enterodiol/enterolactone. During the digestion, the pinoresinol content was decreased in all substrates. After digestion, the rye-bran extract contained plant lignans at 10 mg/100 g and the other samples at 3-5 mg/100 g.

Table 7.5: Plant lignan contents of the processed rye-bran samples, mg/100g dry weight (Karppinen, 2003).

	RYE BRAN			
	Extruded	Extruded, Xylanase treated	Extract	Insoluble residue
Secoisolariciresinol	0.13	0.15	0.32	0.13
Matairesinol	0.15	0.14	0.21	0.13
Lariciresinol	0.14	0.16	0.30	0.25
Pinoresinol	0.32	0.51	0.92	0.43
Isolariciresinol	0.84	1.16	1.12	0.68
Syringaresinol	3.02	3.87	6.17	2.75
Plant lignans, total	**4.6**	**6.0**	**9.0**	**4.4**

8. Rapeseed

Rapeseed (*Brassica napus*) is a bright yellow flowering member of the family Brassicaceae (mustard or cabbage family). The name derives from the Latin for turnip, *rapum* or *rapa*, and is first recorded in English at the end of the fourteenth century (Bassam, 2010). It is an annual plant which originated from the Mediterranean region. The plant germinates quickly, forming a deep growing taproot and a rosette of blue-green leaves from which emerge 7–10 lateral shoots. On the ends of the branched stems grow the gold-yellow flowered racemes. Each plant has approximately 120 long slender seed pods; 40 to 60 of these are found on the main shoot. Each seed pod contains 18–20 seeds (2000–3000 seeds per plant). The seeds are small, round and black. Based on its seed oil, rape belongs to the erucic acid group of oil plants. Of the total fatty acid content, about 6 per cent is saturated fatty acids and 94% is unsaturated fatty acids. Among the unsaturated fatty acids, 14% is oleic, 45% erucic, 14% linoleic and 10% linolenic. Low erucic acid and acid free cultivars (0–rape) and cultivars also low in glucosinolate have been developed in Europe and Canada because of health problems associated with the consumption of oils containing erucic acid. Cultivars with no erucic acid and low glucosinolate content have also been bred (00–rape).

Rapeseed has greatly improved its competitive position in the world, being actually a major crop in many countries (El Bassam, 2010). The seeds of this plant, with very high level of oil, are one of the principal components of the crop. They can be ground into nutritional meals used in animal fodder, or pressed for the oil, which can be used for human food or in the production of biodiesel (Bassam, 2010).

Rapeseed has traditionally been grown for the production of animal feed and vegetable oil for human consumption. In the last years, an increasing fraction of rapeseed oil has been used as raw material for biodiesel production. After seed harvesting, rapeseed straw, left behind on the fields, must be eliminated.

There are reports on the use of rapeseed residues as renewable energy source. Some reports deals with thermal methods; for example, Karaosmanoglu et al. used pyrolysis of the straw and stalk of the rapeseed plant for biofuel production (Karaosmanoğlu et al., 1999). Zabaniotou et al. reported on the integrated utilization of rapeseed suitable to Greek conditions for biodiesel production and parallel use of its solid residues for energy and second generation biofuels production via fast pyrolysis (Zabaniotou et al., 2008a). There are also some reports dealing with rapeseed straw as raw material for ethanol production. The use of sulphuric acid-catalyzed pre-treatment with rapeseed straw has been reported (Lu et al., 2009). Li et al. (2009) reported on rapeseed stover pre-treatment with phosphoric acid–acetone for ethanol production by means of simultaneous saccharification and fermentation (Li et al., 2009). Biogas or ethanol production has also been reported (Petersson et al., 2007).

Figure 8.1: Rapeseed straw (left photo) and rapeseed meal (right photo) (feedipedia, 2016)

8.1 Rapeseed straw

Rapeseed crop (*Brassica napus*) is an attractive feedstock for use in food and bioenergy production. However, rapeseed straw is abundant and inexpensive in European and Asian countries. Consumption of rapeseed oil as raw material for biodiesel production has shown a recent increase. After seed harvesting, rapeseed straw is useful as a resource for biofuels production. In general, rapeseed straw is composed of three main fractions: cellulose, hemicelluloses, and lignin. Cellulose and hemicellulose can be converted into fermentable sugars and produce a large amount of fuels and chemicals by fermentation and chemical processes (Ko et al., 2009; Lu et al., 2009).

Relatively few studies have reported on the use of rapeseed straw as a renewable energy source. Most of these are involved in treatment with thermal applications, like pyrolysis (Castro et al., 2011). Previously studied pretreatments of rapeseed straw include dilute acid pretreatment (Castro et al., 2011), hydrothermal pretreatment (Díaz et al., 2010), and H_2SO_4-catalyzed hydrothermal pretreatment (Lu et al., 2009). Hydrothermal pretreatment of rapeseed straw (Díaz et al., 2010) indicated that enzymatic hydrolysis yields near 100% based on the pretreated materials can be achieved at 210–220°C for 30–50 min, equivalent to near 70% of theoretical glucose yield. In addition, a milder pretreatment at 193°C for 27 min results in 65% of glucose available for fermentation. Castro et al. (Castro et al., 2011) reported that in dilute acid pretreatment of rapeseed straw, total conversion of cellulose from pretreated solids can be achieved at conditions of 200°C for 27 min and 0.4% free acid. Use of a sulfuric acid catalyst in pretreatment of rapeseed straw at 180°C has been reported, with a focus on pretreatment at high solid content (Lu et al., 2009).

The main physicochemical characteristics of rapeseed straw are summarized in Table 8.1.

Table 8.1: Summary of main physicochemical characteristics of rapeseed straw (Abreu & Bruno-Soares, 1998; Chen et al., 2010; ECN, 2016; feedipedia, 2016; Greenhalf et al., 2012; Huang et al., 2015; Kang et al., 2012; Karaosmanoğlu et al., 1999; Lu et al., 2009; Pińkowska & Wolak, 2013; Rasool et al., 1998; Sander, 1997; Vassilev et al., 2010; Zabaniotou et al., 2008a).

PHYSICOCHEMICAL PROPERTIES	AVERAGE	SD	MIN	MAX	N° Samples
ENERGY					
Higher Heating Value (HHV) (MJ/kg)	18.9	1.2	17.6	21.5	8
Lower Heating Value (LHV) (MJ/kg)	17.6	1.5	16.3	20.2	6
Fixed Carbon (%wt)^{db}	17.5	3.4	11.9	23.0	8
Volatile Matter (%wt)^{db}	75.6	3.8	67.6	79.2	8
Ash (%wt)^{db}	5.4	1.8	2.0	8.8	19
Moisture (% wt)^{am}	9.7	2.8	4.6	13.2	11
Carbon (%wt)^{db}	44.8	3.5	38.4	49.8	10
Oxygen (%wt)^{db}	43.0	6.3	33.3	52.1	9
Hydrogen (%wt)^{db}	5.1	1.2	2.2	6.1	10
Nitrogen (%wt)^{db}	0.9	0.5	0.1	1.8	13
Sulfur (%wt)^{db}	0.3	0.2	0.0	0.7	12
FODDER					
Dry matter (%wt)^{am}	90.3	2.8	86.8	95.4	11
Crude protein (%wt)^{db}	5.4	2.9	0.5	11.5	13
Crude fiber (%wt)^{db}	46.7	3.6	44.1	49.2	2
Neutral Detergent Fiber (NDF)	84.1	5.9	74.6	94.8	10

PHYSICOCHEMICAL PROPERTIES	AVERAGE	SD	MIN	MAX	N° Samples
(%wt)[db]					
Acid Detergent Fiber (ADF) (%wt)[db]	42.2	6.6	36.1	52.7	9
Lignin (%wt)[db]	21.1	4.5	18.0	33.3	10
Ether extract (%wt)[db]	2.1	0.2	1.9	2.2	2
Ash (%wt)[db]	5.6	2.1	2.0	9.7	18
Gross energy (MJ/Kg)	18.9	1.2	17.6	21.5	8
FERTILIZER					
Nitrogen (g/kg)[db]	8.6	4.6	0.8	18.4	13
Phosphorus (g/kg)[db]	0.9	0.5	0.2	2.0	11
Potassium (g/kg)[db]	9.7	8.0	1.0	26.8	10
Calcium (g/kg)[db]	12.6	4.1	6.0	21.1	11
Magnesium (g/kg)[db]	1.3	0.8	0.1	2.8	11
Sulfur (g/kg)[db]	2.5	2.0	0.4	6.6	12

8.2 Rapeseed meal

Rapeseed meal - called canola meal in North America, Australia and other countries - is the by-product of the extraction of oil from rapeseeds (*Brassica napus L., Brassica rapa L. and Brassica juncea L.* and their crosses). It is a protein-rich ingredient that is widely used to feed all classes of livestock. Rapeseed meal is the second oil meal ingredient produced in the world after soybean meal (feedipedia, 2016). Rapeseed oil used to have a poor reputation due to the presence of erucic acid, which has a bitter taste and was later found to cause health problems. The use of rapeseed meal as an animal feed was also limited by the presence of glucosinolates, which are antinutritional factors detrimental to animal performance. The term “canola” presently used in Canada is being adopted in the United Kingdom, Australia, and the United States to describe the rapeseed of Brassica napus species yielding oil of less than 2% erucic acid and meal of less than 30 µmol/g of aliphatic glucosinolates (Khajali & Slominski, 2012).

Association of erucic acid consumption with the myocardial lesions in laboratory animals committed Canada and other countries to shift their rapeseed production to low-erucic acid varieties. In Canada, this change was completed in the late 1970s. The second major quality improvement came in the mid 1970s as canola breeders lowered the content of undesirable glucosinolates (GLS) in the seed. A complete changeover to canola varieties was achieved in 1984, where even the high-erucic rapeseed contracted for industrial use was of “canola” characteristics with regard to GLS content. Although canola meal (CM) is commonly used in poultry diets as an economically viable alternative to soybean meal (SBM), its use is still restricted to less than full replacement of SBM due to the low available energy content and the presence of antinutrititional factors (Khajali & Slominski, 2012).

The main components of canola meal (prepress solvent extracted) include protein, carbohydrates (that is, simple sugars, sucrose, oligosaccharides, starch), dietary fiber (that is, nonstarch polysaccharides, lignin with associated polyphenols, glycoproteins), fat, and ash. Although lower in protein, CM compares favorably with SBM with regard to amino acid content. Because CM contains more methionine and cysteine but less lysine, both meals tend to complement each other when used together in rations for livestock and poultry. Also, the fat content is higher than that of SBM due to the presence of gums (that is, phospholipids, glycolipids, triglycerides, and free fatty acids) which are often added back to the meal after oil refining. Canola meal is a good source of available calcium, iron, manganese, selenium, and many of the B vitamins (canola, 2015). Although high in phytate, CM

is also one of the richest sources of nonphytate (available) phosphorus (that is, 0.38% of nonphytate P vs. 0.28, 0.23, 0.09, 0.26, 0.07, and 0.13% for SBM, cottonseed meal, wheat, wheat bran, corn, and barley, respectively) (Khajali & Slominski, 2012).

The main physicochemical characteristics of rapeseed meal are summarized in Table 8.2.

Table 8.2: Summary of main physicochemical characteristics of rapeseed meal (Ballester et al., 1970; Bayley & Hill, 1975; Bell & Keith, 1991; Bunting, 1980; canola, 2015; Çulcuoğlu et al., 2002; ECN, 2016; Eriksson et al., 2009; feedipedia, 2016; Haykiri-Acma et al., 2006; Khajali & Slominski, 2012; Kracht et al., 1999; Krička et al., 2015; Mailer et al., 2008; Özçimen & Karaosmanoğlu, 2004; Piotrowska et al., 2010).

PHYSICOCHEMICAL PROPERTIES	AVERAGE	SD	MIN	MAX	N° Samples
ENERGY					
Higher Heating Value (HHV) (MJ/kg)	20.5	2.7	18.1	24.5	8
Lower Heating Value (LHV) (MJ/kg)	19.5	3.1	16.5	23.4	6
Fixed Carbon (%wt)[db]	16.8	6.0	9.0	25.8	5
Volatile Matter (%wt)[db]	72.2	7.8	67.0	86.0	5
Ash (%wt)[db]	6.6	0.9	5.0	7.9	13
Moisture (% wt)[am]	8.7	2.2	5.4	12.6	13
Carbon (%wt)[db]	47.1	4.1	41.1	53.5	7
Oxygen (%wt)[db]	36.5	6.5	28.3	47.8	7
Hydrogen (%wt)[db]	6.9	0.7	6.0	7.5	7
Nitrogen (%wt)[db]	5.8	0.9	3.8	7.0	16
Sulfur (%wt)[db]	0.6	0.3	0.2	0.9	6
FODDER					
Dry matter (%wt)[am]	91.3	2.2	87.4	94.6	13
Crude protein (%wt)[db]	36.4	5.5	23.6	43.7	16
Crude fiber (%wt)[db]	12.8	1.3	10.7	15.2	13
Neutral Detergent Fiber (NDF) (%wt)[db]	32.5	3.1	28.6	37.1	6
Acid Detergent Fiber (ADF) (%wt)[db]	19.0	1.3	17.5	20.9	6
Lignin (%wt)[db]	7.2	2.2	5.7	8.8	2
Ether extract (%wt)[db]	3.5	1.5	1.8	7.1	10
Ash (%wt)[db]	6.7	1.1	4.6	8.2	16
Gross energy (MJ/Kg)	20.5	2.7	18.1	24.5	8
FERTILIZER					
Nitrogen (g/kg)[db]	58.3	8.8	37.8	69.9	16
Phosphorus (g/kg)[db]	11.6	2.4	9.5	17.4	8
Potassium (g/kg)[db]	13.3	0.9	12.3	14.1	3
Calcium (g/kg)[db]	6.9	1.4	5.1	10.0	8
Magnesium (g/kg)[db]	5.2	0.6	4.5	6.2	3
Sulfur (g/kg)[db]	6.5	2.5	1.5	9.4	8
RECOVERABLE COMPOUNDS					
Sinapine (g/kg)[db]	13.6	1.4	11.3	14.8	5

8.3 Rapeseed AWCB bioactive compounds patent and literature review

There is only a small number of patents using rapeseed by-products for the recovery of added-value products and mainly protein-containing feedstuff and materials. These patents are presented in the following tables.

Patent No	DE 3540179 A1, DE3540179C2
Issue Date	21/05/1987
Title	Process for producing protein-containing feedstuff from rapeseed meal
Description/Abstract	A process is described for producing protein-containing feedstuff from rapeseed meal, in which the rapeseed meal is first fermented by a yeast in an aqueous nutrient solution with supply of air at 20 to 40 DEG C, then the solid is separated off from the liquid phase and finally the solid is processed to form the feedstuff. In the process it is provided that 100 to 200 kg of molasses/t of dry rapeseed meal is added to the nutrient solution and the rapeseed meal is fermented by a yeast of the genus Saccharomyces, the mixture to be fermented of rapeseed meal, nutrient solution, molasses and yeast being circulated at least once by a homogenization machine and the air and the substrate composed of rapeseed meal, nutrient solution and molasses being introduced into the turbulence field of the homogenization machine
Type of AWCB	Rapeseed meal
Recovered high added compound	Protein-containing feedstuff

Patent No	US 4889921 A, CA1311877C, DE3869183D1, EP0289183A2, EP0289183A3, EP0289183B1
Issue Date	26/12/1989
Title	Production of rapeseed protein materials
Description/Abstract	A process of treating meal containing vegetable proteins is disclosed. This process includes the step of extracting the metal with a suitable aqueous solvent in which the vegetable proteins are soluble to obtain an extraction solution. The solubility of the dissolved protein in the extraction solution is then adjusted to precipitate at least some of the protein and therefore obtain a precipitated protein fraction and an unprecipitated protein fraction in solution. The precipitated protein fraction is then separated from the protein fraction in solution, and the unprecipitated protein fraction is separated from the undesirable components in the solution by membrane processing. Each of the protein fractions is then suitably dried to recover the proteins.
Type of AWCB	Rapeseed meal
Recovered high added compound	Protein materials

Patent No	US 4244973 A, CA1102172A, CA1102172A1, DE2962386D1, EP0006654A2, EP0006654A3, EP0006654B1
Issue Date	13/01/1981
Title	Process for producing a detoxified rapeseed protein concentrate
Description/Abstract	A process for the detoxification of rapeseed which involves (a) autolyzing an aqueous mixture of rapeseed meal in the presence of myrosinase and ascorbic acid to achieve hydrolysis of glucosinolates present in the meal and (b) extracting the toxic products resulting from the hydrolysis of said glucosinolates using a polar, organic solvent. The detoxified rapeseed protein concentrate obtained according to the invention is a useful ingredient in foodstuffs for both human and animal consumption.
Type of AWCB	Rapeseed meal
Recovered high added compound	Detoxified rapeseed protein concentrate

9. Rice

Rice (*Oryza sativa*) is one of the most important cereal crops in the world, providing the bulk of daily calories for many companion animals and humans. Rice originates from Asia, where it has been cultivated since 6500 BC, and is now naturalized in most tropical and subtropical regions. Rice grows from 53°N in China to 35°S in Australia. The optimal growing conditions are: 20-30°C average day-temperatures with night temperature over 15°C; fertile, heavy soils; 6.5-7 pH. Most varieties ("swamp rice", "lowland rice") must be planted in stagnant water and require 200 mm rainfall/month or the equivalent amount from irrigation, whereas others ("mountain rice" or "upland rice") require less irrigation and 750 mm rainfall over a 3-4 months period with no desiccation (feedipedia, 2016).

Diverse rice varieties, as characterised by genetics, landraces, and morphology, are cultivated around the world (Figure 9.1). Although rice varieties have been extensively studied for distinct agronomic traits such as yield, many have not yet been thoroughly examined for differences in nutrient composition and bioavailability.

Figure 9.1: Photographic images depicting rice varieties with regard to visual differences in grain size and pigment during each stage of processing (feedipedia, 2016).

Manufacturing and by-products

After threshing, the rough rice is transported to mills for processing into white rice (polished rice) through a series of operations that free it from the hull, germ and bran. In many countries the processing of rice for local use is still carried out in one-stage mills. The by-product of this simplest form of processing is a mixture of hulls and bran that seldom reaches the market as it is usually returned to the rice grower.

In large-scale mills the rough rice undergoes several processes: cleaning, parboiling, hulling, pearling, polishing and grading. The cleaning process removes all extraneous matter, such as ***"dead" grains***, ***stones*** and ***stalks***. For certain varieties it is necessary to parboil (steep) the

cleaned rice in hot water for a time to facilitate removal of the hull and improve the keeping quality of the grain. This process also improves the thiamine content of the grain.

There are several methods of removing the hull. After hulling, the germ and outer bran are removed in a set of huller reels and pearling cones in which the waxy cuticle is scoured off by the friction between the high-speed abrasive cone and its casing. The resultant bran meal is propelled through meshes of wirecloth and collected. The milling space between the cone and the casing is adjustable so that the milling rate can be varied by raising or lowering the cone. In most mills the rice passes through several cones, each with a higher milling rate. The bran from the different settings is usually mixed into one product. For a finer appearance, rice from the pearler is passed through polishers. These machines are similar to pearling cones except that they contain a drum covered with strops of hide rather than an abrasive cone. In this process a part of the starchy kernel (endosperm) is removed. If inner bran layers are included, the product is called fine bran, or pollard. The mixture of whole and broken rice from the polishers is separated in sieves and then remixed in proportions corresponding to the standard at which the rice is to be sold.

The percentage of by-products depends on milling rate, type of rice and other factors. The following figures give an approximate idea of the proportions: **hulls, 20%; bran, 10%; polishings, 3%; broken rice, 1-17%; polished rice, 50-66%.** Rice pollards are a mixture of bran and polishings. Rice mill feed, a mixture of all the by-products obtained in the milling of rice, contains approximately 60% hulls; 35% bran and 5% polishings. The offal obtained from one-stage mills is of similar composition and is often erroneously called "rice bran". Production of rice mill feed in multi-stage mills is somewhat cheaper than separate production of the ingredients.

More than 600 million metric tons (approx. 661 million tons) of paddy rice is milled each year worldwide, which yields approximately 382 million metric tons (421 million tons) of brown rice that is further processed to yield approximately 337 million metric tons (372 million tons) of white rice for consumption by humans (Kahlon, 2009). This results in global production of approximately 60 to 68 million metric tons (66 to 74 million tons) of rice bran available for use in animal feed, pet food, or human food or that is discarded as waste (Figure 9.2).

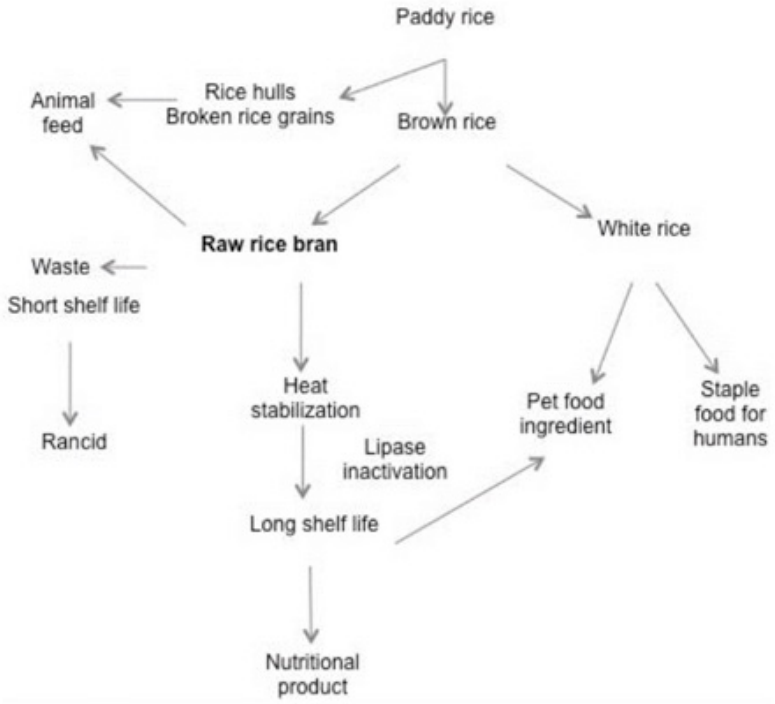

Figure 9.2: Schematic depiction of rice production and processing for bran (Ryan, 2011).

9.1 Rice straw

Rice straw (RS) (or paddy straw) is the vegetative part of the rice plant (*Oryza sativa L.*), cut at grain harvest or after. It may be burned and left on the field before the next ploughing, ploughed down as a soil improver or used as a feed for livestock (Kadam et al., 2000). Rice straw is a major forage in rice-producing areas.

The chemical analysis of raw and treated RS is summarized in Table 9.1. RS contains less lignin than other straws but has a higher silica content. The leaves contain more silica than the stems (Van Soest, 2006). It is, therefore, recommended to cut RS as short as possible to increase the proportion of stems (Göhl, 1982a). Silicas are cell-wall bound or soluble. They are excreted in the urine and some calculi may occur but this does not appear to be a serious problem. RS contains high levels of oxalates (1-2% dry matter), which are known to decrease the Ca concentration, making Ca supplementation necessary (Jackson, 1979).

The quality of RS depends on many factors: variety, time between harvest and storage, N fertilization, plant maturity (lignin content increases with maturity), plant health and weather conditions (Drake et al., 2002). RS is a good source of energy, but is low in protein (2-7%) and its high silica content results in a low digestibility. It is considered as a low quality and variable roughage. Minerals (particularly sulphur) can be limiting factors (Doyle et al., 1986). Other limitations include:

- high NDF content resulting in poor dry matter intakes and low fat-corrected milk yields (Kanjanapruthipong & Thaboot, 2006);
- low concentrations of P, Cu, Zn, Ca and NaCl that do not meet animal requirements (Gowda & Prasad, 2005);
- low energy content compared to maize silage and lower palatability, resulting in poorer N utilization (Odai et al., 2002).

Table 9.1: Summary of main physicochemical characteristics of rice straw (ECN, 2016; feedipedia, 2016).

PARAMETER	VALUE (AVERAGE)				
	rice straw	rice straw urea-treated	rice straw ammonia - treated	rice straw NaOH-treated	Other
ENERGY					
Higher Heating Value (HHV) (MJ/kg)	-	-	-	-	15.09-15.95 (15.5)
Lower Heating Value (LHV) (MJ/kg)	-	-	-	-	13.95-14.92 (14.43)
Fixed Carbon (%wt)[am]	-	-	-	-	14.6
Volatile Matter (%wt)[am]	-	-	-	-	60.28
Ash (%wt)[am]	-	-	-	-	16.47-17.19 (16.83)
Moisture (% wt)[am]	7.2	6.0	29.1	30.6	7.93-9.0 (8.47)
Carbon (%wt)[db]	-	-	-	-	38.24-38.91 (38.58)
Oxygen (%wt)[db]	-	-	-	-	35.31-36.26 (35.79)
Hydrogen (%wt)[db]	-	-	-	-	4.74-5.20 (4.97)
Nitrogen (%wt)[db]	-	-	-	-	0.87-1.37 (1.12)
Sulfur (%wt)[db]	-	-	-	-	0.11-0.18 (0.145)
FODDER					
Dry matter (%wt)[am]	92.8	94,0	70.9	69.4	-
Crude protein (%wt)[db]	4.2	7.9	11,0	2.9	-
Crude fibre (%wt)[db]	35.1	34.2	-	36.2	39.0
Neutral Detergent Fiber (NDF) (%wt)[db]	69.1	68.6	67.5	63.4	67.1
Acid Detergent Fiber (ADF) (%wt)[db]	42.4	42.3	-	37.7	-
Lignin (%wt)[db]	4.8	5.2	-	-	12.5
Ether extract (%wt)[db]	1.4	1.3	-	0.9	-
Ash (%wt)[db]	18.1	19.3	15.2	19,0	18.10-19.09 (18.6)
Gross energy (%wt)[db]	15.5	16,0	-	15.2	-

PARAMETER	VALUE (AVERAGE)				
FERTILIZER					
Nitrogen (g/kg)[db]	6.72	12.64	17.6	4.64	8.7-13.7 (11.2)
Phosphorus (g/kg)[db]	0.9	1.5	-	0.4	1.148-1.165 (1.2)
Potassium (g/kg)[db]	18.0	17.5	-	-	19.06-21.39 (20.2)
Calcium (g/kg)[db]	2.9	3.2	-	2.1	2.59-4.01 (3.3)
Magnesium (g/kg)[db]	1.9	1.7	-	-	1.97-2.07 (2.0)
Sulfur (g/kg)[db]	-	-	-	-	0.534-0.926 (0.7)
Silica (g/kg)[db]	-	-	-	-	65.08-76.07 (68.8)
Manganese (mg/kg)db	454	387	-	-	-
Zinc (mg/kg)[db]	34	37	-	-	-
Copper (mg/kg)[db]	6	3	-	-	-
Iron (mg/kg)[db]	335	-	-	-	801.78-1110.9 (956.3)

9.2 Rice bran

Rice bran (RB) is the most important rice by-product. It is a nutrient-rich by-product that has been primarily used as a low-cost feed for livestock and a fiber source in pet food. RB is primarily used as a source of fiber and fat and may comprise up to 40% of dietary intake for pigs, cows, poultry, and dogs (Bird et al., 2000; Sayre R.N. et al., 1987; Spears J.K. et al., 2004).

The bran fraction contains 14-18% oil. The oil has a marked softening effect on body fat and on the butterfat in milk. With attention to the oil content, RB is a valuable feed for all classes of livestock. RB that has not been defatted is a useful binder in mixed feeds. Defatted RB can be used at higher levels than ordinary RB. RB is often adulterated with rice hulls, as it should have a crude fibre content of 10-15% (Göhl, 1982a).

The chemical analysis of raw and defatted RB for varying fibre content is summarized in Table 10. RB is a good source of B vitamins and is fairly palatable to farm animals. It should be noted that rice milling by-products do not follow strict naming conventions. Many products called "rice brans" are mixtures of by-products obtained at different stages of the milling process, resulting in large variations in chemical composition.

When compared with the nutrient content of other cereal grains, RB provides a nutritious mixture of protein, lipids, energy, and minerals (Nystrom L. et al., 2005; Roth-Maier D.A. et al., 2002). However, a heat-stabilization step is required to prevent RB from spoiling. If the RB is not heat stabilized, a large fraction of it will be lost to oxidative rancidity.

Emerging research is devoted to bran extraction and enrichment for chemical constituents (e.g., antioxidants and sterols) other than fat and fiber content (Renuka Devi & C., 2007). Because the rice genome has been sequenced (Dabestani et al., 2017), the extent to which genetically diverse rice cultivars can be evaluated for differences in bran chemical and nutrient composition (and thus their subsequent health implications) has expanded and may be used for integration into rice breeding programs (Heuberger A.L. et al., 2010). Studies of dietary RB intake in animals are limited and have not included an understanding of how genetic diversity might impact the nutritional value. Crop varietal differences in bioactive compounds from staple foods and the opportunity to improve crops for animal and human health have been recently described as biomedical agriculture (Thompson & Thompson, 2009). This emerging concept of assessing differences in nutrient content of rice varieties and their subsequent effects on health quality can also be applied to other food crops (eg, corn, wheat, and potatoes) (Morris C.E. & Sands, 2006; Sands D.C. et al., 2009).

Rice bran is distinct from other cereal grains in its content of tocotrienols-tocopherols, γ-oryzanol, and β-sitosterol. This is important because there is an emerging body of evidence that indicates these constituents may contribute to decreased concentrations of total plasma cholesterol, triglycerides, and low-density lipoproteins as well as increased concentrations of high-density lipoproteins (Ausman et al., 2005). RB also contains soluble dietary fibers (e.g., β-glucan, pectin, and gum) and ferulic acid from nonlignified cell walls. The United States Department of Agriculture (USDA) nutrient database values for crude rice bran are routinely used when formulating diets for animals (Schmidt & Ahring, 1997) however, care should be exercised because these values may not account for differences across rice varieties (Prakash, 1996).

The unique combinations of lipids (e.g., γ-oryzanol and tocopherols) and ratios of minerals (e.g., calcium and phosphorus) found in RB have led companies to produce stabilized RB and RB oil nutritional products that are marketed to enhance health of humans and other animals. Animal health products may include stabilized rice bran or rice bran oil that are

advertised to enhance energy and muscle condition or improve skin, coat, and digestion for horses. Health claims of RB nutritional supplements for humans are largely related to reports of lipid-lowering effects and cardiovascular benefits (Kuriyan et al., 2005; Most et al., 2005). Continued investigation of the effects of RB in animal species is warranted to substantiate the long-standing historical use of RB for animal health as well as the more recent claims for human health and disease prevention.

Table 9.2: Summary of main physicochemical characteristics of raw and defatted rice bran of varying fibre content (ECN, 2016; feedipedia, 2016).

PARAMETER	VALUE (AVERAGE)							
	fibre <4%	fibre 4-11%	fibre 11-20%	fibre >20%	defatted fibre <11%	defatted fibre 11-20%	defatted fibre >20%	Other
ENERGY								
Higher Heating Value (HHV) (MJ/kg)	-	-	-	-	-	-	-	15.29 [db]
Lower Heating Value (LHV) (MJ/kg)	-	-	-	-	-	-	-	14.17 [db]
Fixed Carbon (%wt)[am]	-	-	-	-	-	-	-	19.53
Volatile Matter (%wt)[am]	-	-	-	-	-	-	-	61.83 (organic)
Moisture (% wt)[am]	10.0	9.9	9.8	8.3	10.3	11.0	8.4	-
Carbon (%wt)[db]	-	-	-	-	-	-	-	38.92
Oxygen (%wt)[db]	-	-	-	-	-	-	-	36.77
Hydrogen (%wt)[db]	-	-	-	-	-	-	-	5.12
Nitrogen (%wt)[db]	-	-	-	-	-	-	-	0.55
Sulfur (%wt)[db]	-	-	-	-	-	-	-	0.0
FODDER								
Dry matter (%wt)[am]	90.0	90.1	90.2	91.7	89.7	89.0	91.6	-
Crude protein (%wt)[db]	14.2	14.8	12.7	8.8	16.0	17.1	6.7	-
Crude fibre (%wt)[db]	4.1	8.6	16.3	28.3	9.8	14.8	30.8	-
Neutral Detergent Fiber (NDF) (%wt)[db]	12.4	25.2	34.4	48.7	26.6	32.6	51.7	54.9
Acid Detergent Fiber (ADF) (%wt)[db]	3.2	11.2	19.6	32.7	12.5	18.0	35.4	25.2
Lignin (%wt)[db]	1.2	4.1	6.8	11.0	4.5	6.3	11.8	10.0
Ether extract (%wt)[db]	13.2	17.2	14.4	10.3	4.1	1.0	4.8	-
Ash (%wt)[db]	6.9	9.4	12.4	13.6	12.3	14.2	19.1	18.64-19.40
Starch (%wt)[db]	42.0	28.8	22.4	14.7	32.2	26.4	14.3	-
Total sugars (%wt)[db]	3.8	2.8	2.8	1.0	2.7	3.0	1.6	-

PARAMETER	VALUE (AVERAGE)							
Gross energy (%wt)[db]	20.5	21.2	20.2	19.3	17.9	17.1	17.0	-
Lipids (%wt)[db]	-	-	-	-	-	-	-	-
FERTILIZER								
Nitrogen (g/kg)[db]	22.72	23.68	20.32	14.08	25.6	27.36	10.72	-
Phosphorus (g/kg)[db]	13.9	17.0	13.8	7.4	12.1	19.2	4.9	-
Potassium (g/kg)[db]	10.8	14.9	12.3	6.3	8.5	7.4	7.3	-
Calcium (g/kg)[db]	0.6	0.7	0.7	4.7	0.8	2.5	1.0	-
Magnesium (g/kg)[db]	6.1	7.8	6.5	2.1	4.6	4.4	2.4	-
Sulfur (g/kg)[db]	-	-	-	-	-	-	-	-
Manganese (mg/kg)db	-	211	138	-	221	164	157	-
Zinc (mg/kg)[db]	-	63	55	-	80	80	34	-
Copper (mg/kg)[db]	-	8	9	-	14	13	7.0	-
Iron (mg/kg)[db]	-	106	-	-	297	2556	443	-
BIOACTIVE COMPOUNDS								
Protein (%wt)[db]	-	-	-	-	-	-	-	6.4
<u>Aminoacids</u>								
Alanine (% protein)	5.9	6.4	5.8	-	6.0	5.7	6.2	-
Arginine (% protein)	7.7	6.6	7.2	-	7.0	6.2	7.4	-
Aspartic acid (% protein)	7.9	9	9.3	-	8.7	8.8	8.1	-
Cystine (% protein)	1.1	1.2	1.7	-	1.7	1.7	1.2	-
Glutamic acid (% protein)	13.5	13	12.7	-	15.5	12.6	12.7	-
Glycine (% protein)	4.9	5.3	5.2	-	5.1	5.0	5.4	-
Histidine (% protein)	2.6	2.6	2.4	-	2.5	2.3	2.4	-
Isoleucine (% protein)	5.8	5.9	5.3	-	4.8	4.2	6.7	-
Leucine (% protein)	6.7	6.7	7	-	7.2	7.0	7.5	-
Lysine (% protein)	4.5	4.7	4.4	-	4.4	3.9	4.6	-
Methionine (% protein)	2.3	2.2	1.9	-	2.4	1.9	2.1	-
Phenylalanine (% protein)	4.6	4.4	4.4	-	4.9	4.7	4.8	-
Proline (% protein)	4.7	5.3	4.6	-	5.1	5.6	6.1	-
Serine (% protein)	4.3	4.6	4	-	4.8	4.5	4.3	-

PARAMETER	VALUE (AVERAGE)							
Threonine (% protein)	3.3	3.8	3.7	-	3.6	3.9	3.6	-
Tryptophan (% protein)	2.0	1.8	2.2	-	1.9	2.1	3.1	-
Tyrosine (% protein)	4.1	3.7	3.4	-	4.6	3.2	3.8	-
Valine (% protein)	5.4	5.5	5.4	-	5.7	5.3	6.2	-

am: as measured; db: dry base

Bioactive compounds in RB

Bioactive food components in rice bran may include, but are not limited to, γ-oryzanol, tocopherols, tocotrienols, polyphenols (ferulic acid and α-lipoic acid), phytosterols (β-sitosterol, campesterol, and stigmasterol), and carotenoids (α-carotene, β-carotene, lycopene, lutein, and zeazanthin). Rice bran also contains essential amino acids (tryptophan, histidine, methionine, cysteine, and arginine) and micronutrients (e.g., magnesium, calcium, phosphorous, manganese, and 9 B-vitamins), all of which may work together for health promotion (Ryan, 2011). Selected compounds from rice bran have been investigated for prevention and control of chronic disease via multiple mechanisms (Table 9.3).

Table 9.3: Selected bioactive compounds in rice bran evaluated for their properties with regard to prevention of chronic disease (Ryan, 2011).

RICE BRAN COMPOUND	DISEASE PREVENTION ACTIVITY
Ferulic acid	Antioxidant, chemopreventive, anti-inflammatory, and lipid-lowering effects
g-Oryzanol	Antioxidant, chemopreventive, anti-inflammatory, and lipid-lowering effects
Inositol hexaphosphate	Inositol hexaphosphate
Campesterol	Antiangiogenic
b-Sitosterol	Blocks cholesterol
Linoleic acid	Anti-inflammatory
a-Tocopherol	Inhibits lipid peroxidation and intracellular signaling
Tocotrienol	Inhibits lipid peroxidation and intracellular signaling
Salicylic acid	Anti-inflammatory
Caffeic acid	Gastrointestinal microbe interactions
Coumaric acid	Antimutagenic, inhibits the cell cycle, antioxidant, and chemopreventive
Tricin	Antimutagenic, inhibits the cell cycle, antioxidant, and chemopreventive

Phytochemical teamwork

RB is a rich source of phytochemicals that may be working both synergistically and in parallel with each other to promote health and fight disease (Boateng et al., 2009). RB is much richer in phytonutrients and antioxidants than are corn, wheat, or oat bran (Kahlon T.S. et al., 1998; Roth-Maier D.A. et al., 2002). Variation has been detected in the amounts and types of phytochemicals in RB with respect to cultivars, growing conditions, bran separation, and kernel thickness (Liu K. & Gu, 2009; Schramm R. et al., 2007). RB fractionation of various cultivars has revealed that both the inner and outer portion of the bran layer contains phenols with anticancer properties; the outer portion contains the highest concentration. Another recent study revealed that significant phytochemical diversity was detected among a set of rice varieties (Heuberger A.L. et al., 2010). This analysis revealed a link between genetic regulation of differences in phenolic and vitamin E contents of cooked brown rice and suggests that genetic variation can control global metabolite diversity.

More information on how the genetic diversity among cultivated rice varieties influences health and nutritional quality of the bran is needed to enhance the value of rice bran as a functional food for promoting health in humans and other animals. Comprehensive data, ranging from gene expression to metabolites that are currently available for rice cultivars, can be used for exploration of health quality and disease prevention traits (Fitzgerald M.A. et al., 2009; Yamakawa H. & Hakata, 2010).

9.3 Rice hulls

Rice hulls (RH) are the by-product of rice dehulling. They are traditionally used as a fuel or silica rich cementitious material (Romano et al., 2011; Williams, 2005). They are also used in some countries for poultry litter that can later be fed to ruminants (feedipedia, 2016). RH can be used in animal feeding in the following ways:

- As raw rice hulls. Low-quality roughages like ground RH can be included in small amounts (up to 15%) in high-concentrate diets for feedlot cattle to help furnish bulk, stimulate appetite and decrease incidence of liver abscesses. In areas with a shortage of roughage, ground RH can be used in place of straw or advantageously as a partial replacement for it. The addition of ground RH has been found in some cases to increase the feed intake.
- As ammoniated rice hulls. A process developed for making livestock feed from hulls includes the addition of monocalcium phosphate, removal of silica, ammoniation under pressure and toasting. Ammoniated RH have been used in proportions of up to 40% of the total ration for sheep, without digestive or mastication problems.
- Together with bran and polishings.

The chemical analysis of WS is summarized in Table 9.4. Due to the high silicon content present rice husks have not yet been exploited in the food and feed industry. In addition, the endogenous phenolic compounds though in significant amounts, are bound to cell walls via linking with polysaccharides, lignin and possibly with silicon and consequently are not easily extractable under mild conditions(Hatfield & Marita, 2010; Inanaga et al., 1995). Drastic ones become, therefore, unavoidable (Butsat & Siriamornpun, 2010; Lee et al., 2003). Numerous publications on uses of rice hulls attest to the many attempts to solve the problem of disposing of this by-product.

Table 9.4: Summary of main physicochemical characteristics of rice hulls (ECN, 2016; feedipedia, 2016; Nenadis et al., 2013).

PARAMETER	VALUE (AVERAGE)
ENERGY	
Higher Heating Value (HHV) (MJ/kg)	12.25-14.11 (13.18)
Lower Heating Value (LHV) (MJ/kg)	11.10-12.92 (12.01)
Fixed Carbon (%wt)[am]	14.45-34.08 (24.62)
Volatile Matter (%wt)[am]	35.70-56.57 (46.13)
Ash (%wt)[am]	18.04-21.50 (19.77)
Moisture (% wt)[am]	8.0-10.94 (9.01)
Carbon (%wt)[db]	37.86-38.86 (38.52)
Oxygen (%wt)[db]	33.49-37.15 (35.37)
Hydrogen (%wt)[db]	4.75-4.86 (4.79)
Nitrogen (%wt)[db]	0.23-0.52 (0.39)
Sulfur (%wt)[db]	0.05-0.31 (0.14)
FODDER	
Dry matter (%wt)[am]	91.9
Crude protein (%wt)[db]	3.7
Crude fibre (%wt)[db]	42.6
Neutral Detergent Fiber (NDF) (%wt)[db]	67.8-83.6 (75.7)
Acid Detergent Fiber (ADF) (%wt)[db]	51.7-52.7 (52.2)
Lignin (%wt)[db]	14.2-35.9 (25.05)
Ether extract (%wt)[db]	1.5
Ash (%wt)[db]	17.5-23.37 (20.52)
Starch (%wt)[db]	5.3
Gross energy (%wt)[db]	16.3

PARAMETER	VALUE (AVERAGE)
FERTILIZER	
Nitrogen (g/kg)[db]	2.3-5.92 (4.47)
Phosphorus (g/kg)[db]	0.38-1.1 (0.74)
Potassium (g/kg)[db]	2.33-6.24 (4.19)
Calcium (g/kg)[db]	0.33-4.64 (1.96)
Magnesium (g/kg)[db]	0.01-1.0 (0.43)
Sulfur (g/kg)[db]	0.58-3.1 (1.84)
Silica (g/kg)[db]	86.5-104.3 (95.4)
Manganese (mg/kg)[db]	442
Zinc (mg/kg)[db]	43
Copper (mg/kg)[db]	2
Iron (mg/kg)[db]	56.0-198.5 (139.4)
BIOACTIVE COMPOUNDS	
Total Polar Phenol (TPP), rice variety Gladio (mgGAE/kg dry hulls)	27898 ± 803
Total Polar Phenol (TPP), rice quality Carolina (mgGAE/kg dry hulls)	25487 ± 1038
Total Polar Phenol (TPP), rice quality Creso (mgGAE/kg dry hulls)	24155 ± 797
Total Polar Phenol (TPP), rice quality Scirocco (mgGAE/kg dry hulls)	19662 ± 334
p-Coumaric acid (mg/kg dry hulls), rice variety Gladio	6367 ± 146
p-Coumaric acid (mg/kg dry hulls), rice variety Carolina	5692 ± 308
p-Coumaric acid (mg/kg dry hulls), rice variety Creso	5565 ± 109
p-Coumaric acid (mg/kg dry hulls), rice variety Scirocco	4879 ± 122
ferulic acid (mg/kg dry hulls), rice variety Gladio	2037 ± 110
ferulic acid (mg/kg dry hulls), rice variety Carolina	1752 ± 76
ferulic acid (mg/kg dry hulls), rice variety Creso	1771 ± 103
ferulic acid (mg/kg dry hulls), rice variety Scirocco	1510 ± 86

The values of bioactive compounds in Table 9.4, indicate that rice hulls, regardless of the tested variety (mean value 24,300 mg GAE/kg dry hulls), contain an amount of phenols that makes such a material to deserve further exploitation by the food industry. This becomes evident if the values are compared with literature ones on the TPP content (mg GAE/kg plant material on dry weight basis) of some agri-food solid wastes, namely carobs (13,830 mg/kg), potato peel (9770 mg/kg) and white grape peels (9700 mg/kg) (Makris et al., 2007). Other sources that may contain significantly higher amounts of phenolics (e.g. grape seeds ~110,000 mg/kg; grape pomace ~51,000 mg/kg; olive leaves 40,270 mg/kg) present the disadvantage of high moisture content (45-72 g/100 g), which raises the cost of processing.

The levels of p-coumaric and ferulic acids given in Table 9.4 are relatively high when compared to the limited data reported for hulls from some Thai rice varieties, ranging from 1561 to 5917 mg/kg for p-coumaric acid and 156e-825 mg/kg for ferulic acid, respectively (Butsat et al., 2009; Butsat & Siriamornpun, 2010). An explanation for such a high amount of these hydroxycinnamic acids

determined in the Greek rice varieties may be the higher efficiency of 4 mol/L boiling NaOH solution to break the bonds of the respective phenols with other organic compounds, as well as with silicon. The respective element was found to be solubilized almost quantitatively (~95%), even at ambient temperature, when using a 4 mol/L NaOH solution (62% in the case of 1 mol/L NaOH) (Nenadis et al., 2013). In addition, silicon levels of the hulls were too low in comparison to the limited information available for certain Asian varieties, which ranged from 5.38 to 26.29 g/100 g (Dai et al., 2005). In this way hydroxycinnamic acids accumulation may possibly be favored. This is further supported by the differences observed with regard to phenolic content (total and individual) and silicon levels among the tested varieties, which seems to be in line with the observations made for the respective element and its relation to p-coumaric and ferulic acid levels in rice leaves (Goto et al., 2003).

9.4 Patent review on the recovery of bioactive compounds from rice by-products

Table 5.5 summarizes the results of the patent research on methods developed for the efficient recovery/extraction/isolation of bioactive compounds from rice by-products. Following the objectives of WP1, the patent research has been focused on the isolation/extraction of high-added value compounds, including phenolics, proteins, anti-oxidants, etc.

Table 9.5: Summary of patents on the recovery of bioactive compounds from rice by-products.

Patent No	Issue Date	Title	Type of AWCB	Recovered high added compound
CN 103351422B CN 103351422A	22/4/2015	Method for extracting natural bioactive protein from unpolished rice or/and rice bran	Rice bran	Rice protein
CN 1366025A	28/8/2002	Process for extracting phytic acid from rice husk (bran)	Rice husk, rice bran, wheat bran, corn	Phytic acid
CN 102516375A	27/6/2012	Subcritical water extraction method for high-denaturation rice bran protein	Rice bran	Rice bran protein
US 5175012A	29/12/1992	Antioxidant extracted from the defatted rice bran	Defatted rice bran	Mix of antioxidants, such as BHA, BHT or tocopherol
CN 101967178B CN 101967178A	5/9/2012	Method for extracting high-content diosgenine hydrolysate	Rice hulls	Diosgenine hydrolysate
US 20110265534A1 CA 2779943A1 CN 102639468A CN 102639468B EP 2319820A1 WO 2011055216A1 WO 2011055216A4	3/11/2011	Plant nutrient obtained from the rice husk and a process of prepartion thereof	Rice husk	Bio silica
US 2818413A	31/12/1957	Continuous process for the production of	Pentosan-containing vegetative materials	Furfural and acetic acid

Patent No	Issue Date	Title	Type of AWCB	Recovered high added compound
		furfural and acetic acid from vegetative material	such as rice hulls	
US 5736384A	7/4/1998	Thermostable xylanase	Xylan and xylan-containing oat spelts bran, wheat bran, pulp, bagasse, corn fiber, agricultural wastes such as rice straw and plant fiber	Xylanase XP1
CN 101311274A	26/11/2008	Process for enhancing extraction rate of ferulaic acid form plant stalks by steam explosion pretreatment	Plant straw including corn stalks, wheat straw, rice straw and the like	Ferulic acid
CA 2401699A1 **DE 60023187D1** **EP 1259631A1** **EP 1259631B1** **US 6927047** **WO 2001064931A1**	7/9/2001	Manufacture and purification of mycophenolic acid	Wheat bran, rice bran, rice husk	Mycophenolic acid
CN 1393434A	29/1/2003	Process for extracting inositol from rice bran (wheat bran)	Rice husk, Wheat bran, Rice bran	Inositol
US 5736384A	7/4/1998	Thermostable xylanase	Xylan and xylan-containing oat spelts bran, wheat bran, pulp, bagasse, corn fiber, agricultural wastes such as rice straw and plant fiber	Xylanase XP1
CN 101311274A	26/11/2008	Process for enhancing extraction rate of ferulaic acid form plant stalks by steam explosion pretreatment	Plant straw including corn stalks, wheat straw, rice straw and the like	Ferulic acid
JP 2004520058A	8/7/2004	Fractionation method of bran cereal	Bran, for example wheat, barley, rye, triticale, and oats or rice cereal grains of the seed coat	Germ rich fractions, endosperm rich fraction and aleurone-rich fractions, glucose, soluble hemicellulose, soluble oligosaccharides

ANIMAL PRODUCTS

10.Pigs

Pig meat represents 9.0 % of the total EU agricultural output; pig meat is the major type of meat produced in the EU28. From 2006 to 2014, the total number of pigs slightly decreased (1.0%), whereas the pig meat production remained stable, and even registered peaks in 2008 and 2011 (EUROSTAT, 2015b). Pig production is concentrated in a number of countries, with Denmark, Germany, Spain, France, the Netherlands and Poland having more than two thirds of the breeding pigs between them. Pork meat is produced throughout the year, however seasonal variation is accounted due to physiological characteristics of the animal (lower fertility in summer) and cultural factors. In 2013 pork meat production in the EU28 reached 252.9 million head, of which more than half (58 %) came from four countries, namely Germany, Spain, France and Poland (EUROSTAT, 2015b).

Raising pigs involves numerous farms and operations, each serving a unique role in the process. The life cycle begins with the piglets, which normally weigh 1.5 - 2 kg. The piglets remain with their mother for 21 to 42 days, depending on the pig management practice of the farm. Piglets are weaned by removing the sow from the pen. Thereafter, they are fed formulated feed. After a few days of adjustment, the weaned pigs are kept in weaner pens for an additional 30 to 60 days until their weight reaches 20 kg. They are then moved into porker pens where they remain until they reach their market weight of 75 - 100 kg. The life span of a porker is anywhere from 150 to 230 days from birth to the abattoir. When slaughtered, the dress weight of the porkers is approximately 70% of live weight.

In EU28, the majority of pigs growing for pig meat production takes place in specialized farms. The number of small pig farms follows a general downward trend, whereas the number of large pig farms is increased. The data confirm the concentration of the pig production sector in large farms where fixed costs are divided by a larger quantity of animal increasing productivity thus reducing the average cost of production (EUROSTAT, 2014). Swine manure is the largest AWCB produced during pig growing, and is usually gathered in large quantities in the pig farms, thus necessitating proper management, to minimize negative effects to the environment and maximize profitability of its use. The amount of manure produced by growing pigs depends on many parameters like the age and weight of the animal, the feeding quantity and characteristic, the amount of water consumed, environmental parameters, the physiological/health animal state etc. A typical manure quantity is 0.05 - 0.08 kg/day per kg of animal size; however, there are significant variations of the aforementioned figure both concerning the quantity, as well as the physicochemical characteristics.

Significant quantities of AWCB, are also produced during the end of life of the animal (slaughtering); typically generated into specific facilities (i.e. slaughterhouses). Slaughterhouse wastes constitute the inedible parts of animals derived from the production of meat, as well as blood and other animal byproducts. Inedible animal tissues (organs, integument, ligaments, tendons, blood vessels, skin, bone) can comprise 35 - 45% of the live weight of the slaughtered pig. Slaughterhouse wastewater quality depends on a number of factors, namely (Masse & Masse, 2000):

1. Blood capture: the efficiency in blood retention during animal bleeding is considered to be the most important measure for reducing the organic content of pig slaughterhouse wastewater;
2. Water usage: water economy usually translates into decrease volumes of wastewater, yet increased pollutant concentration;
3. Type of animal slaughtered: BOD is higher in wastewater from beef than hog slaughterhouses;

4. Amount of rendering or meat processing activities: plants that only slaughter animals produce a stronger wastewater than those also involve meat processing.

Significant quantities of these fractions, inedible by humans, are however used for other uses, namely by pet food companies that use inedible animal tissues as raw material for pet food production. Blood may also be concentrated and dried to an inert powder (blood meal) that can be used as a high-nitrogen organic fertilizer and a high protein animal feed. Other, liquid slaughterhouse wastes due to animal slaughtering and cleaning of the slaughterhouse facilities are usually not of interest and, thus are treated/managed according to the national legislation standards. Again, the quantity of slaughterhouse wastewater is highly site-specific and may vary between 2.5 and 40 m^3 of wastewater per ton of meat produced (World_Bank_Group, 2007).

The current uses of swine manure include mainly spreading to land as an organic fertilizer with or without composting, and its use for biogas production through anaerobic digestion. Pig manure is an excellent fertilizer with high concentration of nitrogen and other minerals (e.g. phosphorus etc.), as well as organic matter. However, swine manure may contain significant pathogenic microorganisms like *E.coli*, salmonella, and parasitic worms and there are concerns related to its direct application into cultivated lands. Composting of swine manure, preferably together with other organic AWCB, is a widely used treatment of swine manure to eliminate or reduce the risk of pathogenic microorganisms due to the development of high temperatures during the composting procedure. There are also some concerns that nitrogen, phosphorus, and trace elements in the manure may build up in the soil to problematic levels. These problems are controlled primarily by setting application rates to match the nutrient needs of the crops following application. Appropriate application practices also account for season and temperature, soil type etc. Swine manure is also widely used as feed in anaerobic digesting alone or in combination with other organic AWCB. Biogas produced from swine manure mainly consists of methane, carbon dioxide and other components, such as hydrogen sulphide, hydrogen, etc. Biogas has high calorific value and after appropriate post-treatment can be used as a renewable fuel for electricity and heat production. Problems with digestion of swine manure as sole substrate have been reported, mainly due to inhibition caused by its high ammonia content; therefore, co-digestion with cattle manure are usually employed in large collective biogas plants (Hansen et al., 1998).

Concerning slaughterhouse wastewater, mainly due to its complex composition of slaughtering by-products (mainly blood and intestinal mucus) is considered detrimental, given also its high content on pathogenic and non-pathogenic microorganisms (Bustillo-Lecompte & Mehrvar, 2015). Currently, the only available valorisation process of slaughterhouse wastewater is through anaerobic treatment for biogas production. Slaughterhouse wastewater are being treated alone (composting) or together with other organic residues (co-composting) for the production of biogas in a great variety of anaerobic reactors. Despite that the biogas production potential is usually satisfactory, the slaughterhouse wastewater organic strength makes it difficult to achieve complete stabilization of the organic compounds, and anaerobically treated effluents usually need additional post-treatment (e.g. aerobic stabilization) to achieve high effluent quality (Bustillo-Lecompte & Mehrvar, 2015).

10.1 Pig Manure

Pig manure refers to the faeces plus urine that are excreted by pig animals (Figure 10.1). Manure is typically 60% faeces and 40% urine. Pig manure, as well as all animal manures have varying composition; however, especially in large farms, that are made up from animals of different ages, weights and growing phases the manure consists as a combination of all types of animals, therefore

its composition may be more stable. Fresh pig manure moisture can reach up to 90% wt and may also contain other organic materials such as bedding material, straws etc.

Concerning energy characteristics, cattle manure can be considered a fuel with rather moderate energy density, ranging around 14.0 - 19.0 MJ/kg of HHV. However, the ability of its use, as is, through combustion is hindered by its high moisture level which is around 60 - 90% wt^{db}. Furthermore, its ash content is rather high around 15 - 35% wt^{db}, which may also render direct combustion problematic. Although, pig manure is not preferably used as fodder supplement, due to hygiene reasons (possibility of spreading pathogenic microorganism) it has been tested, under various portions and through various combinations in the feedlot of cattle and pigs (Muller, 1980). The crude protein is approx. 15 - 30% wt^{db}, higher than the protein content of cattle manure, whereas the Neutral Detergent Fiber (NDF) is between 30 - 60% wt^{db}.

Figure 10.1: Photo of fresh pig manure in a plastic bucket.

Table 10.1: Summary of main physicochemical characteristics of pig manure.

PHYSICOCHEMICAL PROPERTIES	(Tu et al., 2008)	(Shen et al., 2015)	(Choi et al., 2014)	(Komiyama et al., 2013)	(Komiyama et al., 2013)	(Xiu et al., 2009)	(Cu et al., 2015)	(Cu et al., 2015)	(Yousif & Mubarak, 2009)	(ECN, 2016)	(ECN, 2016)	(ECN, 2016)	(ECN, 2016)
FERTILIZER													
Higher Heating Value (HHV) (MJ/kg)	18.8	15.7	19.4±1.8							13.8	17.8	17.9	
Lower Heating Value (LHV) (MJ/kg)										12.8	16.9		
Fixed Carbon (%wt)^{db}	12.1±0.6	10.5±3.8								13.3	21.9	21.7	
Volatile Matter (%wt)^{db}	70.2±0.3	66.1±9.1	65.1±12.4							51.3	62.9	66.2	87.3
Ash (%wt)^{db}	17.7±0.4	24.2±11.1				12.3				35.4	15.2	12.2	
Moisture (% wt)^{am}	68.0±1.1	72.0±9.7	91.3±9.5			72.60				92.1			73.0
Carbon (%wt)^{db}	35.4	37.7±6.4	36.7±4.4	31.0	33.7					35.0	43.7	43.8	45.7
Oxygen (%wt)^{db}	38.8	28.9±5.7	31.6±3.8							21.3	33.5	39.2	44.0
Hydrogen (%wt)db	5.59	5.62±1.00	4.85±1.04							4.38	4.18	5.55	6.45
Nitrogen (%wt)^{db}	2.53	2.79±0.71	3.43±0.68	3.28	3.86	4.69	3.95±0.13	5.95±0.18	9.2±0.02	2.79	2.47	2.45	3.45
Sulfur (%wt)^{db}		0.63±0.30	0.91±0.42			0.42					0.48	0.94	0.38
ENERGY													
Dry matter (%wt)^{am}	32.0±1.1	28.0±9.7	9.70±9.48			27.40	19.4±0.7	37.2±1.1		7.90			27.0
Crude protein (%wt)^{db}	15.8	17.4±4.4	22.1±3.5	20.5	24.1	29.3	24.7±0.8	14.9±0.6	57.5±0.1	17.4	15.4	15.3	21.6
Crude fiber (%wt)^{db}													
Neutral Detergent Fiber (NDF) (%wt)^{db}	45.7±5.0					31.8	35.2±2.4	44.6±1.5	58.9±3.4				

PHYSICOCHEMICAL PROPERTIES	(Tu et al., 2008)	(Shen et al., 2015)	(Choi et al., 2014)	(Komiyama et al., 2013)	(Komiyama et al., 2013)	(Xiu et al., 2009)	(Cu et al., 2015)	(Cu et al., 2015)	(Yousif & Mubarak, 2009)	(ECN, 2016)	(ECN, 2016)	(ECN, 2016)	(ECN, 2016)
Acid Detergent Fiber (ADF) (%wt)^{db}	31.0±3.8					23.6	24.8±1.8	31.7±0.8	51.9±1.8				
Lignin (%wt)^{db}	6.33 ±0.58					3.1	6.88±0.64	16.2±0.3	26.1±1.2				
Ether extract (%wt)^{db}			3.06±1.11			7.46	7.89±0.40	2.10±0.12					
Ash (%wt)^{db}	17.7±0.4					12.30				35.4	15.2	12.2	
Gross energy (%wt)^{db}	18.8	15.7	19.4±1.81							13.8	17.8	17.9	
FERTILIZER													
Nitrogen (g/kg)db	25.3	27.9±7.1	34.3±6.8	32.8	38.6	46.9	39.5±1.3	59.5±1.8	92.0±0.2	27.9	24.70	24.5	34.5
Phosphorus (g/kg)db		19.9±8.2		31.2	31.7	17.10			28.0±0.1		6.10	12.4	
Potassium (g/kg)db		15.4±6.0		24.3	24.4	23.7					14.6	16.0	
Calcium (g/kg)db		18.4±9.9		40.1	39.5	3.30					8.30	11.4	
Magnesium (g/kg)db		12.1±4.1		13.7	13.30	7.10			1.80±0.1		4.30	7.78	
Sulfur (g/kg)db		6.30±3.00	9.10±4.20			4.20					4.80	9.40	3.80

depending on the bedding and other organic material contained within. Furthermore, its lignin content is considered rather low, usually less than 15% wt_{db}. In general, recycling of pig manure to cattle, sheep and pigs is possible at 10 - 30% level in the ration providing the waste is properly balanced and processed, and the content of critical nutrients (cell walls, ash, copper, drugs and other undesired constituents) does not exceed the tolerance level beyond which the performance of livestock would be adversely affected (Muller, 1980). On the other hand, pig manure is an excellent organic fertilizer since it contains significant amounts of nitrogen, phosphorus, and other minerals. The nitrogen content lies between 25.0 - 60.0 mg/kg^{db}, and is considerably higher than the nitrogen content of cattle manure; therefore, application practices should be carefully planned so as to minimize nitrogen loss due to ammonia volatilization or nitrogen run-off. The phosphorus content is also higher than cattle manure, around 15.0 - 30.0 mg/kg^{db}, whereas potassium is also present ranging between 15.0 - 25.0 mg/kg^{db}. The nutrient content of pig manure is higher than the nutrient content of cattle manure and therefore its application rate to cultivated land is usually lower than that of cattle manure. Finally, concerning bioactive compounds, pig manure, does not contain any bioactive compounds of interest for its valorisation. Pig manure is the outcome of the animal feed digestion and most of the plant/feed bioactive compounds, present are either assimilated or degraded during the digestion process. Therefore, no patents concerning bioactive compounds recovery from cattle manure are listed.

10.2 Pig Slaughterhouse Wastewater

Slaughterhouse wastewater comprise the liquid fraction of the wastes produced during the slaughtering of pig animals (Figure 10.2). It mainly comprises blood, intestinal mucus and other water effluents (e.g. cleaning wastewater).

Slaughterhouse wastewater is usually a high polluting effluent that contains faeces, urine, blood, fat, non-digested food in the intestines of the slaughtered animals, as well as other water effluent streams (e.g. cleaning water). The composition of slaughterhouse wastewater varies considerably according to the industrial process and practices, the water demand and the animal characteristics. Nevertheless, it usually contains both high levels of organic matter, nutrients and lipids/fat. Concerning, pH values pig slaughterhouse wastewater is mainly slightly acidic (6.0 - 6.9) with moderate conductivity, usually below 3.0 mS/cm. Both the total and total dissolve solids are quite high, with the majority of the solids being of organic origin. The reported COD and BOD_5 values vary considerably between approx. 1,000 - 16,000 mg COD/L, whereas the Total Nitrogen lies around 100 - 1000 mg N/L.

Figure 10.2: Photo of pig slaughterhouse wastewater.

Table 10.2: Summary of main physicochemical characteristics of pig slaughterhouse wastewater.

PHYSICOCHEMICAL PROPERTIES	(Masse & Masse, 2000)	(Masse & Masse, 2000)	(Pedrazzani et al., 2016)	(Masse et al., 2002)	(Borja et al., 1998)*	(Caixeta et al., 2002)*	(Borja et al., 1995)*	(Torres-Pérez et al., 2014)*
WASTEWATER								
pH	6.4±0.9	6.9±0.2			6.4	6.3-6.6	6.7	6.5-6.9
Conductivity (mS/cm)								2.21
Total Alkalinity (meq/L)					12.4		8.19	
Total Solids (mg/L)	2,812±622	5,748±823			7,120			4,679
Fixed Solids (mg/L)	834 ±406	1,290±1,574			1,980			
Total Suspended Solids (mg/L)	1,067±304	2,099±622				850-6,300	100	3,575
Fixed Suspended Solids (mg/L)	214±64	212±1,172				340-1,400	30	
TOC (mg/L)					2,100			1,220-3,422
COD (mg/L)	3,451±982	8,627±1,669	1,470-5,340	3230±295	10,410	2,000-6,200	5,050	8,250-16,730
BOD_5 (mg/L)					6,600	1,300-2,300	3,120	8,422
Total Nitrogen (TN) (mg/L)			130-340					1,170
Total Kjeldahl Nitrogen (TKN) (mg/L)	213±110	593±95			230	70-240	405	
Total Phosphorus (TP) (mg/L)	42.7±32.6	61.0	31-95		59.0	15.0-40.0	30	
Oil & Grease (mg/L)			90-240	160 ±43		40-600		

* The reported data refer to slaughterhouses of both cattle and swine processing.

The majority of the nitrogen present in cattle slaughterhouse wastewater is in the form of organic nitrogen and ammonia (e.g. Total Kjeldahl Nitrogen - TKN). The phosphorus content is also high between 15 - 95 mg P/L. Oil & grease content is rather high and may reach up to 600 mg/L, and may cause problems in subsequent wastewater treatment. In general, pig slaughterhouse wastewater characteristics are similar to the cattle slaughterhouse wastewater, apart from the pH values which are a little bit more acidic, compared to cattle slaughterhouse wastewater. Concerning bioactive compounds, pig slaughterhouse wastewater, does not contain any bioactive compounds of interest for its valorisation. Despite the fact that some liquid slaughterhouse waste effluents may contain significant quantities of protein, mainly when blood is not efficiently recovered (Bah et al., 2013), serious concerns about the content of pathogenic and non-pathogenic microorganisms and other public health concerns hinder valorisation of these wastes, through recovery of marketable food additives. Therefore, no patents concerning bioactive compounds recovery from pig slaughterhouse wastewater are listed.

11.Chicken

Poultry meat and eggs are important sources of protein for human nutrition in almost all countries in the world. For this reason, poultry sector continues to grow and industrialize in many parts of the globe. This sector influences the development of certain regions due to the effects of the production system (do Nascimento et al., 2015). Poultry production has increased in developing countries and waste management is a critical factor for the sustainability of this activity. Waste materials of the processing poultry industry include offal (feathers, entrails and organs of slaughtered birds), processing wastewater and biosolids. These wastes contain high concentration of nitrogen, phosphorus, potassium, copper, and zinc (Terzich et al., 2000). Inappropriate disposal of poultry processing industry wastes may cause environmental problems related to contamination of superficial and ground waters, besides the impacts on air quality (do Nascimento et al., 2015).

Studies on a diversity of poultry waste aspects have been carried out, from generation and characterisation to planning and implementation. However, in the topic of recycling and reuse, wastes have been used for fertilization, improving soil attributes, and contributing to plant growth (Bolan et al., 2010; Endale et al., 2010; Penn et al., 2011). This is a very interesting topic, since the waste is used without either environmental or health risks, once it is applied according to plant needs and the effects of its application are constantly monitored (do Nascimento et al., 2015).

Due to the intensive poultry farming, poultry litter raise serious concerns about treatment and disposal. It is traditionally used as fertilizer, but potential environmental problems such as spread of pathogens and emission of greenhouse gases and odorous compounds are reported due to its overuse as fertilizer (Font-Palma, 2012). The other waste produced in a huge amount by the poultry industry is poultry meal. It consists of ground, rendered, clean parts of poultry carcasses and can contain bones, offal, undeveloped eggs, and in a few cases, feathers, that are unavoidable parts in the poultry meat processing. It was used in formulated animal feed, but today it can be only used in formulated pet feed according to EU Regulation 1774/2002. Therefore, the poultry industry is facing difficulties in the proper treatment of surplus poultry litter and meal and seeking an alternative technology for the utilization of these wastes (Kantarli et al., 2016).

Existing technologies such as combustion, anaerobic digestion, gasification, pyrolysis and hydrothermal conversion may be an alternative way for proper management of the wastes from poultry industry. Direct combustion would not be suitable due to the high water and nitrogen contents of these wastes. Also, anaerobic digestion may not be a good alternative due to the high nitrogen content of poultry wastes which would inhibit microbial activities (Kantarli et al., 2016).

11.1 Manure

The value of manure as a source of plant nutrients has long been recognized, and poultry manure is a concentrated plant food containing two to three times as much nitrogen, three to five times as much phosphorus, and about the same amount of potassium as other farm manures. In addition to being a valuable source of plant nutrients, chicken manure is an important soil conditioner, and it increases the soil's moisture-holding and nutrient-holding capacities. Fresh manure contains about 76% water. The weight of fresh manure voided by hens is slightly less than two times that of the feed consumed. One hen will produce 130 pounds of manure in 1 year, or 1000 hens will produce 65 tons. On the dry basis as sold (approximately 30% water), this amounts to about 51 pounds per hen or 25 tons for 1000 hens per year.

The composition of chicken manure varies according to age of the chicken, moisture content and age of the manure, kind and amount of litter, and storage and handling practices. The only sure way to know the composition is to analyse the material. The value of chicken manure decreases with age.

Those manures that are several years old have little nutritive value, but they serve as excellent organic soil amendments (Smith et al., 1998).

Chicken manure contains both organic and inorganic forms of the plant nutrients as described in Table 11.1. Nitrogen occurs as ammonia and uric acid. The uric acid converts to urea, and the urea rapidly decomposes to ammonia gas, which causes the stron offensive odor often noticeable with chicken manure. Use preservatives or litters to prevent the loss of ammonia gas. Conversion of the uric acid and urea to ammonia is rapid during the first 2 weeks after the addition of manure to a warm moist soil, but conversion of the organic forms of nitrogen to an available form is slow during the first 4 weeks after its addition. About 60% of the nitrogen becomes available during the first 6 weeks in the soil; the remaining nitrogen is converted very slowly and may not be available until the next crop or season. Phosphorus is primarily organic and becomes available as the manure decomposes, but all may not be available until the next -crop or season. Potassium is present in the inorganic form and readily available to plants. Proper handling is required to prevent the loss of potassium and other soluble nutrients by leaching. Other plant nutrients become available during decomposition of chicken manure and, like phosphorus, may not all be available until the next crop or season.

Chicken manure may be applied to the soil fresh or at any age. In general, commercially available manure is air dried, pulverized, and packed in plastic bags of varying sizes. The manure may be scattered on the surface of the soil and worked in with a rotary tiller, plow, spading fork, shovel, or similar tool. It should be mixed thoroughly and evenly so no "pockets" of unmixed material remain in the soil and applied in rows or hills as recommended for the type of crop grown. The manure should be mixed with or covered by soil to prevent offensive odors. Chicken manure, used wisely, brings excellent results as a top dressing for pasture and turf. It may be used in potting mixtures for container-grown plants, and it may be used to increase the growth of flowers, fruits, and vegetables in home gardens.

Chicken manure must be applied with care as it may 'bum" plants if used in large amounts, if placed too close to plants, or if planting follows too soon after application. It should be mixed with the soil at least 1 week before planting when applied at the rate of 5 tons per acre (23 pounds per 100 square feet) or less and 2 weeks for greater amounts (Smith et al., 1998).

Table 11.1: Summary of main physicochemical characteristics of chicken manure.

PHYSICOCHEMICAL PROPERTIES	(Shen et al., 2015)	(Shen et al., 2015)	(Huang et al., 2011)	(Cantrell et al., 2012)	(Choi et al., 2014)	(Komiyama et al., 2013)	(Komiyama et al., 2013)	(Komiyama et al., 2013)	(Fernandez-Lopez et al., 2015)	(McCall, 1980)	(Laasonen, 2014)	(Laasonen, 2014)	(Quiroga et al., 2010)	(Anakalo et al., 2009)	(Anakalo et al., 2009)	(Pinto-Ruiz et al., 2012)	(Smith et al., 1998)	(Cu et al., 2015)	(Yousif & Mubarak, 2009)
ENERGY																			
Higher Heating Value (HHV) (MJ/kg)	12,4	13,2		15.1±0.35	11.9±3.6				16,1		13,1	15,1	13,1						
Lower Heating Value (LHV) (MJ/kg)											12,2	14,1	12,3						
Fixed Carbon (%wt)^{db}	6.48±6.51	10.5±6.0	7.20±0.70	8.80±1.10					19,6										
Volatile Matter (%wt)^{db}	62.6±7.1	62.5±11.0	57.5±1.2	74.3±0.8	55.3±6.5				66,3			67,3						66.7±1.0	
Ash (%wt)^{db}	32.4±9.8	27.8±13.6	32.2±0.2	20.9±0.4					9,72		33,7	23,1	33,7						
Moisture (% wt)^{am}	72.3±10.0	63.9±8.8			68.6±13.9					76,0	75,5	65,6	74,5					62.1±0.3	
Carbon (%wt)^{db}	33.0±6.2	33.6±8.8		42.2±0.02	26.7±6.1	27,6	25,1	35,7	40,6		36,2	38,0	36,2				24.8 ±7.0		
Oxygen (%wt)^{db}	25.7±7.0	30.8±7.3		37.8±0.1	30.5±3.3				41,5			27,5							
Hydrogen (%wt)^{db}	4.81±1.14	5.06±1.94		5.23±0.03	3.33±0.99				5,78		4,60	4,60	4,60						
Nitrogen (%wt)^{db}	3.39±1.25	3.70±1.26	2.50±0.10	3.67±0.06	2.25±0.58	4,47	2,62	3,55	1,72	6,70	5,90	6,30	5,90	4.80±0.27	4.16±0.19	4.77±0.30	2.98 ±1.83	2.94±0.06	4.00±0.03
Sulfur (%wt)^{db}	0.81±0.39	0.89±0.55		0.58±0.02	0.49±0.19				0,64	0,31	0,11	0,47	0,11						
FODDER																			
Dry matter (%wt)^{am}	27.7±10.0	36.1±8.8			31.4±13.9					24,0	24,5	34,4	25,5					37.9±0.3	
Crude protein (%wt)^{db}	21.2±7.8	23.1±7.9	15.6±0.6	22.9±0.4	20.0±6.3	27,9	16,4	22,2	10,8	41,9	36,9	39,4	36,9	30.0±1.7	26.0±1.2	29.8±1.9	18.6 ±11.4	18.4±0.4	25.0±0.2
Crude fiber (%wt)^{db}														15.2±2.5	11.5±1.8				
Neutral Detergent Fiber (NDF) (%wt)^{db}																21.6±3.3	41.6 ±10.9	36.1±1.1	70.2±2.7
Acid Detergent Fiber (ADF) (%wt)^{db}																9.76±2.43	29.6 ±12.9	25.0±0.8	37.9±1.6
Lignin (%wt)^{db}																		5.17±0.18	14.9±1.1
Ether extract (%wt)^{db}					2.02±1.01									1.80±0.90	1.60±0.40			2.35±0.11	
Ash (%wt)^{db}	32.4±9.8	27.8±13.6	32.2±0.2	20.9±0.4					9,72		33,7	23,1	33,7	12.0±1.1	29.0±3.4				
Gross energy (%wt)^{db}	12,4	13,2		15.1±0.35	11.9±3.6				16,1		13,1	15,1	13,1						
FERTILIZER																			
Nitrogen (g/kg)^{db}	33.9±12.5	37.0±12.6	25.0±1.0	36.7±0.6	25.2±5.8	44,7	26,2	35,5	19,0	67,0	59,0	63,0	59,0	48.0±2.7	41.6±1.9	47.7±3.0	29.8 ±18.3	29.4±0.6	40.0±0.3
Phosphorus (g/kg)^{db}	12.8±5.3	11.1±5.5	9.68±0.44			23,4	20,3	21,8	17,56	19,6	6,50	23,0	6,50	25.0±0.4	37.0±1.1	14.4±0.9			28.0±0.1

PHYSICOCHEMICAL PROPERTIES	(Shen et al., 2015)	(Shen et al., 2015)	(Huang et al., 2011)	(Cantrell et al., 2012)	(Choi et al., 2014)	(Komiyama et al., 2013)	(Komiyama et al., 2013)	(Komiyama et al., 2013)	(Fernandez-Lopez et al., 2015)	(McCall, 1980)	(Laasonen, 2014)	(Laasonen, 2014)	(Quiroga et al., 2010)	(Anakalo et al., 2009)	(Anakalo et al., 2009)	(Pinto-Ruiz et al., 2012)	(Smith et al., 1998)	(Cu et al., 2015)	(Yousif & Mubarak, 2009)
Potassium (g/kg)^{db}	23.9±7.6	23.4±7.6	34.9±0.8			25,8	26,5	33,7		16,6			23,8	21.0±4.0	34.0±8.0	30.2±2.6			
Calcium (g/kg)^{db}	45.2±24.7	23.5±15.1				11,2	15,8	38,2	10,1	32,0			48,4	26.0±3.0	55.0±13.0	26.9±3.1			17.0±0.2
Magnesium (g/kg)^{db}	10.5±5.6	7.88±3.31				9,30	7,60	8,3	4,46	2,90			4,30			5.90±0.60			10.3±0.4
Sulfur (g/kg)^{db}	8.10±3.90	8.90±5.50			4.90±1.90					3,10	1,10	4,70	1,09						

11.2 Slaughterhouse Wastewater

The generation of wastewater from slaughterhouses has become an environmental concern due to the growth of the poultry industry, as demand for poultry products has increased. Poultry slaughterhouses consume significant quantities of fresh water during slaughtering and cleaning of surfaces, resulting in the generation of a significant quantity of high strength wastewater (Debik & Coskun, 2009), containing high organic matter, with high nitrogen and phosphorus constituents (Avula et al., 2009). The high phosphorous concentration is due to blood, cleaning and sanitizing agents, and the phosphorous is in the form of organic or inorganic phosphates (Arvanitoyannis & Ladas, 2008; Avula et al., 2009). Residual blood, fat from skin, oils desorbed during scalding for feather removal and immersion chilling and feces are the main sources of organic matter in these wastewaters. Residual blood, urine and feces are also significant sources of nitrogen, especially organic nitrogen The phosphorus contained in this wastewater results from blood, manure and cleaning and sanitation compounds (Bayar et al., 2011). Furthermore, slaughterhouse wastewater contains a high quantity of biodegradable organic matter with a biological oxygen demand (BOD_5) range of 1.2 to 2.6 g/L, with the soluble fraction of the BOD, ranging between 40 to 60% (de Nardi et al., 2008; de Nardi et al., 2011). The primary pollutants contributing to the BOD in the poultry slaughterhouse wastewater are insoluble proteins from carcass debris, blood, fats, including non-biodegradable matter from feathers (Avula et al., 2009; Manjunath et al., 2000; Yordanov, 2010). The wastewater predominantly contains 35% more protein, resulting in a much higher BOD and COD, as compared to municipal sewerage (Avula et al., 2009; Zhang et al., 2008). However, wastewater characteristics vary from plant to plant, depending on the type of industrial process and the water consumption per fowl slaughtered (Bayar et al., 2011). Therefore, the poultry slaughterhouse wastewater should be treated efficiently prior to disposal to receiving fresh water sources to reduce environmental pollution (Debik & Coskun, 2009).

Aerobic and anaerobic methods have been traditionally used for the treatment of poultry slaughterhouses wastewater. Aerobic treatment processes are limited by their high energy consumption needed for aeration and high sludge production (Parawira et al., 2005). Both biological processes require long hydraulic retention time and large reactor volumes, high biomass concentration and controlling of sludge loss, to avoid the wash-out of the sludge (Kobya et al., 2006).

Biological anaerobic treatment technology is one of the most recommended treatment methods worldwide in the treatment of wastewater from the food industry due to the technology's ability to treat high strength wastewater. Anaerobic digestion has been used in treating poultry slaughterhouse wastewater as it can efficiently handle variations in particulate matter and fats, oil and grease (FOG) loading rates. Anaerobic bioreactors such as an up-flow anaerobic sludge bed (UASB) reactor have been successfully used to treat poultry slaughterhouse wastewater. Del Nery et al. (2007) obtained treatment efficiency rates of 65% for total COD and 85% for soluble COD reduction at an average organic loading rate (OLR) of 1.64 kg COD/m^3 per day using a full scale UASB reactor (Del Nery et al., 2016). Similarly, (Debik & Coskun, 2009) used a static granular bed reactor (SGBR) to treat the poultry slaughterhouse wastewater, achieving averaged COD removal rates of 95%. Similarly, the EGSB, which is well known to increase sludge expansion for improved efficiency due to its recirculation stream, was reported to achieve COD removal of 67% by Nunez & Martinez (2009), treating poultry slaughterhouse wastewater without a pretreatment process (Basitere et al., 2016; Núñez & Martínez, 1999).

Electrocoagulation is an alternative technology for wastewater treatment systems and most effective in removing inorganic and organic contaminants and pathogens. Many studies have reported the potentials of electrocoagulation in treating a variety of wastewater, including arsenic, dyes, paper mills, breaking oil emulsions in water, phosphate, boron and bacteria, viruses and cysts. Compared with conventional chemical coagulation, electrocoagulation has many advantages such as simple

equipment, easy operation and automation, a short retention time, low sludge production and no chemical requirement (Bayar et al., 2011).

Table 11.2: Summary of main physicochemical characteristics of chicken slaughterhouse wastewater.

PHYSICOCHEMICAL PROPERTIES	(Rajakumar et al., 2011)	(Del Nery et al., 2016)	(Del Pozo & Diez, 2005)	(Debik & Coskun, 2009)	(Bayar et al., 2011)	(Basitere et al., 2016)	(Chávez P et al., 2005)	(Coskun et al., 2016)	(Oliveira et al., 2011)	(Godini et al., 2012)
WATER										
pH	7.0-7.6	6.8-7.8		6.9±1.3	6,7	6.5-8.0	6.1-7.1	6.6±0.1	6,9	
Conductivity (mS/cm)					2.858		8.6-14.7	2.75±0.10		
Total Alkalinity (meq/L)	12.0-26.8		4.59-15.2	26.3±15.7		0-9.76	2.68-4.32			
Total Solids (mg/L)	1,400-3,900						1,082-4,558		1.500	
Fixed Solids (mg/L)							124-1,492		210	
Total Suspended Solids (mg/L)	300-950		230-760	2,800±950		315-1,273	726-1,462	2,760±700		880-1,130
Fixed Suspended Solids (mg/L)							66-172	350±1,300		
COD (mg/L)	3,000-4,800	4,060 ±687	1,820±60	6,880±1,400	2.171	2,133-4,137	5,800-11,600	7,970±140	2.490	26,500-28,959
BOD_5 (mg/L)	750-1,890	2,133 ±373	900±200		1.123	1,100-2,750	4,524-8,700			
Total Nitrogen (TN) (mg/L)							10.5-111.5			
Total Kjeldahl Nitrogen (TKN) (mg/L)	109-325	169 ±71	190±50	675±110		77-352				998-1,005
Total Phosphorus (TP) (mg/L)	16.0-32.0			8.95±3.15	9,65	8.0-27.0	7.2-12.7		3,5	200-215
Oil & Grease (mg/L)	800-1,385	125 ±44	170		143	131-684	147-666			1,473-1,720

12.Cattle

In terms of value, bovine animals represent 8.1% of total agricultural output and 18.8% of animal output, without taking animal products (e.g. milk) into account. Between 2009 and 2014, production of meat from heifers and bulls fell in the EU28 by 7 %. However, there has been an increase for veal, i.e. meat from calves (aged under 8 months) and young cattle (aged between 8 and 12 months), and for which production increased by around 4 % in the EU28 during the same period.

Raising cattle involves numerous farms and operations, each serving a unique role in the process. It usually takes anywhere from 2-3 years to bring beef from farm to fork and during this period significant quantities of AWCB (e.g. manure) is produced. In EU28, the majority of cattle growing for cattle meat production takes place in specialized farms with intensive livestock farming usually employing confined animal feeding operations. At farms where animals are allowed to graze on pasture, much - if not all - of their manure is excreted directly onto the land, serving as a fertilizer and recycling nutrients back into the soil. On industrial livestock farms, however, animals drop their manure in the houses where they live. From there, the manure must be properly managed so as to minimize negative effects to the environment and maximize profitability of its use. The amount of manure produced by growing cattle depends on many parameters like the age and weight of the animal, the feeding quantity and characteristic, the amount of water consumed, environmental parameters, the physiological/health animal state etc. A typical manure quantity is 0.06 kg/day per kg of animal size; however, variations of the aforementioned figure may come up to about 25%, due to the aforementioned reasons.

Significant quantities of AWCB, are also produced during the end of life of the animal (slaughtering); typically generated into specific facilities (i.e. slaughterhouses). Slaughterhouse wastes constitute the inedible parts of animals derived from the production of meat, as well as blood and other animal byproducts. Inedible animal tissues (organs, integument, ligaments, tendons, blood vessels, skin, bone) can comprise up to 45% or more of the slaughtered animal. Significant quantities of these fractions, inedible by humans, are however used for other uses, namely by pet food companies that use inedible animal tissues as raw material for pet food production. On the other hand, liquid slaughterhouse wastes due to animal slaughtering and cleaning of the slaughterhouse facilities are usually not of interest and, thus are treated/managed according to the national legislation standards. Again, the quantity of slaughterhouse wastewater is highly site-specific and may vary between 2.5 and 40 m^3 of wastewater per ton of meat produced (World_Bank_Group, 2007).

The current uses of cattle manure include as fertilizer, for energy production and as building material. Dried cow manure is an excellent fuel. In some cultures dung from domestic cows or buffalo is routinely collected and dried for fuel, sometimes after being mixed with straw. Pieces of dung are lit to provide heat and a flame for cooking. A more efficient way for energy exploitation of cattle manure comprise the anaerobic digestion. Biogas produced from cattle manure mainly consists of methane, carbon dioxide and other components, such as hydrogen sulphide, hydrogen, etc. Biogas has high calorific value and after appropriate post-treatment can be used as a renewable fuel for electricity and heat production. Manure is also a valuable fertilizer for any farming operation and has been used for centuries to supply needed nutrients for crop growth. Cow manure is rich in minerals, especially nitrogen, phosphorus and potassium. It can support the growth of beneficial microorganisms when it is mixed with soil. Manure can also improve the texture of the soil and help it to maintain moisture. Often, however, manure is too rich in certain chemicals and needs to be treated (composting) so as to be safely used. In some developing countries, cattle manure is often used as a building material; cow manure paste is applied to the floors and walls of rural homes, as an insulating material forming a waterproof layer that also thermally insulates the house. A relatively new process is to make building bricks from cow dung mixed with straw dust. The bricks are much lighter than conventional ones and are constructed using renewable raw materials (Smithsonian, 2011).

Concerning slaughterhouse wastewater, mainly due to its complex composition of slaughtering by-products (mainly blood and intestinal mucus) is considered detrimental, given also its high content on pathogenic and non-pathogenic microorganisms. Currently, the only available valorisation process of slaughterhouse wastewater is through anaerobic treatment for biogas production. Slaughterhouse wastewater are being treated alone (composting) or together with other organic residues (co-composting) for the production of biogas in a great variety of anaerobic reactors. Despite that the biogas production potential is usually satisfactory, the slaughterhouse wastewater organic strength makes it difficult to achieve complete stabilization of the organic compounds, and anaerobically treated effluents usually need additional post-treatment (e.g. aerobic stabilization) to achieve high effluent quality (Bustillo-Lecompte & Mehrvar, 2015).

12.1 Cattle Manure

Cattle manure refers to the faeces plus urine that are excreted by cattle animals (Figure 12.1). Manure is usually more than 80% water and when collected is usually mixed with other organic materials such as bedding material, straws etc.

Figure 12.1: Photo of fresh cattle manure in the field.

Table 12.1: Summary of main physicochemical characteristics of cattle manure.

PHYSICOCHEMICAL PROPERTIES	(TU ET AL., 2008)	(FEEDIPEDIA, 2016)	(SHEN ET AL., 2015)	(SHEN ET AL., 2015)	(AMON ET AL., 2007)	(HUANG ET AL., 2011)	(CANTRELL ET AL., 2012)	(CHOI ET AL., 2014)	(CHOI ET AL., 2014)	(KOMIYAMA ET AL., 2013)	(KOMIYAMA ET AL., 2013)	(FERNANDEZ-LOPEZ ET AL., 2015)	(ECN, 2016)	(OSHITA ET AL., 2015)	(HASSAN ET AL., 2011)	(SORENSEN ET AL., 2003)	(CHEN ET AL., 2003)
ENERGY																	
Higher Heating Value (HHV) (MJ/kg)	17.0	16.9	15.2	13.6			17.6±0.3	16.1±0.4	16.6±1.6			18.4	18.2	16.7±0.4			
Lower Heating Value (LHV) (MJ/kg)													16.9	15.2			
Fixed Carbon (%wt)^{db}	15.4±2.1		13.7±4.1	11.7±4.5		10.3±0.3	4.50±3.20					11.9					
Volatile Matter (%wt)^{db}	71.2±2.2		64.6±8.1	60.6±12.6		60.9±1.6	80.7±3.1	80.4±2.9	86.3±6.4			64.1		83.4±1.7			
Ash (%wt)^{db}	13.4±0.1	14.0	22.6±11.9	28.2±16.3	15.4±1.3	31.9±0.9	14.8±0.2					20.8	8.96				17.1±3.2
Moisture (% wt)^{am}	81.4±0.4	83.3±1.7	75.7±7.8	75.6±9.2	85.5±1.2		86.5±0.4	75.6±3.1	73.3±6.2	64.5	71.5		70.0	81.8±1.4	80.3		84.1±5.0
Carbon (%wt)^{db}	36.4		37.6±6.2	34.4±9.0			46.5±0.1	37.6±1.9	38.1±4.0	32.5	26.2	40.7	44.7	42.7±0.2			44.2±1.0
Oxygen (%wt)^{db}	43.8		31.9±6.8	30.4±8.5			33.2±0.7	28.6±2.4	28.2±2.5			31.4	38.2				
Hydrogen (%wt)db	4.85		5.26±1.12	4.91±1.39			5.49±0.01	5.06±0.25	5.18±0.45			5.32	5.85	5.70±0.30			
Nitrogen (%wt)^{db}	1.52	1.87±0.56	2.16±0.64	1.92±0.50	3.73±1.90	2.60±0.10	2.29±0.03	1.87±0.40	1.85±0.42	1.35	1.87	1.38	2.05	2.30±0.20	1.28	2.68±0.59	2.52±0.51
Sulfur (%wt)^{db}			0.59±0.28	0.65±0.41			0.25±0.02	0.18±0.05	0.25±0.07			0.42	0.31				0.25±0.05
FODDER																	
Dry matter (%wt)^{am}	18.6±0.4	16.7±1.7	24.3±7.8	24.4±9.2	14.5±1.2		13.5±0.4	24.4±3.1	26.7±6.2	35.5	28.5		30.0	18.2±1.4	19.7		15.9±5.0
Crude protein (%wt)^{db}	9.47	11.7±3.5	13.5±4.0	12.0±3.1	23.3±11.9	16.3±0.6	14.3±0.2	11.8±2.7	12.3±2.0	8.44	11.7	8.63	12.8	14.4±1.3	7.98	16.8 ±3.7	15.8±3.2
Crude fiber (%wt)^{db}		22.4			27.4±2.1											26.0±5.9	
Neutral Detergent Fiber (NDF) (%wt)^{db}	60.8±4.1	64.1			53.7±8.8										52.1	47.1±8.6	48.6±6.0
Acid Detergent Fiber (ADF) (%wt)^{db}	37.3±2.0	43.9			33.6±5.3										32.2	28.4±5.7	31.6±10.3
Lignin (%wt)^{db}	19.0±1.4	14.5			15.2±3.1												10.4±3.8
Ether extract (%wt)^{db}		2.8			3.21±0.78			2.49±0.90	1.17±0.30					1.50			
Ash (%wt)^{db}	13.4±0.1	14.0	22.6±11.9	28.2±16.3	15.4±1.3	31.9±0.9	14.8±0.2					20.8	8.96				

PHYSICOCHEMICAL PROPERTIES	(TU ET AL., 2008)	(FEEDIPEDIA, 2016)	(SHEN ET AL., 2015)	(SHEN ET AL., 2015)	(AMON ET AL., 2007)	(HUANG ET AL., 2011)	(CANTRELL ET AL., 2012)	(CHOI ET AL., 2014)	(CHOI ET AL., 2014)	(KOMIYAMA ET AL., 2013)	(KOMIYAMA ET AL., 2013)	(FERNANDEZ-LOPEZ ET AL., 2015)	(ECN, 2016)	(OSHITA ET AL., 2015)	(HASSAN ET AL., 2011)	(SORENSEN ET AL., 2003)	(CHEN ET AL., 2003)
Gross energy (%wt)^{db}	17.0	16.9	15.2	13.6			17.6±0.3	16.1±0.4	16.6±1.6			18.4	18.2				
FERTILIZER																	
Nitrogen (g/kg)^{db}	15.2	18.7±5.6	21.6±6.4	19.2±5.0	37.3±19.0	26.0±1.0	22.9±0.3	18.7±4.0	18.5±4.2	13.5	18.70	13.8	20.5	23.0±2.0	12.8	26.8±5.9	25.2±5.1
Phosphorus (g/kg)^{db}			6.07±4.12	6.00±3.33		6.60±0.18				8.2	16.6	16.2	5.14				5.70±2.10
Potassium (g/kg)^{db}			12.0±8.2	9.39±7.30		14.1±0.8				9.80	20.5	5.81	7.00				17.4±10.0
Calcium (g/kg)^{db}			12.4±11.1	16.0±15.6						25.4	32.7	17.0	20.5				9.83±2.64
Magnesium (g/kg)^{db}			6.54±3.07	8.59±3.72						5.40	8.70	6.43	5.32				3.97±1.94
Sulfur (g/kg)^{db}			5.90 ±2.80	6.50±4.10			2.50±0.20	1.80±0.50	2.50±0.70			4.20	3.10				2.57±0.50

Concerning energy characteristics, cattle manure can be considered a fuel with rather moderate energy density, ranging around 16.0 - 18.0 MJ/kg of HHV. However, the ability of its use, as is, through combustion is hindered by its high moisture level which is around 70 - 85% wt^{db}. Furthermore, its ash content is rather high around 15 - 25% wt^{db}, which may also render direct combustion problematic. Although, cattle manure is not preferably used as fodder supplement, due to hygiene reasons (possibility of spreading pathogenic microorganism) it has been added, dried and pulverized at levels of 20 to 60 % to feedlot cattle rations (Ferrell & Garrett, 1973b). The energy and protein content is considered rather low, due to high fiber and ash content. The crude protein is approx. 10 - 15% wt^{db}, whereas the Neutral Detergent Fiber (NDF) is between 50 - 60% wt^{db}. Furthermore, its lignin content is considered moderate to high (10 - 20% wt^{db}) and the fat content is low, usually less than 3.0% wt^{db}. Cattle manure is an excellent organic fertilizer since it contains significant amounts of nitrogen, phosphorus, potassium and other minerals. The nitrogen content lies between 15.0 - 25.0 mg/kg^{db}, the phosphorus content is around 5.0 - 15.0 mg/kg^{db}, whereas potassium is also present ranging between 5.0 - 15.0 mg/kg^{db}. The mineral content of cattle manure is among the highest of all the AWCB listed in the present study. Finally, concerning bioactive compounds, cattle manure, does not contain any bioactive compounds of interest for its valorisation. Cattle manure is the outcome of the cattle feed digestion and most of the plant bioactive compounds, present in the cattle feed are either assimilated or degraded during the digestion process. Therefore, no patents concerning bioactive compounds recovery from cattle manure are listed.

12.2 Cattle Slaughterhouse Wastewater

Slaughterhouse wastewater comprise the liquid fraction of the wastes produced during the slaughtering of cattle animals (Figure 12.2). It mainly comprise blood, intestinal mucus and other water effluents (e.g. cleaning wastewater).

Figure 12.2: Photo of slaughterhouse wastewater treatment facility.

Table 12.2: Summary of main physicochemical characteristics of cattle slaughterhouse wastewater

PHYSICOCHEMICAL PROPERTIES	(Maroneze et al., 2014)	(Bazrafshan et al., 2012)	(Ozyonar & Karagozoglu, 2014)	(Jensen et al., 2015)	(White et al., 2013)	(McCabe et al., 2013)	(Pereira et al., 2016)	(Borja et al., 1998)*	(Caixeta et al., 2002)*	(Borja et al., 1995)*
WATER										
pH	7.0±0.2	7.3±0.1	6.7-7.3				7.3±0.6	6.4	6.3-6.6	6.7
Conductivity (mS/cm)		9.14±1.51	1.62-2.27				3.22±2.62			
Total Alkalinity (meq/L)						70-906	85.6±37.2	12.4		8.19
Total Solids (mg/L)	2,725±646			2,036-15,485			7,528±8,627	7,120		
Fixed Solids (mg/L)	1,193±822						1,661 ±1,702	1,980		
Total Suspended Solids (mg/L)	540.0±212.3	3,247±845	980-1,200		2,000	457-6,870	4,195±5,879		850-6,300	100
Fixed Suspended Solids (mg/L)							428±412		340-1,400	30
TOC (mg/L)								2,100		
COD (mg/L)	7,692±5,193	5,817±473	3,337-4,150	3,163-31,600	7,250	1,040-12,100	6,242±1,549	10,410	2,000-6,200	5,050
BOD5 (mg/L)		2,543±362	1,950-2,640		3,000	163-7,020	2,401±2,751	6,600	1,300-2,300	3,120
Total Nitrogen (TN) (mg/L)					450	296-785	522±267			
Total Kjeldahl Nitrogen (TKN) (mg/L)	155±80	137±12		130-1,163			466±243	230	70-240	405
Total Phosphorus (TP) (mg/L)	23.0±10.1			16.8-173	45		28.0±17.0	59.0	15.0-40.0	30
Oil & Grease (mg/L)		34.0±9.0	275-376	11-5,540	120	5-2,110			40-600	

* The reported data refer to slaughterhouses of both cattle and swine processing

Slaughterhouse wastewater is usually a high polluting effluent that contains faeces, urine, blood, fat, non-digested food in the intestines of the slaughtered animals, as well as other water effluent streams (e.g. cleaning water). The composition of slaughterhouse wastewater varies considerably according to the industrial process and practices, the water demand and the animal characteristics. Nevertheless, it usually contains both high levels of organic matter, nutrients and lipids/fat. Concerning, pH values cattle slaughterhouse wastewater is mainly neutral (6.5 - 7.5) with moderate conductivity, usually below 3.0 mS/cm. Both the total and total dissolve solids are quite high, with the majority of the solids being of organic origin. The reported COD and BOD_5 values vary considerably between approx. 1,000 - 12,000 mg COD/L, whereas the Total Nitrogen lies around 300 - 800 mg N/L. The majority of the nitrogen present in cattle slaughterhouse wastewater is in the form of organic nitrogen and ammonia (e.g. Total Kjeldahl Nitrogen - TKN). The phosphorus content is also high between 10 - 50 mg P/L. Finally, a specific characteristic of cattle slaughterhouse wastewater is the rather high oil & grease content, due to fat residues from slaughtered animals. Oil & grease content may reach up to 5,500 mg/L, and may cause problems in subsequent wastewater treatment. Therefore, cattle slaughterhouse wastewater is usually pre-treated through coagulation and Dissolved Air Flotation (DAF) so as to remove the majority of the fat/oil present in the wastewater stream. Concerning bioactive compounds, cattle slaughterhouse wastewater, does not contain any bioactive compounds of interest for its valorisation. Slaughterhouse wastewater contains significant amounts of pathogenic and non-pathogenic microorganisms and the recovery of specific compounds is hindered due to public health concerns. Therefore, no patents concerning bioactive compounds recovery from cattle slaughterhouse wastewater.

13. Cow's Milk

The European dairy sector is a highly important sector that comprises almost 600,000 dairy farms, 12,000 processing facilities and more than 300,000 job positions; in fact milk accounts for 15% of EU agricultural revenue (Lemoine, 2016). In EU-28, approx. 162.8 million tons of cow's milk have been produced and almost 152.0 million tons have been processed by the dairy industry. The main products include: drinking milk (31.3 million tons), other fresh products (15.6 million tons) and cheese (9.5 million tons). At the same time, almost 50.0 million tons of whey are produced as the main by-product of European dairy industry. Over one fifth (21.0 %) of all the cows' milk collected by EU-28 dairies in 2015 was collected in Germany, while slightly more than a sixth of the total (16.7 %) was collected by dairies in France (EUROSTAT, 2015c).

The production of dairy products mainly involve two main stages:

A. Cow's milk production and collection in the farms, and
B. Cow's milk processing in the dairy industry.

Concerning AWCB production, each stage of dairy products production results in significant (in terms of quantity), yet distinctively different (in terms of quality characteristics) AWCB streams. During cow's milk production and collection, the main AWCB is the cow's manure produced throughout the life of the dairy cows. On the other hand, cow's milk processing in dairy industry results in various milk-related AWCB streams; the most significant one is whey, produced during cheese and yogurt production. Another major difference is that cow's manure is mainly considered a waste stream, with little or no commercial value, whereas whey is a significant by-product of the dairy industry that after appropriate processing can, and does become a significant commercial co-product (Królczyk Jolanta et al., 2016).

Dairy cows usually live for about 5 - 6 years in average (Nor et al., 2013); lameness, mastitis and poor fertility are common reasons for culling. Dairy cows will probably give birth from approx. 2-3 years old usually through artificial insemination. About nine months later, Dairy cows give birth to a calf, which is fed her colostrum, and when her lactation begins, the cow becomes part of the milking herd where she will produce milk for about 10 months. The cow will stop producing milk during a two-month dry period before the birth of her next calf. Each dairy cow will go through approx. 3-4 milking cycles before culling. During her life, dairy cow will produce approx. 50 - 80 tons of manure. Regardless of its housing systems (e.g. tie-stall, cubicles, straw yard or outdoor), significant part of the cow's life involves housing indoors (e.g. during winter, at night etc.), thus most of the manure produced should be collected and properly managed together with the bedding material that is regularly replaced. The amount of manure produced by dairy cows depends on many parameters like the age and weight of the animal, the feeding quantity and characteristic, the amount of water consumed, environmental parameters, the physiological/health animal state etc. Furthermore, in addition to livestock excreta, manure collected on dairy farms may contain other materials, for example, soil, animal bedding, waste feed, waste milk, weed seeds, pathogens, and cleaning and foot bath compounds.

Significant amounts of AWCB, are also produced during the processing of the milk which is the main commodity of dairy cows. Milk is almost entirely processed into industrial facilities, therefore dairy processing AWCB should be properly managed by the dairy industry. A significant proportion of AWCB generated by the dairy industry is in the form of whey, which creates a lot of environmental concerns. Fifty years ago, whey was considered as wastewater from the processing of cheese and it was mainly disposed along with wastewater generated by the washing of equipment and floors of the cheese manufacturing units (Valta et al., 2017). However, whey contains all the natural constituents of the milk, which are not retained into the cheese curd, thus it is surprisingly that for many years, whey was considered as a waste stream, or was under-utilised as animal feed (post drying) or as a liquid fertilizer (Ganju & Gogate, 2017). Currently, the majority of the whey, almost 60%, is valorised into many different products inside the dairy industry or by other whey processing

facilities (Tsakali et al., 2010). The quantity of the whey produced during dairy processing, varies, depending on the dairy product produced, the methods and technology applied, the milk properties etc. In general, the cheese yield is approx. 10% of the initial milk mass, the rest (90%) is whey. There are two main different types of whey: sweet whey and acid whey. Sweet whey is a by-product of ripened cheese production (pH 5.8 - 6.6) whereas acid whey is obtained from cottage cheeses (pH 3.6 - 5.1)(Królczyk Jolanta et al., 2016).

The current uses of cattle manure include as fertilizer, for energy production and as building material. Dried cow manure is an excellent fuel. In some cultures dung from domestic cows or buffalo is routinely collected and dried for fuel, sometimes after being mixed with straw. Pieces of dung are lit to provide heat and a flame for cooking. A more efficient way for energy exploitation of cattle manure comprise the anaerobic digestion. Biogas produced from cattle manure mainly consists of methane, carbon dioxide and other components, such as hydrogen sulphide, hydrogen, etc. Biogas has high calorific value and after appropriate post-treatment can be used as a renewable fuel for electricity and heat production. Manure is also a valuable fertilizer for any farming operation and has been used for centuries to supply necessary nutrients for crop growth. Cow manure is rich in minerals, especially nitrogen, phosphorus and potassium. It can support the growth of beneficial microorganisms when it is mixed with soil. Manure can also improve the texture of the soil and help it to maintain moisture. Often, however, manure is too rich in certain chemicals and needs to be treated (composting) so as to be safely used. In some developing countries, cattle manure is often used as a building material; cow manure paste is applied to the floors and walls of rural homes, as an insulating material forming a waterproof layer that also thermally insulates the house. A relatively new process is to make building bricks from cow dung mixed with straw dust. The bricks are much lighter than conventional ones and are constructed using renewable raw materials (Designother90network, 2011).

Concerning whey, approx. 40% of its global production is wasted or under-utilised since it is used as animal feed, after drying or used as liquid fertilizer; this is the case mainly at developing countries. The rest, approx. 85 million tons in global scale, is used to produce various by-products including whey powder and lactose (50% of whey industrially utilized), whey protein concentrates and whey protein isolates (35% of whey industrially utilized), and the rest (15% of whey industrially utilized) for other uses e.g. whey cheese, fermentation, production of soft drinks, lactic acid, and bio-ethanol. However, whey valorisation processes, usually present a number of limitation and barriers, technological and economical, which should be overcome prior to applications, especially when concerning small and small-to-medium sized dairy industries (Valta et al., 2017).

Another promising and economical viable process for whey valorization is anaerobic digestion for the production of biogas, which can be burned to produce electrical energy and thermal heat that can cover part of the needs of the dairy industry. Economic analysis have shown that despite the relative high investment costs of anaerobic digestion units, such an investment may be profitable even within the first 10 years of operation due to the probable government financial subsidization and the shelling prices of the produced electricity from renewable energy sources (Valta et al., 2017). Another advantage of the anaerobic digestion process is that whey apart from being treated alone (composting) it can be digested together with other organic residues (co-composting) for the production of biogas in a great variety of anaerobic reactors. On the other hand, despite that the biogas production potential is usually satisfactory, the anaerobically treated effluents usually need additional post-treatment (e.g. aerobic stabilization) to achieve high effluent quality (Prazeres et al., 2012).

13.1 Dairy cow Manure

Dairy cow manure refers to the faeces plus urine that are excreted by cattle animals (Fig. 1). Manure is usually more than 80% water and when collected is usually mixed with other organic materials

such as bedding material, straws etc. As already mentioned, the characteristics of manure greatly vary and depend on many different parameters like the age and weight of the animal, the feeding quantity and characteristic, the amount of water consumed, environmental parameters, the physiological/health animal state etc. Dairy cows have different physiological characteristics, and their diet may be quite different than beefs for bovine meat production. Dairy cows tend to eat more forage, or grassy foods, such as hay and alfalfa, while beefs often eat in feedlots that offer food rich in grains such as corn and grain sorghum. Different diets result in different manure characteristics, however the differences are rather minor as can been seen at the following Table 13.1, which compares main physicochemical characteristics from dairy and beef manure.

Table 13.1: Comparative summary of means, medians, maximums and minimums for total N, ammonium, organic N, P, K, and DM for solid beef and dairy manures (Manitoba_Agriculture, 2015).

TYPE	SAMPLE N°	TKN (LB/TON)	N-NH4 (LB/TON)	ORG N (LB/TON)	P (LB/TON)	K (LB/TON)	DM (%)
Beef manure	93	Mean: 10.6 Median: 10.3 Min: 5.40 Max: 16.9	Mean: 1.50 Median: 1.20 Min: 0.00 Max: 8.50	Mean: 9.00 Median: 8.80 Min: 2.90 Max: 15.3	Mean: 2.00 Median: 1.90 Min: 0.60 Max: 7.00	Mean: 10.5 Median: 9.50 Min: 3.30 Max: 37.2	Mean: 26.1 Median: 24.7 Min: 14.3 Max: 50.2
Dairy manure	20	Mean: 11.5 Median: 11.4 Min: 6.60 Max: 16.4	Mean: 2.30 Median: 2.00 Min: 0.00 Max: 6.00	Mean: 9.20 Median: 8.80 Min: 3.30 Max: 15.1	Mean: 3.20 Median: 2.80 Min: 1.00 Max: 11.8	Mean: 9.00 Median: 8.60 Min: 2.60 Max: 17.8	Mean: 26.3 Median: 24.9 Min: 22.0 Max: 37.6

The variation and differences between the various samples of the same origin (e.g. dairy or beef) is greater than the differences between the mean or median values of dairy and beef manure. For example, the mean and median values of DM (%) for beef manure is 26.1% and 24.7% respectively, whereas the same values for dairy manure are 26.3% and 24.9%, respectively. At the same time, the min. and max. of DM (%) of beef manure are 14.3% and 50.2%, respectively. The same observation holds for all the main physicochemical parameters that are presented in Table 1. Therefore, it is obvious that it does not make much sense of discriminating between manure samples from dairy or beef origin, and thus the data presented in Table 12.1, can be safely considered that refer to both beef and dairy manure characteristics.

Figure 13.1: Photo of fresh cattle manure in the field.

Concerning energy characteristics, dairy cattle manure can be considered a fuel with rather moderate energy density, ranging around 16.0 - 18.0 MJ/kg of HHV. However, the ability of its use, as is, through combustion is hindered by its high moisture level which is around 70 - 85% wt^{db}. Furthermore, its ash content is rather high around 15 - 25% wt^{db}, which may also render direct combustion problematic. Although, dairy cattle manure is not preferably used as fodder supplement, due to hygiene reasons (possibility of spreading pathogenic microorganism) it has been added, dried and pulverized at levels of 20 to 60 % to feedlot cattle rations (Ferrell & Garrett, 1973a). The energy and protein content is considered rather low, due to high fiber and ash content. The crude protein is approx. 10 - 15% wt^{db}, whereas the Neutral Detergent Fiber (NDF) is between 50 - 60% wt^{db}. Furthermore, its lignin content is considered moderate to high (10 - 20% wt^{db}) and the fat content is low, usually less than 3.0% wt^{db}. Dairy cattle manure is an excellent organic fertilizer since it contains significant amounts of nitrogen, phosphorus, potassium and other minerals. The nitrogen content lies between 15.0 - 25.0 mg/kg^{db}, the phosphorus content is around 5.0 - 15.0 mg/kg^{db}, whereas potassium is also present ranging between 5.0 - 15.0 mg/kg^{db}. The mineral content of cattle manure is among the highest of all the AWCB listed in the present study. Finally, concerning bioactive compounds, cattle manure, does not contain any bioactive compounds of interest for its valorization. Cattle manure is the outcome of the cattle feed digestion and most of the plant bioactive compounds, present in the cattle feed are either assimilated or degraded during the digestion process. Therefore, no patents concerning bioactive compounds recovery from cattle manure are listed.

Table 13.2: Summary of main physicochemical characteristics of cattle manure (Amon et al., 2007; Cantrell et al., 2012; Chen et al., 2003; Choi et al., 2014; ECN, 2016; feedipedia, 2016; Fernandez-Lopez et al., 2015; Hassan et al., 2011; Huang et al., 2011; Komiyama et al., 2013; Oshita et al., 2015; Shen et al., 2015; Sorensen et al., 2003; Tu et al., 2008).

PHYSICOCHEMICAL PROPERTIES	AVERAGE	SD	MIN	MAX	N° SAMPLES
ENERGY					
Higher Heating Value (HHV) (MJ/kg)	16.6	1.42	13.6	18.4	10
Lower Heating Value (LHV) (MJ/kg)	16.1	1.20	15.2	16.9	2
Fixed Carbon (%wt)^{db}	11.3	3.75	4.5	15.4	6
Volatile Matter (%wt)^{db}	72.5	10.31	60.6	86.3	9
Ash (%wt)^{db}	18.7	7.13	9.0	31.9	10
Moisture (% wt)^{am}	77.8	6.52	64.5	86.5	14
Carbon (%wt)^{db}	38.5	5.78	26.2	46.5	12
Oxygen (%wt)^{db}	33.2	5.30	28.2	43.8	8
Hydrogen (%wt)^{db}	5.3	0.34	4.9	5.9	9
Nitrogen (%wt)^{db}	2.1	0.60	1.3	3.7	17
Sulfur (%wt)^{db}	0.4	0.17	0.2	0.7	8
FODDER					
Dry matter (%wt)^{am}	32.2	36.15	13.5	155.9	14
Crude protein (%wt)^{db}	13.0	3.77	8.0	23.3	17
Crude fiber (%wt)^{db}	25.3	2.58	22.4	27.4	3
Neutral Detergent Fiber (NDF) (%wt)^{db}	54.4	6.75	47.1	64.1	6
Acid Detergent Fiber (ADF) (%wt)^{db}	34.5	5.44	28.4	43.9	6
Lignin (%wt)^{db}	14.8	3.52	10.4	19.0	4
Ether extract (%wt)^{db}	2.2	0.87	1.2	3.2	5

PHYSICOCHEMICAL PROPERTIES	AVERAGE	SD	MIN	MAX	Nº SAMPLES
Ash (%wt)[db]	18.9	7.54	9.0	31.9	9
Gross energy (%wt)[db]	16.6	1.51	13.6	18.4	9
FERTILIZER					
Nitrogen (g/kg)[db]	20.7	6.04	12.8	37.3	17
Phosphorus (g/kg)[db]	8.8	4.77	5.1	16.6	8
Potassium (g/kg)[db]	12.0	5.08	5.8	20.5	8
Calcium (g/kg)[db]	19.1	7.87	9.8	32.7	7
Magnesium (g/kg)[db]	6.4	1.74	4.0	8.7	7
Sulfur (g/kg)[db]	3.6	1.73	1.8	6.5	8

13.2 Whey

Whey is the liquid remaining after milk has been curdled and strained (Figure 13.2). There are two main types of whey: sweet whey (pH = 5.1 - 6.4) that is produced from the production of hard cheese, and acid whey (pH < 5.1) that is produced when making acid types dairy products such as cottage cheese or greek yogurt. Whey comprise the liquid fraction of the milk components that does not curd, e.g. water, lactose, whey proteins like α-lactalbumin, β-lactoglobulin, serum albumin, immunoglobulins, and proteose-peptones (Farrell et al., 2004), minerals and traces of fat.

Figure 13.2: Photo of whey remaining after cheese curd removal.

Whey composition in terms of nutritional characteristics is presented in Table 13.3. The data summarized there refer to both sweet and acid whey originating from different dairy processes (e.g. hard cheese, soft cheese, yogurt, casein etc.).

Table 13.3: Nutritional properties of whey on wet base.

PARAMETER	VALUE (% W/W)
Water	93.0 - 95.0
Lactose	4.0 - 5.0
Proteins	0.5 - 1.0
Fat	0.1 - 0.5

PARAMETER	VALUE (% W/W)
Minerals	0.5 - 0.8
Other organic solids	0.2 - 0.5

Table 13.4: Summary of main physicochemical characteristics of whey (Antonopoulou et al., 2008; Bylund 2015; Ebrahimi et al., 2010; Ergüder et al., 2001; Farizoglu et al., 2004; Ghaly & Singh, 1989; Ghaly & Kamal, 2004; Janczukowicz et al., 2008; Saddoud et al., 2007; Siso, 1996).

PHYSICOCHEMICAL PROPERTIES	AVERAGE	SD	MIN	MAX	N° SAMPLES
WASTEWATER					
pH	5.2	0.82	3.9	6.3	10
Conductivity (mS/cm)	109.3	28.57	78.0	140.5	4
Total Alkalinity (meq/L)	7.8	2.55	6.0	9.6	2
Total Solids (mg/L)	39792.0	29576.16	5930.0	66830.0	5
Fixed Solids (mg/L)	4610.0	6066.98	320.0	8900.0	2
Total Suspended Solids (mg/L)	21960.0	21699.64	1350.0	67700.0	7
Fixed Suspended Solids (mg/L)	300.0	-	300.0	300.0	1
COD (mg/L)	63600.0	23925.42	6000.0	79500.0	8
BOD_5 (mg/L)	37740.0	8097.10	29500.0	50000.0	5
Total Nitrogen (TN) (mg/L)	1096.7	40.41	1050.0	1120.0	3
Total Kjeldahl Nitrogen (TKN) (mg/L)	1571.7	1053.51	146.0	2960.0	7
Total Phosphorus (TP) (mg/L)	336.0	184.20	124.0	500.0	4
Oil & Grease (mg/L)	5614.3	3088.38	1000.0	9900.0	7

Whey wastewater is usually a high polluting effluent that contains significant quantities of organic matter, namely proteins, simple sugars, fat, and other organic compounds. The COD values of whey vary between 50-70 g/L, which is approx. 10 times higher than typical COD values of municipal wastewater streams. The majority of the whey's organic constituents are readily biodegradable, as it is obvious by the high BOD_5 values that range between 30 and 50 g/L. Therefore, whey can be treated through conventional biological wastewater processes, either aerobic, or preferably anaerobic. As already noted, the pH of the whey streams varies from 3.9-4.0 (acid whey) to 6.0-6.5 (sweet whey). Another point, which should be taken into consideration when designing whey treatment facilities, is the high mineral content, which results in typical conductivities of approx. 80-100 mS/cm. Such high conductivity values may have a negative impact upon biological processes especially for anaerobic ones. The same stands for the low alkalinity of whey, that probably necessitates the use of an alkaline medium (NaOH, $Ca(OH)_2$, $NaHCO_3$) to maintain proper pH values within the anaerobic bioreactor. However, the addition of mineral alkaline medium may further increase the process conductivity, thus there should be extra care when operating anaerobic facilities that treat whey streams.

Both the total and total suspended solids are quite high, with the majority of the solids being of organic origin. Total Nitrogen lies around 1000 mg N/L, due to the presence of milk proteins. The former can be also concluded by the fact that majority of the nitrogen present in whey is in the form of organic nitrogen and ammonia (e.g. Total Kjeldahl Nitrogen - TKN). The phosphorus content is also high between approx. 1500-500 mg P/L. Finally, a specific characteristic of cattle slaughterhouse wastewater is the rather high oil & grease content, due to fat residues from milk; values up to 10 g/L

have been presented in the literature, whereas most whey samples have between 4.0-5.0 g/L of fats. The high fat content may cause problems in subsequent wastewater treatment and special care should be given on its removal.

13.3 Milk AWCB bioactive compounds patent and literature review

As already mentioned, dairy cows manure do not contain any bioactive compounds. However, whey is a AWCB stream with high nutritional value. It contains proteins, simple sugars, fat, and other organic compounds, therefore it can be valorised through producing various products for the food industry like whey powder, whey protein concentrates and isolates, lactose etc. All these products, despite their undoubtedly significant nutritional value, cannot be considered as "bioactive", which mainly refers to compounds that are not essential nutrients, which are essential for general body function, but have a rather specific biological effect, having a positive influence on human health. Based on this consideration the following patent review, does not contain any data on patents referring on whey deriving food ingredients or food product formulations, but is focused on technologies and processes that mainly involve production and/or separation of specific bioactive compounds mainly of protein origin (e.g. specific peptides).

Individual whey protein components and their peptide fragments show various bioactivities including antimicrobial and antiviral actions, immune system stimulation, anticarcinogenic activity, and other metabolic features (Park & Nam, 2015). Whey proteins are comprised of 50% β - lactoglobulin; 12% a - lactoglobulin; 10% immunoglobulins; 5% serum albumin, and 0.23% proteose peptones, lactoferrin (LF), and lactoperoxidase (LP). Bioactive properties have been found to both the parent proteins, but mainly to specific peptides fragments, which may be inactive when comprising part of the parent protein, but exhibit regulatory, hormone-like activity when released after partial hydrolysis of the parent proteins (Park & Nam, 2015). Various α-La and β-Lg derived peptides show antihypertensive effects; the active peptides are usually short and apart from ACE-inhibitory (antihypertensive) they effect radical-scavenging activity. A typical α-La derived peptide, α-lactorphin, is a tetrapeptide (Tyr - Gly - Leu - Phe) that dependently lowered blood pressure without affecting heart rate in rats. Another enzyme hydrolyzed peptide (β-lactotensin) from β-Lg shows hypocholesterolemic activity in mice. Other effects, include antimicrobial activity against Gram- positive or -negative bacteria, antiviral activity, and anticarcinogenic activity. Lactoferricin is another peptide derived from LF exhibiting antimicrobial activity against various bacteria due to its iron-chelating properties, and its ability to bind to membrane's lipopolysaccharides of Gram-negative bacteria. LF is also a key factor in the modulation of antiinflammatory processes through simulation of the immune system. Finally, IGs have shown significant antimicrobial and antiviral activity and it also provides protection against diseases through passive immunity. Oral administration of milk IGs significantly enhanced the immunological functions of gastrointestinal - associated lymphoid tissue cells (Park & Nam, 2015).

Whey proteins are hydrolyzed enzymatically into peptides using acids, alkali and enzymes, as well as supercritical water. From the above methods, enzymatic hydrolysis is generally preferred because peptides are produced under mild pH and temperature conditions, thus eliminating formation of by-products. Furthermore, through proper adjustment of the enzymes used and the operating parameters, tailor-made hydrolysis can be achieved that results to less free amino acids, unlike chemical hydrolysis processes (Cheison & Kulozik, 2017). Enzymatic hydrolysis of whey proteins to produce bio-active peptides can be produced in the following ways (a) enzymatic hydrolysis, and (b) hydrolysis by proteolytic active microorganisms. The most common way to produce bioactive peptides is through enzymatic hydrolysis of whole protein molecules. Many of the known bioactive peptides have been produced using gastrointestinal enzymes, usually pepsin and trypsin. Other digestive enzymes and different enzyme combinations of proteinases—including alcalase, chymotrypsin, pancreatin, pepsin and thermolysin as well as enzymes from bacterial and fungal sources—have also been utilized to generate bioactive peptides from various proteins. Bioactive

peptides can, also, be generated by the starter and non-starter bacteria used in the manufacture of fermented dairy products that exhibit wall-bound proteinases and a number of intracellular peptidases (Korhonen & Pihlanto, 2006).

After peptides production, the most commonly used methods for their recovery are ultrafiltration and diafiltration. These methods offer cost reduction, high processing speed, and the absence of denaturation or protein - structure modification. Ultrafiltration is routinely employed to enrich bioactive peptides from protein hydrolysates. Enzymatic hydrolysis can be performed through conventional batch hydrolysis or continuous hydrolysis using ultrafiltration membranes. The traditional batch method has several disadvantages, such as the relatively high cost of the enzymes and their inefficiency as compared with a continuous process. Ultrafiltration membrane reactors have been shown to improve the efficiency of enzyme-catalysed bioconversion and to increase product yields, and they can be easily scaled up. Stepwise ultrafiltration using cut-off membranes of low molecular mass have been found useful for separating out small peptides from high molecular mass residues and remaining enzymes (Korhonen & Pihlanto, 2006).

Patent No	WO 2008108649 A2
Issue Date	06/03/2008
Title	**Ace-inhibitory peptides from whey and methods for providing the same**
Abstract	The invention relates to methods for providing compounds having an antihypertensive effect. More in particular, the invention relates to ACE (angiotensin I- converting enzyme)-inhibitory peptides that can be released enzymatically from whey proteins. Provided is a method for providing a protein hydrolysate having ACE-inhibitory activity, comprising treating a whey protein- containing substrate with a bacterial heat-labile neutral protease to produce a primary hydrolysate and treating said primary hydrolysate with a thermolysin to produce a secondary hydrolysate. Also provided are hydrolysates and isolated peptides obtainable by said method and uses thereof for the preparation of a medicament for inhibiting ACE activity in a mammal; for lowering the blood pressure; and/or for preventing the occurrence of hypertension.
Type of AWCB	Whey
Recovered compound	ACE-inhibitory peptides
Details	The method comprises: - treating a whey protein-containing substrate with a bacterial heat-labile neutral protease, derived from Bacillus subtilis or from Bacillus amyloliquefaciens, to produce a primary hydrolysate; and -treating said primary hydrolysate with a thermolysin (heat-stable metalloproteinase), derived from B. stearothermophilus, to produce a secondary hydrolysate. If desired, downstream processing takes place, for instance in the form of an ultrafiltration (UF) treatment. The enzymes have a much larger molecular weight than the peptides and can be separated from the ACE-inhibitory peptides by means of UF. An additional advantage of a UF step is that the protein substrates which have not been degraded by the enzymes can also be separated from the biologically active hydrolysate.

Patent No	CN101775429 B
Issue Date	26/03/2010
Title	**Whey protein antioxidant peptides, preparation method thereof and application thereof**
Abstract	The present invention relates to a whey protein antioxidant peptides and preparation and their use. The present invention utilizes cheese byproduct whey protein and enzymes, by enzymatic hydrolysis, prepared whey protein hydrolysates antioxidant peptide, then these hydrolysates by macroporous adsorption static or dynamic preliminary purification, gel filtration chromatography After preparative high performance liquid chromatography and high performance liquid chromatography analysis of pure whey protein purified antioxidant peptide products, and amino acid sequence determination of peptides, the product has a good resistance to digestion, acid and heat resistant storage stability, small molecular weight and specific amino acid sequence, can effectively eliminate free radicals, blocking the oxidation reaction, reduce the generation of oxidative damage, so it has a very broad application prospects in the food, pharmaceutical, feed and cosmetic fields
Type of AWCB	Whey

Patent No	CN101775429 B
Recovered compound	Anti-oxidant peptides
Details	A method for preparing whey proteins antioxidant peptides, characterised by the steps of enzymatic hydrolysis, degree of hydrolysis 18 - 20% at constant pH, inactivation of enzymes through heating. Hydrolysate is then purified in a macroporous resin column, eluted with ethanol solution (65 - 75% v/v). The whey hydrolysate is then concentrated into a rotary evaporator and freeze-dried to obtain the final whey protein antioxidant peptide lyophillisate.

Patent No	US6919314 B1
Issue Date	14/06/1999
Title	**Bioactive whey protein hydrolysate**
Abstract	The invention relates to a partial hydrolysate of whey protein which contains bioactive peptides but does not have a bitter flavor. The hydrolysate is carried out using selective enzymes which produce the active peptides and is terminated at a degree of hydrolysis before substantial bitter flavors are created. There are also described novel peptides and a method of reducing systolic blood pressure through the administration of the peptides.
Type of AWCB	Whey
Recovered compound	ACE-inhibitory peptides
Details	Accordingly the invention includes a process for preparing a whey protein hydrolysate containing bioactive peptides which comprises: i) hydrolysing a whey protein-containing substrate with at least one heat labile protease, at a temperature of between about 20° C. and 65° C. at a pH of about 6 to about 8 when said enzyme is a neutral protease, at a pH of about 3 to about 5 when said enzyme is an acid protease, and at a pH of about 5 to about 10 when said enzyme in an alkaline protease; ii) terminating said hydrolysis when a degree of hydrolysis of no greater than 10% has been reached by deactivating said protease under conditions which produce a water soluble hydrolysate

Patent No	WO2010000801 A2
Issue Date	02/07/2009
Title	**Whey protein hydrolysate containing tryptophan peptide consisting of alpha lactalbumin and the use thereof**
Abstract	The invention relates to a whey protein hydrolysate, in particular a hydrolysate consisting of whey protein enriched with α-lactalbumin and α-lactalbumin, and the use thereof for producing pharmaceuticals, anti-hypertensive agents, food supplements, foodstuffs and animal feed, and to pharmaceuticals, anti-hypertensive agents, food supplements, foodstuffs and animal feed produced in this manner. The whey protein hydrolysate according to the invention, which has an ACE inhibiting and anti-hypertensive action, contains a physiologically active quantity of at least one peptide containing tryptophan, preferably at least one of the bio-active dipeptides Ile-Trp and Trp-Leu, and can be obtained by

Patent No	WO2010000801 A2
	the extensive hydrolysis of whey protein isolates or of pure α-lactalbumin.
Type of AWCB	Whey
Recovered compound	ACE-inhibitory peptides
Details	A method for producing a whey protein hydrolyzate with ACE-inhibitory and antihypertensive activity, characterized in that the hydrolysis is carried out enzymatically with at least the enzymes Alcalase® and trypsin. The method is characterized in that the hydrolysis is carried out until more than 50% of the protein contained has a molecular weight of less than 4 kDa. The enzyme / substrate ratio (g enzyme / g substrate) is preferably between 1: 10 and 1: 10,000. The progress of the hydrolysis is monitored for example by gel permeation chromatography (GPC) and after reaching the desired degree of hydrolysis, stopped by inactivating the enzymes, preferably by heating at a temperature from 80 °C to 100 °C.

Patent No	US20120322745 A1
Issue Date	27/07/2011
Title	**Optimized method for obtaining ace activity inhibitory peptides from whey, ace inhibitory peptides and food comprising them**
Abstract	An optimized method for obtaining ACE activity inhibitory peptides includes the steps of whey ultrafiltration for obtaining a whey concentrate, enzymatic hydrolysis, hydrolysate ultrafiltration and inhibitory peptide separation. The method includes selecting and adding a mixture having suitable proportion and amount of two microbial proteases and having complementary action to the whey concentrate for the hydrolysis thereof in order to obtain peptides with an ACE inhibition percentage greater than 70% and an IC50 index of 30 to 100 µg/ml.
Type of AWCB	Whey
Recovered compound	ACE-inhibitory peptides
Details	An optimized method is provided using whey as the raw material in which it includes ultrafiltration of whey in order to obtain a whey concentrate, an enzymatic hydrolysis of this whey concentrate for a minimum time of 30 minutes, protein hydrolysate ultrafiltration and ACE inhibitory peptide separation and production, which comprises: selecting and adding a mixture having a suitable proportion and amount of two microbial proteases and having complementary action to said whey concentrate for the hydrolysis thereof, in which said proportion of enzyme/substrate ranges between 0.5 and 3 enzyme units/mg of whey protein concentrate in order to obtain peptides with an ACE inhibition percentage greater than 70% and an IC50 index of 30 to 100 µg/ml. Purification is performed by means of an ultrafiltration membrane. Ultrafiltration is carried out in two steps: first, a first ultrafiltration in which the hydrolysates are fractioned using membranes with a 10 kDa cut-off, and the permeate obtained was then fractioned through a second ultrafiltration using membranes with a 1 kDa cut-off. A permeate with extracts of 1 kDa peptides is thus obtained. After ultrafiltration, peptides with greater ACE inhibitory activity are selected. To that end a separation is performed by means of high performance liquid chromatography (HPLC) with reverse phase columns.

Patent No	US6998259 B1
Issue Date	30/10/2000
Title	**Enzymatic treatment of whey proteins for the production of antihypertensive peptides and the resulting products**
Abstract	Enzymatic digests of whey protein concentrates were prepared using animal, bacterial and fungal proteases, and evaluated for antihypertensive activities. The highest ACE-inhibitory activity was obtained with the purified peptide β-1g (f142–148) obtained by chemical synthesis, for which an IC50 value of 0.04 mg powder.ml−1 was found. The hydrolysates derived from BiPRO™ whey protein isolate and β-1g both gave higher antihypertensive activities (IC50 values of 0.29 to 0.90 mg powder.ml−1) than the other hydrolysates tested (IC50 values of 0.96 and 1.30 mg powder.ml−1). The recovered hydrolysate can be used to treat hypertension in mammals such as humans and domestic pets such as dogs and cats.
Type of AWCB	Whey
Recovered compound	ACE-inhibitory peptides
Details	A process for preparing an angiotensin-converting enzyme (ACE)-inhibiting composition comprising: (a) preparing an aqueous solution of a whey protein fraction and trypsin; (b) holding said solution under conditions effective for partially hydrolyzing said whey protein fraction to provide a hydrolysate having increased ACE-inhibiting activity; (c) stopping the hydrolyzation; and (d) drying hydrolysate to provide the ACE-inhibiting composition comprising a mixture of peptides

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FRUITS

14.Grape fruit

Grapevine (*Vitis vinifera* L.) is a woody vine cultivated worldwide for its edible berries (grapes) that are eaten fresh or pressed into juice. Grape crops are one of the main extended agro economic activities in the world with more than 60 million tons produced globally every year (Teixeira et al., 2014). Most of grape juice is fermented and macerated to make wine, and the rest is used as a refreshing beverage. Grape processing generates massive amounts of by-products (solid waste up to 30%, *w*/*w* of the material used (Teixeira et al., 2014) that can be broadly classified as follows: solid by-products (*leaves, stems, seeds, skins and pulp*), highly viscous by-products (*lees*), and low-viscosity by-products (*wastewater*) (Bordiga, 2016). The wine processing with the by-products produced during the various production stages are shown schematically in Figure 14.1 (Barba et al., 2016). *Grape pomace (or grape marc)* is the main solid residue of grape processing including at least the pressed skins and the disrupted cells of grape pulp, and, depending on the process, the stems and the seeds.

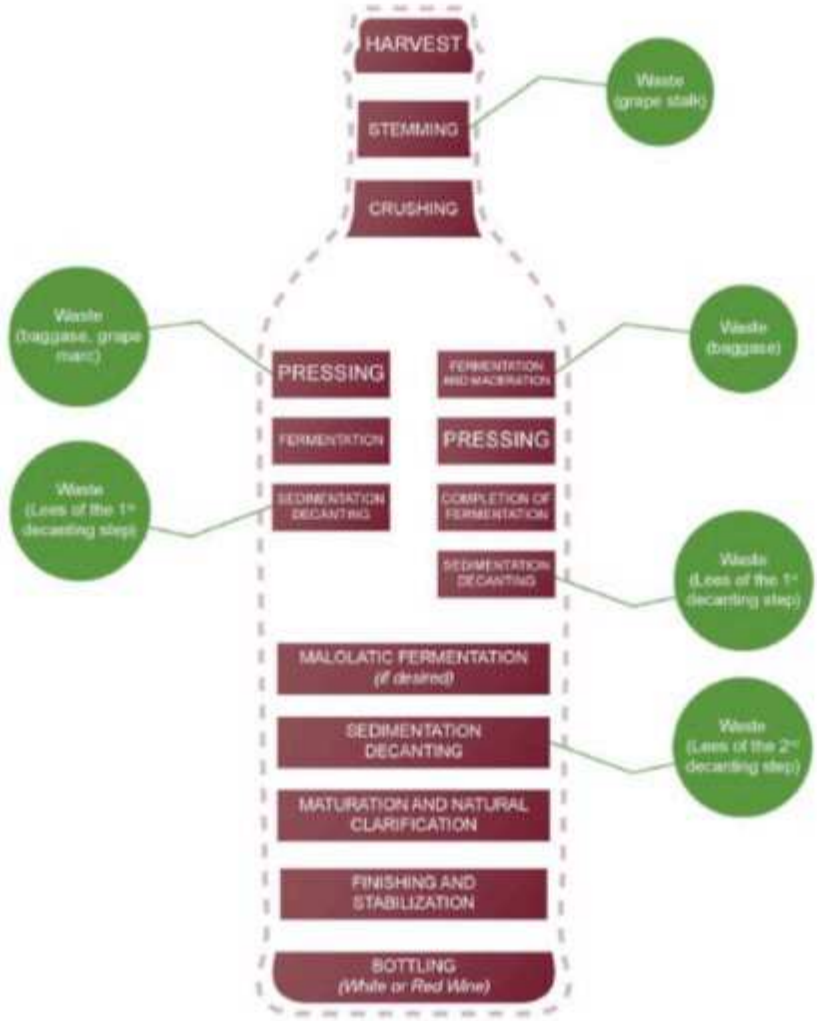

Figure 14.1: Overview of wastes and by-products during wine making industry (Barba et al., 2016).

The physical and chemical composition of wine and grape juice by-products depend on many factors: purpose of the crop (white wine, red wine, spirits, juice etc.), grape variety, grape maturity and the wide range of techniques and machinery used for grape separation, crushing, fermentation, maceration and distillery. As a result, the nature and nutritional value of those products should be ideally determined on a case-by-case basis (Bordiga, 2016).

Currently, after grape juice extraction, the remaining pomace and stems are not valued as highly profitable waste, being mainly directed to composting or discarded in open areas potentially causing environmental problems leading to serious surface and groundwater pollution. The use of these products for fertilizers or composts can cause the increase of nitrogen leaching in soils and oxygen depletion due to the presence of tannins and other compounds (Bordiga, 2016). These products also contain heavy metals that can cause problems. Thus, the increasing demand for environment-friendly industrial production in addition to the challenge for gaining operational efficiency and minimizing by-product treatment cost in the wine industry has started to move this sector towards the adoption of preventative integrated waste approaches (Teixeira et al., 2014). In this report, the two major by-products, grape pomace/marc and wine lees, with their physicochemical characteristics will be described and analyzed. Furthermore, the potential high added value compounds which could be recovered from these by-products will be reported.

14.1 Grape pomace/marc/pulp

Grape pomace includes the skins and pulp (10-12% of grapes), the seeds (3-6%) and, in some cases, the stems, whereas grape pulp is composed only of skins and pulp (Bordiga, 2016). Due to the lower fibre content of grape pulp, it is the grape by-product with the best nutritional value for livestock.

Current wine-making practices favor destemming and many wines are made with grapes crushed after the removal of the stems. Leaving the stems is still required for certain red wines when the organoleptic properties provided by the stems are desirable. Some white wines do not require destemming, as the stems do not come in contact with the juice during the process. Grape pomace made of non-destemmed berries is composed of about 30% stems, 30% seeds and 40% skins and pulp, while grape pomace made from destemmed berries consists of about 40% seeds and 60% skin and pulp (Gohl, 1981). Grape pomace is often further processed to extract the residual ethanol for the production of liquors, resulting in "exhausted" pomace.

Table 14.1 summarizes the main physicochemical characteristics of grape pomace.

Table 14.1: Summary of main physicochemical characteristics of grape pomace (Baglieri et al., 2014; Bordiga, 2016; Brenes et al., 2016; Celma et al., 2007; feedipedia, 2016; Teixeira et al., 2014; Vassilev et al., 2010).

PHYSICOCHEMICAL PROPERTIES	RANGE	COMMENTS
ENERGY		
Higher Heating Value (HHV) (MJ/kg)	18.2-22.2	
Lower Heating Value (LHV) (MJ/kg)	16.4-20.5	
Fixed Carbon (%wt)^{db}	21.4-26.4	
Volatile Matter (%wt)^{db}	65.8-74.4	
Ash (%wt)^{db}	4.2-9.5	
Moisture (% wt)^{am}	10-11.5 (dehydrated), 50-72 (fresh)	
Carbon (%wt)^{db}	47.2-54.9	
Oxygen (%wt)^{db}	30.4-38.6	
Hydrogen (%wt)db	5.6-6.3	
Nitrogen (%wt)^{db}	1.9-2.4	
Sulfur (%wt)^{db}	0.03-0.21	
FODDER		
Dry matter (%wt)^{am}	90-93 (dehydrated) or 33-47 (fresh pomace)	Values are average values from a lot of samples.

PHYSICOCHEMICAL PROPERTIES	RANGE	COMMENTS
Crude protein (%wt)^{db}	12.4-15.3	Values are average values from a lot of samples.
Crude fiber (%wt)^{db}	36.1-62.6	Values are average values from a lot of samples.
Neutral Detergent Fiber (NDF) (%wt)^{db}	57-78.7	Values are average values from a lot of samples.
Acid Detergent Fiber (ADF) (%wt)^{db}	48-78.2	Values are average values from a lot of samples.
Lignin (%wt)^{db}	33.3-52.8	Values are average values from a lot of samples.
Ether extract (%wt)^{db}	3-13	Values are average values from a lot of samples.
Ash (%wt)^{db}	2.7-7.8	Values are average values from a lot of samples.
Gross energy (%wt)^{db}	18.2-19.1	Values are average values from a lot of samples.
FERTILIZER		
Nitrogen (g/kg)^{db}	19.8-24.5	Values are average values from a lot of samples.
Phosphorus (g/kg)^{db}	2-3	Values are average values from a lot of samples.
Potassium (g/kg)^{db}	11.9	Values are average values from a lot of samples.
Calcium (g/kg)^{db}	5-9	Values are average values from a lot of samples.
Magnesium (g/kg)^{db}	0.8	
BIOACTIVE COMPOUNDS		
Total polyphenolic content (g GAE/kg)^{db}	10-43	
Tannins (g tannic acid eq./kg)^{db}	22-203	
Condensed tannins (g catechin eq./kg)^{db}	116	

14.2 Wine lees

Wine lees are the residues formed at the bottom of wine vessels, after fermentation, during storage or after authorized treatments, as well as the residue obtained following the filtration or centrifugation of this product. Lees are mainly composed of microorganisms (mainly yeasts), tartaric acid, inorganic matter, and phenolic compounds (Teixeira et al., 2014) (Table 14.2) and account for approx. 25% of the total solid waste in wine making industry (Oliveira & Duarte, 2016). The composition of wine lees depends on the winemaking technology. Therefore, red wine lees also contain skins, pips and polymeric phenolic compounds whereas white lees do not contain the phenolic compounds from pips and skins. These lees are rested in tanks or barrels to precipitate the solid particles to the bottom. Additionally, white and red wine lees composition differs depending not only on the kind of wine but also on the number of decanting steps performed (Pérez-Bibbins et al., 2015). Table 14.2 summarizes the main physicochemical characteristics of wine lees. The widely reported importance of lees for natural removal of undesirable compounds from wine makes advisable the exploitation of this phenomenon in other fields such as water detoxification and filters production, in which lees could play a key role as natural and cheap decontaminant. Lees could be used as a supplement in animal feed, but when recovered by centrifugation after column distillation, they have a very poor nutritional value, making them unsuitable for this purpose (Bordiga, 2016).

Table 14.2: Summary of main physicochemical characteristics of wine lees (Bordiga, 2016; feedipedia, 2016; Teixeira et al., 2014).

PHYSICOCHEMICAL PROPERTIES	RANGE
pH	3.6-7.2
el. Conductivity (mS/cm)	4-13.8
Total nitrogen (TN) (g/kg)^{db}	17.2-59.7
ENERGY	
Fixed Carbon (oxidizable organic carbon) (%wt)^{db}	22.6-37.6
Ash (%wt)^{db}	22.3-22.6
Moisture (% wt)^{am}	52-54
FODDER	
Proteins (%wt)^{db}	14.5-15.7
Dietary fiber (%wt)^{db}	21.2-21.9
Ether extract (%wt)^{db}	5-5.9
Ash (%wt)^{db}	22.3-22.6
FERTILIZER	
Phosphorus (g/kg)^{db}	1.6-10.3
Potassium (g/kg)^{db}	17.6-158.1
Calcium (g/kg)^{db}	3.6-15.5
Magnesium (g/kg)^{db}	0.4-3.7
BIOACTIVE COMPOUNDS	
Total polyphenolic content (g GAE/kg)^{db}	1.9-50
anthocyanins (g/kg)^{db}	6-11.7
Tartaric acid (%wt)^{db}	24.5-24.7

14.3 Grape AWCB bioactive compounds patent and literature review

The conventional uses of solid wine by-products are animal feed and fertilizer/compost without or with little further processing (Bordiga, 2016). Due to the high content of fibre (and particularly lignin) and the presence of phenolic compounds, grape pomace is poorly digestible. It can be used to feed ruminants, horses and rabbits, in association with feeds having a better nutritive value, but it is not recommended for pigs and poultry, at least not as a source of energy and major nutrients. However, in recent years, there has been a growing interest in the exploitation of wine industry waste in other applications and mainly for the recovery of several compounds such as ***oil*** (12%–17% of the grape seeds weight), ***protein***, ***carbohydrates*** (up to 15% sugars and 30%–40% ***fiber***), ***phenolics/pigments (anthocyanins, flavonols, flavanols, phenolic acids, and resveratrol)*** (0.9%), ***lactic acid***, ***laccase***, ***biosurfactants*** and ***bioemulsifiers***, ***methanol***, ***ethanol***, ***xanthan***, ***citric acid*** and ***tartrate*** (0.05%–0.08%), which are suitable for a range of useful products that can be used in food, pharmaceutical, and agricultural industries (Barba et al., 2016; Bordiga, 2016; Oliveira & Duarte, 2016; Teixeira et al., 2014). Grape pomace is already used industrially for the extraction of ***anthocyanins***. Furthermore, since the mid-2000s, the scientific literature about the feed utilization of grape pomace, which used to be extremely scarce, has been largely dedicated to investigations of grape pomace as a source of beneficial polyphenols and antioxidants, notably for ruminants and poultry (Bordiga, 2016).

Furthermore, Braga et al. in their study presented results ranging from 100 to 150 kg/t (wine lees) and 50 to 75 kg/t (grape pomace) with respect to the potential production of the food preservative ***calcium tartrate***. The average figures for the ***grape pigment*** (enocyanin) varied from 12 kg/t (red wine lees) to 9 kg/t (red grape pomace), the final product being in the form of a liquid concentrate

with 30 g of pigments per kilogram of solution (Braga et al., 2002). Finally, recovery of squalene (squalene obtained in extract 1.69 % wt), which is the biosynthetic precursor of sterols and terpenoids and is present in all cell types, has been investigated (Naziri et al., 2016)

The "HANDBOOK on BIOACTIVE COMPOUNDS from GRAPE PROCESSING RESIDUES", published as a part of BIOACTIVE-NET project, a Specific Support Action (SSA) funded by the European Commission under the 6th Framework Program, collected the most relevant knowledge and technologies related to bioactive compounds in grape processing residues, from techniques of extraction, to application fields and economic feasibility of the extraction (Casas et al., 2008a). The main bioactive compounds extractable from grape processing residues reported in this manual include polyphenols and more specifically ***Resveratrol***, ***Anthocyanins***, ***Procyanidins***, ***Quercetin*** and ***Catechins*** but also ***Grape seed oil***. Additionally, in this handbook the state of competition, regarding companies supplying the aforementioned compounds, has been summarized (Casas et al., 2008a).

Many patents have been issued on recovery of various bioactive compounds from grape AWCB and are summarized in the following tables.

Patent No	US 6,534,678 B1
Publication Date	18/03/2003 (Issue date)
Title	Process for producing tartaric acid from a raw material containing potassium hydrogentartrate.
Description/Abstract	Process for producing tartaric acid from a raw material whose dry matter comprises at least 5 wt% potassium hydrogen tartrate wherein the raw material containing potassium hydrogen tartrate (KHT) is mixed with aqueous potassium hydroxide solution in a first reaction stage, where KHT is virtually completely reacted to form dipotassium tartrate (DKT), the aqueous solution containing DKT is then mixed with added acid in a precipitation stage at a pH value of 2.0 to 5.0, to produce a suspension containing crystallized KHT; crystallized KHT is then separated from the suspension, washed with water, and there is produced a solution at least 80 wt-% saturated with KHT and then the potassium is removed, to obtain an aqueous tartaric acid product solution, from which water is then at least partly removed.
Type of AWCB	*Yeast from wine production*
Recovered high added compound	Tartaric acid

Patent No	US 7,311,837 B2
Publication Date	25/12/2007 (issue date)
Title	Process for the continuous recovery of free tartaric acid from raw materials containing potassium hydrogentartrate.
Description/Abstract	In a process for the continuous recovery of free tartaric acid from raw materials containing potassium hydrogentartrate, the same are mixed with water and the potassium hydrogentartrate is dissolved. The process is improved in that the suspension is decanted, the clarified liquid is refiltered, the filtrate is cooled to crystallization temperature under a vacuum, the potassium hydrogentartrate crystals formed are dissolved, the solution is subjected to a cation exchange, and the tartaric acid solution obtained is evaporated.
Type of AWCB	*wine yeast, tartar, or a byproduct material obtained during wine preparation*
Recovered high added compound	Tartaric acid

Patent No	EP1302251 B1
Publication Date	27/8/2008 (Issue date)
Title	Method for producing a vegetable flour using residues of agroindustrial processes, and method for producing papers and cardboards using said flour.
Description/Abstract	The present invention relates to a method for producing a vegetable flour that uses, as a raw material, vegetable materials that are residues of agroindustrial processes, particularly shells, pits and peels, to a method for producing papers and cardboards featuring particular tactile and visual characteristics that uses the same vegetable flour, and to the use of said flour as filler for plastics, rubbers, panels, pre-shaped components and the like.
Type of AWCB	*Residues of agroindustrial processes, particularly shells, pits and peels (nuts, hazelnuts, peanuts, pistachios, pine seeds, peaches, apricots, plums, prunes, olives, cherries, coffee, dates and the like), (bananas, pears, apples, peaches, apricots, grapes, tomatoes, fennels, artichokes, peas, beans and pineapple and the like).*
Recovered high added compound	Vegetable flour production and papers and cardboards.

Patent No	EP 2308323 A1
Publication Date	13/4/2011 (application date)
Title	METHOD FOR PRODUCING AN EXTRACT OF VITIS VINIFERA HAVING HIGH ORAC VALUES AND THE EXTRACT PRODUCED BY SAID METHOD
Description/Abstract	A method for producing a vitis vinifera extract and the extract produced by said method are disclosed. Said method comprises drying the raw materials of vitis vinifera, dipping them into ethanol to provide an extract, after removing ethanol, partially separating and removing the inactive residue from the extract, passing the extract through macroporous resin, eluting the resins with ethanol to give an intermediate, after removing ethanol, refining the intermediate containing the active components, separating and collecting high concentrations ofpolyphenols and free phenols, affording the extract having high contents ofpolyphenols, and at least more than 10,000 µmol TE/g of ORAC values, drying them to give a desired powder, ultimately testing and packing.
Type of AWCB	*grape fruit, grape skin, grape seed*
Recovered high added compound	polyphenols
Details/methodology applied	solvent extraction, resin adsorption

Patent No	EP 0096481 A1 and EP 0096481 B1, 19871125
Publication Date	21/12/1983 (publication date)
Title	Extraction and intensification of anthocyanins from grape pomace and other material
Description/Abstract	Anthocyanin extracts, known as enocianina, extracted from grape pomace with sulphure dioxide, are treated with enzymes, e.g. pectinase and amylase, to reduce or remove solids from the extract. The colour of the enocianina can be intensified by treatment of the clarified extract with acetaldehyde.
Type of AWCB	*grape pomace*
Recovered high added compound	Anthocyanin extracts
Details/methodology applied	treatment with enzymes

Patent No	EP 1937091 B1 20150429
Publication Date	29/04/2015 (publication date)
Title	Grape extract, dietary supplement thereof, and processes therefor
Description/Abstract	A purified polyphenol extract from grapes produced according to Process A or Process B, wherein Process A comprises: (1) contacting a member selected from the group consisting of whole grapes, grape seeds, grape pomace, and mixtures thereof with water at an elevated temperature to obtain a crude grape-water extract; and (2) treating the crude grape-water extract with a live culture selected from the group consisting of yeast, bacteria, fungi, and mixtures thereof at an elevated temperature to obtain the purified polyphenol extract; wherein Process B comprises: (1) contacting a member selected from the group consisting of whole grapes, grape seeds, grape pomace, and mixtures thereof with water at an elevated temperature to obtain a crude grape-water extract; and (2) treating the crude grape-water extract with a tannase enzyme at an elevated temperature to obtain the purified polyphenol extract, wherein the extract comprises 2% by weight or less epicatechin-gallate terminal units and 12% by weight or less epicatechin-gallate extension units.
Type of AWCB	grape seeds, grape pomace and mixtures
Recovered high added compound	purified polyphenol extract
Details/methodology applied	water extraction and enzymes

Patent No	United States Patent 6544581
Publication Date	04/08/2003 (publication date)
Title	Process for extraction, purification and enrichment of polyphenolic substances from whole grapes, grape seeds and grape pomace
Description/Abstract	The present invention provides a novel process for the extraction, purification and concentration of polyphenolics from whole grapes, grape pomace and grape seeds. The liquid and powdered products of the present processes are particularly rich in polyphenolics, including anthocyanins, catechin monomers and their oligomers. These oligomers are frequently referred to as procyanidins in the field of polyphenol chemistry.
Type of AWCB	whole grapes, grape pomace and grape seeds.
Recovered high added compound	polyphenolics
Details/methodology applied	water extraction and resins

Patent No	United States Patent 6479081
Publication Date	11/12/2002 (publication date)
Title	Method for obtaining grape tannin, resulting tannin and uses
Description/Abstract	The invention concerns a method for obtaining grape pomace and/or seed tannin, comprising steps which consist in: (a) from fresh black or white grapes pomace and/or seed, carrying out a solid-liquid extraction of raw tannin fraction in an aqueous solvent; (b) eliminating the first solvent from the resulting extract to obtain a concentrate of the raw tannin fraction; and (c) purifying the raw tannin fraction to obtain said tannin: The method is characterised in that in step (a) sulphite water (H2O+SO2) is used as solvent, and in step (c) the raw tannin fraction is purified by selectively adsorbing the tannin polyphenol compounds on resin and by subsequent filtering. The invention also concerns the resulting tannin and its uses in particular as endogenous tannin in wine.
Type of AWCB	grape pomace and/or seed
Recovered high added compound	tannin polyphenols compounds
Details/methodology applied	solvent extraction and resins

Patent No	United States Patent Application 20070003644 A1
Publication Date	1/4/2007 (application date)
Title	Concentrated polyphenolic product and process for making the same
Description/Abstract	A process for preparing a concentrated polyphenolic product is disclosed. The process generally includes the extraction of polyphenoliccompounds from grape material using a solvent containing ethanol and water, and further includes steps of extract filtration and extract concentration to provide either a liquid polyphenolic concentrate or a powdered polyphenolic extract. The concentrated polyphenolic product may be used in food products and dietary supplements to afford the health benefits of consuming red wine. An additional process for preparing a concentrated ethanol product with a prefermentation step in addition to a concentrated polyphenolic product also is disclosed.
Type of AWCB	grape pomace, grape seeds, grape clusters, a grape fermentation product, and combinations thereof
Recovered high added compound	concentrated polyphenolic product
Details/methodology applied	extraction with ethanol/water

Patent No	United States Patent Application 20050129790 A1
Publication Date	16/06/2005 (publication date)
Title	Polyphenol-containing stem and vine extracts and methods of use
Description/Abstract	The present invention relates to extracts of polyphenolic-containing stems and/or vines. There are provided methods for extractingpolyphenols from polyphenolic-containing stems and vines as well as extracts produced by these methods. In other aspects, the invention provides dietary supplements, nutraceutical and pharmaceutical compositions containing the stem and/or vine extracts and methods of using the extracts to prevent or treat coronary artery disease and other diseases.
Type of AWCB	mixture comprising polyphenolic-containing stems, vines, or combinations thereof
Recovered high added compound	extract containing polyphenolic compounds
Details/methodology applied	solvent extraction and chromatography

Patent No	European Patent Application EP2875822 A4 and WO 2014013122 A1
Publication Date	15/6/2016, 23/01/2014
Title	POLYPHENOL EXTRACT FROM WHITE-GRAPE RESIDUE
Description/Abstract	The invention relates to a polyphenol extract from white-grape residue. The invention relates to a straightforward method with few steps for obtaining extracts having anti-oxidant and anti-bacterial properties from white-grape residue. Due to the characteristics white-wine production, which is carried out by exclusively fermenting the must squeezed from the grapes, without any contact with the remains of pulp, skin and seeds, the residue generated during the method (white-grape bagasse) is very rich in polyphenols, since smaller amounts of same are transferred to the wine. The proposed procedure uses non-contaminating materials, takes place under gentle conditions and prevents the obtained eluates from containing suspended solids, enabling extracts rich in bioactive polyphenols to be obtained, which can be used on an industrial scale, essentially in the cosmetic, pharmaceutical and/or food industries.
Type of AWCB	white grape residue
Recovered high added compound	polyphenol extract
Details/methodology applied	solvent extraction under mild conditions

Patent No	United States Patent 7226627
Publication Date	05/06/2007 (Issue date)
Title	Grapeseed, cold-pressed grape oil, crushed grape and grape flour
Description/Abstract	The present application relates to a process for preparing cold-pressed grape seed oil, and to food, food supplements, food additives, animal food, animal food supplements, medicaments and cosmetics comprising the cold-pressed grape seed oil prepared by said process, and to the enrichment of various media with active substances, especially cyclic polyphenols, from the meal of the crushed seeds obtained in the process.
Type of AWCB	grape seeds
Recovered high added compound	grape oil
Details/methodology applied	cold pressing

15.Tomatoes

Tomato (*Lycopersicon esculentum*) is one of the major vegetable crops around the world, used as salad, food preparation, and as juice, soup, puree, ketchup or paste (Kaur et al., 2008). Tomato is a key element of the Mediterranean diet and the second most important vegetable crop worldwide, being consumed either fresh or in the form of processed products (Pinela et al., 2016).

The demand for tomato processing arises from a need to preserve the product for cooking purposes out of season. Traditionally, the most important tomato processed products are tomato concentrates: passata, puree, paste. The by-products produced during the tomato transformation process are defined as Secondary Raw Materials. Council Directive 96/25/EC, legislates the re-use in particular of "tomato pulp obtained by pressing tomatoes during the production of tomato juice" for animal feeding. Currently the pomace is sold, transferred to other companies without financial exchange or removed with payment from the tomato processors. Existing research has identified that tomato pomace still constitutes an excellent source of nutrients such as carotenoids, proteins, sugars, fibres, waxes and oils (75% unsaturated fatty acids) which might then be used in food applications and in the cosmetic industry (bioactive-net, 2008).

The industrial processing of tomato namely tomato pomace, seeds and peels, representing 10-40% of total processed tomatoes (Strati & Oreopoulou, 2011). These by-products represent a major disposal problem for the industry, intended mainly for animal feed or fertiliser (Knoblich et al., 2005), whereas they usually constitute a promising source of compounds that can be used for their nutritional properties and biological potential (Pinela et al., 2016; Strati & Oreopoulou, 2011) .

Tomato pomace is currently disposed of or used as animal feed, but the abundance of lycopene in the peel suggests the possibility of utilizing it as a cheap source of lycopene, providing also revenues that could partially off-set the cost for further effective management of the remaining wastes (Papaioannou & Karabelas, 2012). According to Knoblich et al. (2005), the carotenoid content of dry tomato by-products collected from a commercial tomato processing plant amounted to 793.2 and 157.9 $\mu g \cdot g^{-1}$, for peel and seed by-product, respectively (Knoblich et al., 2005).

Tomato byproducts have a high moisture content, which incurs a drying expense if they are to be used in the dry form. Wet byproduct can be ensiled with corn plants and the resulting silage supported good milk production. On a dry matter basis, the tomato byproduct contained 200 g kg^{-1} crude protein and 439 g kg^{-1} acid detergent fiber. Dry tomato byproduct was included in lamb diets at 100, 200 or 300 g kg^{-1}. The results suggested that tomato byproduct was equivalent to soybean meal as a protein source (Knoblich et al., 2005).

Figure 15.1: Tomato fruits (left photo) and tomato plant (right photo) (feedipedia, 2016).

15.1 Tomato pomace

Tomato pomace constitutes the major part of the waste that comes from the pulper. The wet pomace contains 33% seed, 27% skin and 40% pulp while the dried pomace contains 44% seed and 56% pulp and skin. Pomace consists of skin that could be utilized for extracting lycopene (Kaur et al., 2008). Skin can be separated by a floatation-cum-sedimentation technique, from other constituent seed and fibrous matter, to facilitate better pigment extraction (Kaur et al., 2005). Most of the lycopene is associated with the water-insoluble fraction and the skin (Sharma & Le Maguer, 1996). Results indicate that 72–92% of the lycopene is associated with the water insoluble fraction and the skin. Therefore, skin extracts are especially rich in lycopene. The fresh skin has a high moisture content that makes it susceptible to microbial proliferation and spoilage. Therefore, skin can be preserved by drying and then used for lycopene extraction (Kaur et al., 2006).

The main physicochemical characteristics of tomato pomace are summarized in Table 15.1.

Table 15.1: Summary of main physicochemical characteristics of tomato pomace (ECN, 2016; feedipedia, 2016; Kaur et al., 2008; Sabio et al., 2016).

PHYSICOCHEMICAL PROPERTIES	MEAN VALUE
ENERGY	
Higher Heating Value (HHV) (MJ/kg)	22.8
Fixed Carbon (%wt)^{db}	10.8
Volatile Matter (%wt)^{db}	85.1
Ash (%wt)^{db}	4.6
Moisture (% wt)^{am}	6.5
Carbon (%wt)^{db}	58.0
Oxygen (%wt)^{db}	33.2
Hydrogen (%wt)^{db}	7.5
Nitrogen (%wt)^{db}	2.23
Sulfur (%wt)^{db}	0.2
FODDER	
Dry matter (%wt)^{am}	93.5
Crude protein (%wt)^{db}	21.0
Crude fiber (%wt)^{db}	39.0
Neutral Detergent Fiber (NDF) (%wt)^{db}	54.9
Acid Detergent Fiber (ADF) (%wt)^{db}	44.3
Lignin (%wt)^{db}	25.4
Ether extract (%wt)^{db}	11.9
Ash (%wt)^{db}	5.2
Gross energy (MJ/Kg)	21.8
FERTILIZER	
Nitrogen (g/kg)^{db}	33.6
Phosphorus (g/kg)^{db}	3.6
Potassium (g/kg)^{db}	8.7
Calcium (g/kg)^{db}	4.4
Magnesium (g/kg)^{db}	2.2
VALUE-COMPOUNDS	
Lycopene (g/kg)^{db}	0.02

15.2 Tomato wastewater

Tomato processing industries consume plenty of water resulting in great amounts of wastewater effluents. The average amount of wastewater produced in a medium-sized tomato processing factory is about 300 M^3/d. Wastewater from the tomato industry is characterised by a large amount of suspended solids from various stages of processing and consequently high chemical oxygen demand (COD). In the tomato processing industry, wastewater is comprised of water from tomato washing and trimming (47% total wastewater flow), effluent from scalding and peeling (32% total wastewater flow), canning water (19% total wastewater flow), and concentrator wastewater flows from tomato paste production (2% total wastewater flow) (Alghooneh et al., 2016). The effluent coming directly from cleaning, sorting, and moving tomatoes has a red color, is highly malodorous and polluted mainly by organics, suspended solids, and ground particles (Iaquinta et al., 2009).

Additionally, tomato packinghouses use freshwater (adding chlorine sanitizers in dump tanks) to rinse, wash, and sanitize field-harvested tomatoes before packing each day. The amount of water required depends on the type of tomato packed (Chahal et al., 2011).

One of the important issues with this kind of wastewater streams is that it is seasonal (the tomato harvesting lasts 90 d a year) and deteriorates very quickly (Alghooneh et al., 2016).

The main physicochemical characteristics of tomato processing wastewater are summarized in Table 15.2.

Table 15.2: Summary of main physicochemical characteristics of tomato wastewater (Chahal et al., 2011; Iaquinta et al., 2009; Maninder et al., 2012).

PHYSICOCHEMICAL PROPERTIES	MEAN VALUE
FERTILIZER	
Phosphorus (g/kg)^{db}	0.0041
Potassium (g/kg)db	0.0345
Calcium (g/kg)^{db}	0.0515
Magnesium (g/kg)^{db}	0.126
WATER	
pH	6.54
Conductivity (mS/cm)	2.24
Total Suspended Solids (mg/L)	1400
TOC (mg/L)	340
COD (mg/L)	4100
Total Kjednal Nitrogen (TKN) (mg/L)	151
Total Phosphorus (TP) (mg/L)	47.5

15.3 Tomato AWCB bioactive compounds patent and literature review

Lycopene, a bright red pigment, belongs to the carotenoid family and has received great interest due to its various biological activities. Lycopene acts as a potent antioxidant and contributes towards reducing the risk of chronic diseases by protecting cells against oxidative damage (Poojary & Passamonti, 2015). Studies have also revealed its protective effect on cardiovascular (Arab & Steck, 2000) and coronary heart diseases (Clinton, 1998). It inhibits low-density lipoprotein oxidation and helps to reduce cholesterol levels in the blood (Rao & Agarwal, 1999). Lycopene exhibits anti-inflammatory activity by inhibiting the activation of inducible nitric oxide synthase proteins (Rafi, Yadav, & Reyes, 2007). In the food industry, lycopene from tomato products is used as a food additive to enhance storage stability, nutritional properties and health benefits (Østerlie & Lerfall, 2005).

Though lycopene is found in watermelon, pink grapefruit, guava, and rosehip, the richest source is tomato. Not only can it be extracted from fresh tomato, but adequate quantities can also be obtained from tomato processing waste or tomato pomace (Zuorro et al., 2011). The lycopene content present in the skin fraction of tomato pomace is about 5 times higher than in the pulp (Papaioannou & Karabelas, 2012; Poojary & Passamonti, 2015).

Several advanced methods to extract lycopene from tomato have been described, amongst them extraction with organic solvents (such as hexane, acetone, ethanol, chloroform etc.), supercritical fluid extraction (Zuknik et al., 2012), ultra- sound assisted extraction (Eh & Teoh, 2012), ultrasound-micro- wave extraction (Lianfu & Zelong, 2008), and enzyme assisted extraction etc. (Poojary & Passamonti, 2015; Zuorro et al., 2011).

Many patents have been issued on recovery of lycopene and various other bioactive compounds from tomato AWCB and are summarized in the following tables.

Patent No	US 9434886 B2, CN103354721A, CN103354721B, US20140316175, WO2013097055A1
Issue Date	31/12/2011
Title	Process for extracting lycopene
Description/Abstract	A process for extracting lycopene, comprising the following steps: pressing and dehydrating tomato pomace which is the by-products of tomato processing production, then drying it to control the water content in the range from 10% to 20%; crushing the dried tomato pomace, and separating tomato skins and tomato seeds by air blast process, granulating the separated tomato skins and extracting them, then purifying by removing impurity from the extracted lycopene with active carbon. The process uses the by-products of tomato production as raw material, thus increasing the utilization ratio of tomatoes; the way of separating the seeds and skins after dehydrating and drying can save water and reduce the discharge of pollutant; the addition of antioxidant in the process of drying avoids the impact of high temperature on lycopene; extracting after granulating the tomato skins significantly increases the extracting efficiency; treating the extracting solution with active carbon effectively can remove the pesticide residues, impurities, odor etc., and thus increase the quality of lycopene.
Type of AWCB	Tomato pomace
Recovered high added compound	Lycopene

Patent No	CN 101085988 A
Issue Date	12/12/2007
Title	Production process of biological enzyme concentration method for extracting tomatine from tomato peel slag
Description/Abstract	The invention relates to a process of extracting lycopene from dehydrated tomato pulp with enzyme concentration method, belonging to biological technique. The raw material of dehydrated tomato pulp is leftover bits and pieces of catsup production, the enzyme and multistep enrichment are employed to enrich lycopene protein complex, then extracts with acetone dissolvent, the extract rate is not less than 45mg/ 100g. The invention is characterized by low consumption of acetone dissolvent and low production cost.
Type of AWCB	Tomato peel
Recovered high added compound	Tomatine

Patent No	EP 1103579 B1, DE69903645D1, DE69903645T2, EP1103579A1, WO2001038443A1
Issue Date	23/10/2002
Title	A process for the extraction of lycopene
Description/Abstract	The present invention concerns a process for the extraction of lycopene. Lycopene,which belongs to the family of the carotenoids, is an important natural food coloring agent in the red region. Lycopene is present naturally in a number of fruits, primarily in tomatoes and watermelon. It is possible to extract this coloring agent by different extraction processes. The US Patent No. 4'781'936 for example, concerns already a process for isolating a yellow coloring component from tomato peel, which comprises exposing tomato peel to a non-toxic polar extraction solvent, said solvent being ethanol, lower alcohols, ethers, ketones and aldehydes. The pure lycopene compound has more a red color, whereas the product obtained by this above mentioned process allows the production of a final compound having more a yellow color. The reason of this difference is that according to this process, it is not possible to obtain a real pure lycopene compound, but more a mixture of the different carotenoids present in the basic raw material. The European Patent Application EP 0 818 225 A relates to a process for the preparation of pure lycopene or of lipophilic extracts containing it from tomatoes. This process involves extraction with aliphatic or aromatic hydrocarbons or water-immiscible solvents in the presence of phospholipids as surfactant and stabilizing agents.
Type of AWCB	Tomato pomace
Recovered high added compound	Lycopene

Patent No	CN 101449801 A
Issue Date	10/06/2009
Title	Lycopene extraction method from tomato peel
Description/Abstract	The invention relates to a method for extracting lycopene from tomato peel residue, which includes steps of (1) carrying out peel and seed separating process for tomato peel residue to obtain tomato peel and tomato seed; (2) crushing the obtained tomato peel to obtain tomato peel slurry; (3) pre-treating the tomato peel slurry, dewatering and removing impurities; (4) adding the treated tomato peel slurry into organic solvent to carrying out extracting, and collecting extract; and (5) concentrating in vacuum to obtain lycopene oil resin. The method for extracting lycopene provided by the present invention uses tomato processing industry waste-tomato peel residue as raw material to obtain lycopene product with high content. The method is easy, has wide raw material source and low cost, is favourable to supple raw material source of lycopene production, avoids resource waste and environmental pollution, increases economic benefit of tomato industry, and has wide development prospect.
Type of AWCB	Tomato peel
Recovered high added compound	Lycopene

Patent No	CN 1799674 A
Issue Date	12/07/2006
Title	Supercritical carbon dioxide method for extracting lycopene from dry powder of tomato peel
Description/Abstract	The invention discloses an above-critical carbon dioxide extraction method of lycopene in the dry powder of tomato pericarp, which is characterized in following steps: arranging dry powder of tomato pericarp in the extraction kettle; importing the mixed liquid of above-critical CO2 liquid and extraction assistant; controlling the extraction pressure in 28-50Mpa, the extraction temperature in 45-70Deg. C, the extraction time in 1.5-5 hours, the cost of carbon dioxide in 20-60 times (carbon dioxide volume/material weight); the extraction assistant as lower alcohol and its cost at 5-30% (extraction assistant volume/material weight); after extraction, reducing pressure and separating the extracted material, and the carbon dioxide will be feedback to the CO2 source. Said method is simple with high efficiency, high productivity and high application value.
Type of AWCB	Tomato peel
Recovered high added compound	The tomato peel powder added to the extraction kettle lid was closed through a supercritical carbon dioxide fluid extraction cycle. Its conditions for extraction pressure 30MPa, extraction temperature 65 ℃extraction time was 3 hours. The amount of carbon dioxide: 40 times (carbon dioxide volume / weight of the material), to help put agents Category: help raise the dosage of ethanol, 20% (assisted extraction agent volume / weight of the material). Was added at a flow rate of: 50Kg ~ 100Kg / hr. After the extraction is complete, the pressure was reduced to 4 ~ 6Mpa, isolated substance is extracted, the extraction rate of more than 65%, to obtain oleoresin extract 4Kg. Extract lycopene content: 1.8%.

Patent No	CN 101121631 B
Issue Date	02/06/2010
Title	Method for fast extracting lycopene
Description/Abstract	The present invention discloses a method to extract tomato element fast, which belongs to the food material technology region. The present invention is to extract the tomato element from the materialabundant of tomato element; the material including tomato element is treated firstly; and the method uses an ultrasonic / microwave cooperation technology to assistant the solution refluence to extract the tomato element; and the tomato element oil resin will be obtained after being condensed; finally, the solution is callback. The present invention has the advantages of simple step; the extraction time can be shortened greatly so as to avoid the losing of the tomato element in the extraction process; the extraction ratio is much higher even up to 97 percent; the extraction process is in a sealing system with much less solution consumption and much lower cost; besides, the method can enhance the production safety; the method uses the microwave as the heat resource, so the energy can be functioned on the extraction system directly; the method is characterized in that: the method can decrease the consumption waste and save energy.
Type of AWCB	Tomato pomace
Recovered high added compound	Lycopene

Patent No	CN 101987809 A
Issue Date	23/03/2011
Title	Production technology for extracting purified lycopene from tomato waste residue
Description/Abstract	The invention discloses production technology for extracting purified lycopene from tomato waste residue serving as a raw material, which comprises the following steps of: firstly, separating tomato skin from tomato seeds; secondly, extracting lycopene extract from the tomato skin by subcritical extraction technology; and finally, separating and purifying the lycopene in the lycopene extract by using a silica gel short column. The extraction ratio of the lycopene is 80 to 90 percent, and the lycopene content of extracted lycopene oleoresin can reach 6 to 50 percent.
Type of AWCB	Tomato waste residue
Recovered high added compound	Lycopene

Patent No	CN 1298904 A, CN1121455C
Issue Date	13/06/2001
Title	Process for preparing crystal lycopene and/or lycopene oil resin from tomato paste
Description/Abstract	The present invlention relates to an industrial prodn. method of lycopene crystal containing more than 10% of lycopene and/or lycopene oleoresin containing more than 2% of lycopene by using tomato paste as main raw material. It includes the following steps: (1) use water to extract soluble component in tomato paste; (2) separate tomato clear juice to obtain potato paste dreg; (3) the tomato pastedreg is washed with alkali liquor, then dried and ground; (4) use organic solvent to extract lycopene; (5) filter out containing lycopene; (6) the liquid extract is flash-evaporated and concentrated,lower temperature to crystalize lycopene; (7) separate and dry lycopene crystal to obtain the lycopene product containing more than 10% of lycopene.
Type of AWCB	Tomato paste
Recovered high added compound	Lycopene crystal, lycopene oil resin

Patent No	CN 101928473 B
Issue Date	25/09/2013
Title	Method for producing lycopene oleoresin
Description/Abstract	The present invention relates to a method of lycopene oleoresin extracted. In this method, dehydration tomato pieces, diced tomatoes or tomato sauce production by-products as raw tomato pomace, the choice of a suitable hydrofluorocarbon and a co-solvent for the extraction solvent, using subcritical extraction method to extract lycopene oleoresin. The method has simple process, less investment in equipment, less environmental pollution, low energy consumption, high production efficiency per unit of time.
Type of AWCB	Tomato pomace
Recovered high added compound	Lycopene oleoresin

Patent No	US 7572468 B1
Issue Date	11/08/2009
Title	Extraction of carotenoids from plant material
Description/Abstract	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 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.
Type of AWCB	Tomato pomace, tomato peel, tomato skin
Recovered high added compound	Carotenoids

Patent No	WO 2014095342 A1, CA2893888A1, CN104902763A, EP2934179A1, EP2934179B1, US20150335054
Issue Date	26/06/2014
Title	A tomato fibre composition and method for the preparation thereof
Description/Abstract	One aspect of the invention relates to tomato fibre composition having a dry matter content of at least 1 wt.%, wherein at least 80 wt.% of said dry matter is water-insoluble, said fibre composition comprising, by weight of dry matter:15-50% cellulose; 5-45% pectin; 0-10% of monosaccharides, said monosaccharides being selected from fructose, glucose and combinations thereof; and 0.003-1% lycopene; wherein the fibre composition contains less than 60% pectin by weight of cellulose. The tomato fibre composition of the present invention has excellent water structuring properties. Another aspect of the invention relates to a method of manufacturing a product selected from a foodstuff, a beverage and a nutritional formulation, said method comprising incorporating into said product the aforementioned tomato fibre composition. The invention further provides a process of manufacturing a tomato fibre composition
Type of AWCB	Tomato pomace
Recovered high added compound	Tomato fibre

Patent No	CN 102660380 A
Issue Date	12/09/2012
Title	Method for extracting lycopene oil with dried tomato skin as raw material
Description/Abstract	The invention discloses a method for extracting lycopene oil with dried tomato skin as a raw material, comprising the following steps of: crushing the dried tomato skin which is obtained by carrying out dehydration drying and dry skin-seed separation on skin-seed residues from a ketchup factory to be used as the raw material, so as to obtain dried tomato skin powder; carrying out normal-pressure solvent extraction on the dried tomato skin powder to obtain lycopene oil extraction liquor; before recovering the solvent, regulating the content of crude fat in the lycopene oil extract liquor and recovering the solvent through normal-pressure evaporative condensation to obtain crude lycopene oil; carrying out vacuum desolventizing refining on the crude lycopene oil to obtain the lycopene oil; and removing the solvent residue in the crude lycopene oil by using a centrifugal thin-filmed vacuum evaporator. The method has the beneficial effects that the industrial production of lycopene oil extracted from tomato skin is easy to realize; the active ingredients of the tomato skin-seed residue are fully utilized; production of pure lycopene oil which has high lycopene content and conforms to hygienic standard is facilitated; and the method is low in investment and production cost and is beneficial for environment protection.
Type of AWCB	Tomato skin
Recovered high added compound	Lycopene oil

Patent No	CN 102020331 A
Issue Date	20/04/2011
Title	Energy-saving and environmentally-friendly processor for purifying and dewatering tomato sauce waste water
Description/Abstract	The technical plant of the invention discloses a magic energy-saving and environmentally-friendly processor for purifying and dewatering tomato sauce waste water, which has a structure that water enters from top to bottom, a special filter screen is used for adsorbing superfine substances for straining, and the strained superfine substances are put on the bottom of a processor tank; finally, the high-density chroma waste water generated through producing tomato sauce is processed.
Type of AWCB	Tomato wastewater

16.Olives fruits

The olive tree is member of the family *Oleaceae*, which comprises 30 species such as jasmine, ash, lilac, and privet. The only edible species is *Olea europeaea L.*, which is cultivated for its plump, fleshy and oil-containing fruits (Niaounakis & Halvadakis, 2006). Olive cultivation is widespread throughout the Mediterranean region and is important for the rural economy, local heritage, and environment. The countries around the Mediterranean basin and in the Middle-East provide 98% of the total surface area for olive tree culture and total productive trees, and 99% of the total olive production, with Spain being first regarding total culture surface and number of productive trees, followed by Italy and Greece (these three countries have the 75% of the total production).

The traditional press extraction method as well as the continuous three-phase decanter process, which is most widely used for the production of olive oil, generate three products: olive oil (20%) and two streams of waste: a wet solid waste (30%) called ''crude olive cake'' or ''olive husk'' and an aqueous waste called ''olive mill wastewater'' or ''olive mill effluent'' or ''alpechin'' (50%) (Oreopoulou & Russ, 2007). It is estimated that for every 100 kg of treated olives, 35 kg of solid waste (olive cake) and from 55 to 200 L liquid waste are produced depending on the oil extraction process (Figure 16.1) (feedipedia, 2016; Krishnaswamy et al., 2014; Niaounakis & Halvadakis, 2006; Roselló-Soto et al., 2015). Essentially, the OMWW composition is water (80–83%), organic compounds (15–18%), and inorganic compounds (mainly, potassium salts and phosphates) 2%, and it varies broadly depending on many parameters such as olive variety, harvesting time, climatic conditions, oil extraction process, etc. (Niaounakis & Halvadakis, 2006).

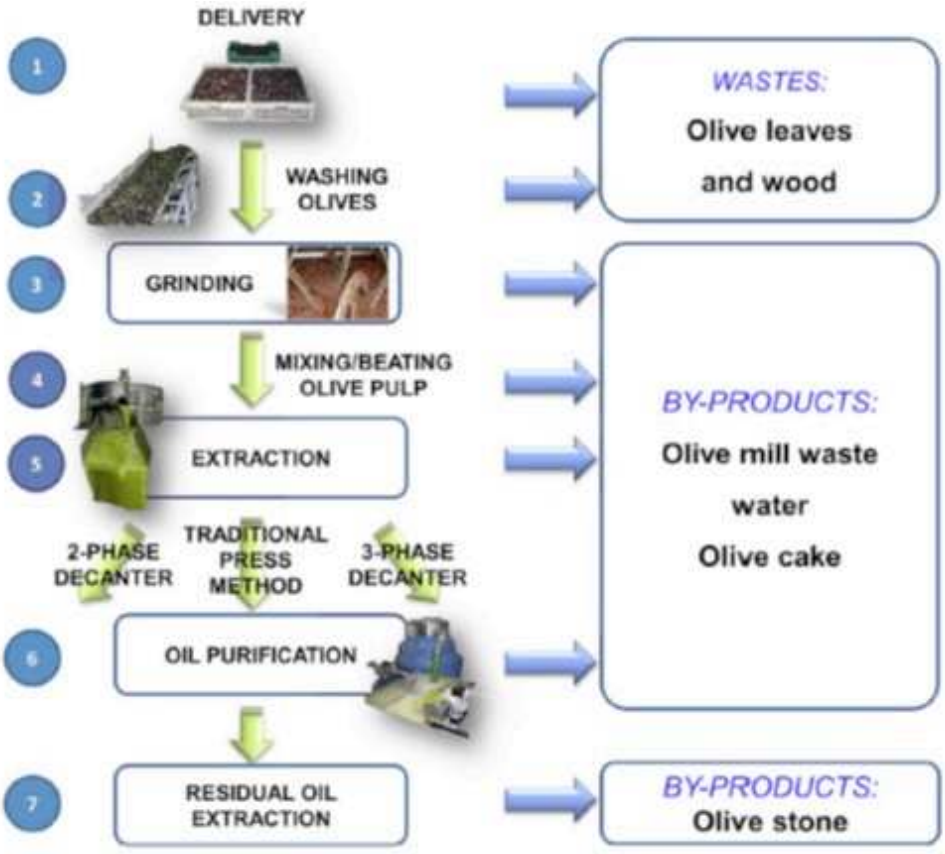

Figure 16.1: Wastes and by-products generated during olive oil production process (Roselló-Soto et al., 2015).

16.1 Olive mill waste water (OMWW)

The OMWW composition is not constant - both qualitatively and quantitatively- and it varies according to:

i. composition of the vegetation water;
ii. olive oil extraction process;
iii. storage time.

As far as its chemical synthesis is concerned, the OMWW is characterised by the following special features and components (Niaounakis & Halvadakis, 2006; Oreopoulou & Russ, 2007):

- intensive violet-dark brown up to black color,
- strong specific olive oil smell,
- high degree of organic pollution (COD values up to 220 g/L), and a COD to BOD_5 ratio between 2.5 and 5 (hardly degradable).
- pH between 3 and 6 (slightly acid),
- high electrical conductivity,
- high content of polyphenols (0.5–24 g/L), which are not easily biodegradable and toxic to most microorganisms.

In terms of pollution effect, 1 m^3 of OMWW is equivalent to 100 – 200 m^3 of domestic sewage. Its uncontrolled disposal in water reservoirs leads to severe problems for the whole ecosystem and especially for the natural water bodies (ground water reservoirs, surface aquatic reservoirs, seashores, and sea). The most visible effect is discoloration, a result of oxidation and subsequent polymerization of tannins. OMWW also has a considerable content of reduced sugars, high phosphorus content, and phenolic load that has a toxic action to some organisms. Attempts to alleviate the problem, especially in the major olive oil-producing countries, are more than 50 years old; yet, there has been little success in finding an environment friendly and economically viable solution to be generally adopted. The problems mentioned above make the technological design of an OMWW treatment plant difficult. Factors that make the economic design of such a plant much more difficult is the intense and seasonal production of the waste (maximum 4 months each winter), the great variability both of synthesis and quantity, the high regional scattering of olive mills, and the small size of the majority of them in the olive oil producing regions (Oreopoulou & Russ, 2007). The main physicochemical characteristics of OMWW are summarized in Table 16.1.

Table 16.1: Summary of main physicochemical characteristics of OMWW (feedipedia, 2016; Kapellakis et al., 2008; Niaounakis & Halvadakis, 2006).

PHYSICOCHEMICAL PROPERTIES	RANGE	COMMENTS
ENERGY		
Moisture (% wt)^{am}	80-92	
FODDER		
Crude protein (%wt)^{db}	5.8	Average values from various samples
Crude fiber (%wt)^{db}	0.1	Average values from various samples
Neutral Detergent Fiber (NDF) (%wt)^{db}	0.5	Average values from various samples
Acid Detergent Fiber (ADF) (%wt)^{db}	0.9	Average values from various samples
Lignin (%wt)^{db}	0.6	Average values from various samples
Ether extract (%wt)^{db}	1.2	Average values from various samples
Ash (%wt)^{db}	14.3	Average values from various samples
Gross energy (%wt)^{db}	15.3	Average values from various samples
FERTILIZER		
Phosphorus (mg/L)	950-2470	
Potassium (g/L)	2.9-9.1	
Calcium (mg/L)	69-162	
Magnesium (mg/L)	90-194	
WATER CHARACTERISTICS		
pH	4.2-7	
Total Solids (mg/L)	14000-126000	
Total Suspended Solids (mg/L)	400-24000	
COD (mg/L)	60000-180000	
BOD_5 (mg/L)	20000-100000	
Total Nitrogen (TN) (mg/L)	1000-3000	
Total Kjeldahl Nitrogen (TKN) (mg/L)	9-3200	
BIOACTIVE COMPOUNDS		
polyphenols (g GAE/L)	0.5-24	
Hydroxytyrosol (mg/L)	127-353	
Sugars (% wt)^{db}	0.5-2.6	
Organic acids (% wt)^{db}	0.2-0.4	
Polyalcohols (% wt)^{db}	0.3-0.5	
Tannins (% wt)^{db}	0.2-0.5	

16.2 Crude olive cake

The solid waste (crude olive cake) is the residue that remains after the first pressing of the olives and is a mixture of olive pulp, crushed stones, skin, water (~ 25%) and a remaining quantity of oil (4.5–9%). The exhausted olive cake is a dry material (8–10% moisture) composed of ground olive stones and pulp. The exhausted olive cake has a high lignin, cellulose, and hemicellulose content (Niaounakis & Halvadakis, 2006). Both crude and exhausted olive cake can be used as solid fuels (due to their high heating value), for animal feed supplement, or return to the olive grove as mulch. The

crude olive cake should be distributed to animals or ensiled as soon as possible before its spoilage. However, extracting oil from olive cake remains economically a better choice than its distribution to animals later on (Oreopoulou & Russ, 2007; Roselló-Soto et al., 2015), taking also into account the low nutritive value of this by-product.

The commercial value of olive cake depends on its oil and water content, thus, the three-phase pomace, with low moisture content, has a better commercial value than the one obtained in a two-phase process system (Kapellakis et al., 2008). Nutrient composition varies greatly between different olive by-products. This may be due to olive variety or environmental conditions: for instance, during dry years, stones may represent up to 70% of the fruit. Mineral content depends on harvesting methods: 7-8% when the fruits are picked directly from the tree, 11% when they are collected with a net, and 16-24% when the olives are dropped onto the ground before harvesting. However, these values are not usually found in olive oil manufacture since olives are washed before crushing. Crude protein, crude fibre and crude fat also depend on extraction method (2-phase or 3-phase process) as well as on the method of de-stoning. Crude fibre is mostly constituted of lignin, which limits the feed value of olive cake (feedipedia, 2016; Krishnaswamy et al., 2014). The main physicochemical characteristics of the various forms of solid waste generated during olive oil production are summarized in Table 16.2.

Table 16.2: Summary of main physicochemical characteristics of solid olive cakes (ECN, 2016; feedipedia, 2016; Niaounakis & Halvadakis, 2006).

PHYSICOCHEMICAL PROPERTIES	RANGE	COMMENTS
ENERGY		
Higher Heating Value (HHV) (MJ/kg)	22	
Lower Heating Value (LHV) (MJ/kg)	20.6	
Fixed Carbon (%wt)^{db}	17.3	
Volatile Matter (%wt)^{db}	77.2	
Ash (%wt)^{db}	5.6	
Moisture (% wt)^{am}	6.9 (dry), 25-57 (fresh)	
Carbon (%wt)^{db}	51.4	
Oxygen (%wt)^{db}	34.4	
Hydrogen (%wt)db	6.6	
Nitrogen (%wt)^{db}	2.0	
Sulfur (%wt)^{db}	0.11	
FODDER		
Dry matter (%wt)^{am}	77.8-88.7	Range for the various forms of olive cakes (average values from various samples)
Crude protein (%wt)^{db}	7.8-12.7	Range for the various forms of olive cakes (average values from various samples)
Crude fiber (%wt)^{db}	21.1-38.1	Range for the various forms of olive cakes (average values from various samples)
Neutral Detergent Fiber (NDF) (%wt)^{db}	48.9-70.5	Range for the various forms of olive cakes (average values from various samples)
Acid Detergent Fiber (ADF) (%wt)^{db}	37.8-56.1	Range for the various forms of olive cakes (average values from various samples)
Lignin (%wt)^{db}	20.6-27.2	Range for the various forms of olive cakes (average values from various samples)
Ether extract (%wt)^{db}	3-34.5	Range for the various forms of olive cakes (average values from various samples)

PHYSICOCHEMICAL PROPERTIES	RANGE	COMMENTS
Ash (%wt)[db]	5.3-14.5	Range for the various forms of olive cakes (average values from various samples)
Gross energy (%wt)[db]	18.4-25.4	Range for the various forms of olive cakes (average values from various samples)
FERTILIZER		
Phosphorus (mg/L)	0.8-2.2	
Potassium (g/L)	5.1-14.4	
Calcium (mg/L)	6.3-15.2	
Magnesium (mg/L)	0.4-1.4	
BIOACTIVE COMPOUNDS		
Total extractable polyphenols (g GAE/kg DM)	13.9	
Total extractable tannins (g/kg DM)	5-24	

16.3 Olives AWCB bioactive compounds patent and literature review

Hydroxytyrosol, 2-hydroxytyrosol, tyrosol, oleanolic acid, and maslinic acid, flavonoids, anthocyanins, and tannins that are found in OMWW are considered as natural antioxidants with considerable commercial and economic interest. The most interesting one appears to be ***hydroxytyrosol***, a compound of high added value, due to its antioxidant and potentially beneficial (to human health) properties (Oreopoulou & Russ, 2007). Possibly it arises from the hydrolysis of oleuropein by an esterase during the milling process. Results of in vitro research demonstrate that hydroxytyrosol inhibits human LDL oxidation, scavenges free radicals, inhibits platelet aggregation and the production of leukotriene for human neutrofils, and confers cell protection. It also acts against both gram (+) and gram (-) bacteria. It could be used as a food preservative, in agriculture for the protection of olive trees, and in cosmetics industry in antiaging preparations. Since it is commercially unavailable, a method for its chromatographic purification has been developed to produce it from OMWW (Niaounakis & Halvadakis, 2006). Also, phenolic substances are the major contributors to OMWW's antimicrobial properties.

Finally, several techniques exist, which allow some potentially valuable organic compounds contained in the OMWW to be extracted. Roselló-Soto et al. (Roselló-Soto et al., 2015) in a review paper summarized the current state-of-the-art for the recovery of high-added value compounds from OMWW, including ***polyphenols*** and ***squalene*** (a naturally occurring polyprenyl compound primarily known for its key role as an intermediate in cholerestol) (Roselló-Soto et al., 2015). Furthermore, it has also been reported the recovery of pectin, and the synthesis of enzymes, biosurfactants or biopolymers (Niaounakis & Halvadakis, 2006) from OMWW.

The recovery of polyphenols from olive cake, pomace, kernel, paste, stone and seeds can constitute an important strategy to give an added value to these by-products. Roselló-Soto et al. (Roselló-Soto et al., 2015) summarized the non-conventional techniques being applied for the recovery of bioactive compounds from olive pomace including ***polyphenols***, ***proteins***, ***tocopherols*** or ***squalene***.

Finally, the "HANDBOOK on BIOACTIVE COMPOUNDS from OLIVE PROCESSING RESIDUES", published as a part of BIOACTIVE-NET project, a Specific Support Action (SSA) funded by the European Commission under the 6th Framework Program, collected the most relevant knowledge and technologies related to bioactive compounds in olive processing residues, from techniques of extraction, to application fields and economic feasibility of the extraction (Casas et al., 2008b). The main bioactive compounds extractable from olive processing residues, reported in this manual, are Polyphenols and more specifically Hydroxytyrosol and Oleuropein. Finally, the state of competition, regarding companies supplying these compounds, has been recorded (Casas et al., 2008b).

A lot of patents exist regarding the recovery of valuable compounds from the waste generated during olive oil production, which are presented in the following tables.

Patent No	US 20150045449 A1 and United States Patent 9420820
Publication Date	12/02/2015 (publication date), 23/08/2016 (issue date)
Title	Method for isolating polyphenols from olive mill water
Description/Abstract	The present invention relate to a highly efficient and novel method, using clean technologies, for obtaining a natural bioactive concentrate that is rich on polyphenols from olive mill water (OMW). The clean technologies integrate centrifugation, a drowning-out crystallization-based separation process, and vacuum evaporation. The method provides a highly-concentrated polyphenol isolate (up to 99% (mass fraction)) from other components presents in OMW, with up to half of the polyphenol content being hydroxytyrosol. The isolated polyphenols exhibit anti-oxidant, anti-microbial, anti-inflammatory, and anti-carcinogenic activities; they can be prepared as solid particles, as an aqueous solution, in an emulsion, or as lipidic-based nanoparticles. The isolated polyphenols can be used in the food industry, cosmetic industry, or pharmaceutical industry.
Type of AWCB	*olive mill water*
Recovered high added compound	polyphenols
Details/methodology applied	This present invention relates to a process for isolating polyphenols from OMW, combining different process units: centrifugation, flash evaporation, drowning-out crystallization-based separation process, and distillation, for the isolation of polyphenols from the TDS in OMW based on the solubility behavior changing after addition of EtOH as solvent chosen in the present invention. Further, distillation process unit is applied for the regeneration of EtOH which is used in a later process.

Patent No	ES2143939 B1 (2000)
Publication Date	16/12/2000
Title	Process for obtaining mannitol from pulp extracted from olives
Description/Abstract	The novelty of the invention consists in the revalorization of the extracted pulp, a waste by-product derived from the extraction of oil from olives which, after being subjected to a steam explosion process, has allowed all the mannitol present therein to be separated out and recovered, and which, by means of various simple purification stages (ultrafiltration, ion exchange and fractionated crystallization) permissible in food technology, has achieved a yield with a high degree of purity.
Type of AWCB	*olive cake coming from a three-phase centrifugation system*
Recovered high added compound	mannitol
Details/methodology applied	Steam explosion process and purification stages

Patent No	WO0145514 A1 (2001)
Publication Date	28/6/2001 (Publication date)
Title	Antioxidant compositions extracted from olives and olive by-products.
Description/Abstract	The present invention provides methods of extracting antioxidant compositions from olive-based starting materials, including olives, olive pulps, olive oil, and wastewater from olive oil manufacturing. One method includes the steps of extracting the olives, olive pulp or olive oil with a polar aqueous solvent to form an aqueous phase containing antioxidant components, passing the aqueous phase through a solid matrix to trap the antioxidant components on the matrix, and washing the matrix with a polar organic solvent to yield a solution of the antioxidant composition in the polar organic solvent. Another method includes the steps passing the wastewater from olive oil production containing antioxidant components through a solid matrix to trap the antioxidant components on the matrix, and washing the matrix with a polar organic solvent to yield a solution of the antioxidant composition in the polar organic solvent. The present invention also provides antioxidant compositions and methods of increasing the antioxidant activity of a product using such compositions.
Type of AWCB	*olives, olive pulp, olive oil, wastewater from olive oil manufacturing*
Recovered high added compound	antioxidant compositions
Details/methodology applied	(solid-liquid) extraction with AMBERLITE resins

Patent No	EP1310175 B1
Publication Date	13/10/2004
Title	Process for the isolation of antioxidants
Description/Abstract	The invention is in the field of antioxidants, and relates to a novel process for isolating antioxidants from residues of the olive oil production.
Type of AWCB	*residues from the production of olive oil*
Recovered high added compound	antioxidants
Details/methodology applied	olive water is subjected to fluidized bed adsorption on a suitable adsorbent, the adsorbed antioxidants are eluted with a suitable solvent and the eluate is freed from the solvent again.

Patent No	WO2005003037 A1
Publication Date	13/1/2005 (Publication date)
Title	A method for the treatment of olive mill waste waters
Description/Abstract	A system of filters for use in the treatment of olive mill waste waters is disclosed as well as a method in which said system of filters is used. The profitable outcome of using said system of filters in the treatment of olive mill waste waters is an effluent which may be used for agricultural irrigation and the retention and recovery of highly valuable products present in the waste waters to be treated.
Type of AWCB	*olive mill waste water*
Recovered high added compound	water for irrigation and phenolics solution

Patent No	WO02064537 A1
Publication Date	22/8/2002
Title	Method for obtaining purified hydroxytyrosol from products and by-products derived from the olive tree
Description/Abstract	The present addendum certificate relates to a method for obtaining purified hydroxytyrosol from products and by-products derived from the olive tree by means of two-step chromatographic treatment. The invention uses a non-activated ion exchange resin chromatographic method, followed by a second treatment on an XAD-type absorbent non-ionic resin which concentrates and completely purifies the hydroxytyrosol by means of elution with a methanol or ethanol:water dissolution (from 30 to 33%). The inventive method can also be applied to two-phase pomaces, three-phase pomaces and stones if they are subjected to a steam explosion process.
Type of AWCB	*products and by-products derived from the olive tree*
Recovered high added compound	hydroxytyrosol
Details/methodology applied	Chromatographic treatment, resin treatment.

Patent No	WO2000004794 A1 and US6936287 B1
Publication Date	3/2/2000
Title	Water-soluble extract from olives
Description/Abstract	The invention provides olive-derived vegetation water substantially free of monophenolic compounds (e.g., tyrosol and its derivatives) from olive pits. According to one aspect of the invention, the pits or seeds are removed from the olives prior to pressing. The pitless pulp or meat is then pressed to obtain a liquid-phase mixture including olive oil, vegetation water, and solid by-products. The vegetation water is separated from the rest of the liquid-phase mixture and collected. The vegetation water is useful as a source of oleuropein.
Type of AWCB	*olive pits*
Recovered high added compound	oleuropein
Details/methodology applied	

Patent No	WO1998004331 A1
Publication Date	05/02/1998 (Publication date)
Title	Process for the industrial recovery of oleanolic and maslinic acids contained in the olive milling subproducts
Description/Abstract	Process for the recovery of oleanolic and maslinic acids contained in the subproducts resulting from the milling and processing of olives or parts thereof, either proceding from three-phases or two-phases presses. This process enables to obtain, by separation and with purities higher than 80 %, of both acids with yields comprised between 0.2 and 1.5 %, as a function of the product and prime material processed. Fundamentally, it comprises selective extractions and fractionation of resulting mixtures with the use of solvents.
Type of AWCB	*subproducts resulting from the milling and processing of olives or parts thereof, either proceding from three-phases or two-phases presse*
Recovered high added compound	oleanolic and maslinic acids
Details/methodology applied	solvent extraction

Patent No	WO0212159 (2002)
Publication Date	14/02/2002 (Publication date)
Title	Process for producing oleanolic acid and/or maslinic acid
Description/Abstract	A process for producing oleanolic acid and/or maslinic acid and physiologically acceptable salts thereof characterized by comprising extracting with water and/or an organic solvent olive plant and/or products formed in the course of the production of olive oil and then concentrating and/or fractionating and purifying.
Type of AWCB	*olive plant and/or products formed in the course of the production of olive oil*
Recovered high added compound	oleanolic acid and/or maslinic acid
Details/methodology applied	Solvent extraction

Patent No	US20040102657 A1
Publication Date	27/05/2004 (Publication date)
Title	Method for obtaining purified hydroxytyrosol from products and by-products derived from the olive tree.
Description/Abstract	The present invention relates to a method for obtaining purified hydroxytyrosol from products and by-products derived from the olive tree by means of two-step chromatographic treatment. The invention uses a non-activated ion exchange resin chromatographic method, followed by a second treatment on an XAD-type absorbent non-ionic resin which concentrates and completely purifies the hydroxytyrosol by means of elution with a methanol or ethanol:water dissolution (from 30 to 33%). The method of the invention can also be applied to two-phase pomaces, three-phase pomaces and stones if they are subjected to a steam explosion process.
Type of AWCB	*products and by-products from olive tree*
Recovered high added compound	hydroxytyrosol
Details/methodology applied	two-step chromatographic treatment

Patent No	US9420820 B2
Publication Date	23/08/2016 (issue date)
Title	Method for isolating polyphenols from olive mill water
Description/Abstract	The present invention relate to a highly efficient and novel method, using clean technologies, for obtaining a natural bioactive concentrate that is rich on polyphenols from olive mill water (OMW). The clean technologies integrate centrifugation, a drowning-out crystallization-based separation process, and vacuum evaporation. The method provides a highly-concentrated polyphenol isolate (up to 99% (mass fraction)) from other components presents in OMW, with up to half of the polyphenol content being hydroxytyrosol. The isolated polyphenols exhibit anti-oxidant, anti-microbial, anti-inflammatory, and anti-carcinogenic activities; they can be prepared as solid particles, as an aqueous solution, in an emulsion, or as lipidic-based nanoparticles. The isolated polyphenols can be used in the food industry, cosmetic industry, or pharmaceutical industry.
Type of AWCB	*olive mill water*
Recovered high added compound	Highly-concentrated polyphenol isolate (up to 99% (mass fraction)) from other components presents in OMW, with up to half of the polyphenol content being hydroxytyrosol.
Details/methodology applied	The clean technologies integrate centrifugation, a drowning-out crystallization-based separation process, and vacuum evaporation.

Patent No	EP 2044848 A1 20090408
Publication Date	8/4/2009 (application date), 16/12/2009 (granted)
Title	Process for the treatment and the recovery of humid pomace produced by two-phase oil mills.
Description/Abstract	Process for the treatment and the recovery of humid pomace produced by two-phase olive oil mills, in order to obtaining dry pomace through processes which involve the dehumidification of the humid pomace in an appropriate equipment and the subsequent drying of the dehumidified pomace. The vegetable waste water that is recovered can be treated to obtain purified water and polyphenol concentrate through a combination of processes of mechanical separation and processes of a membrane separation.
Type of AWCB	*two-phase olive oil pomace*
Recovered high added compound	polyphenol concentrate and water
Details/methodology applied	decanting and membrane processes

Patent No	EP 2102110 B1 20121128
Publication Date	28/11/2012 (issue date)
Title	OLIVE WASTE RECOVERY
Description/Abstract	Process for isolating soluble dietary fibers and valuable polyphenols from olive mill wastewater, characterized by the following steps: the olive mill wastewater is (a) defatted by removing the fat by centrifugation and; (b) concentrated by removing the water content and; (c) extracted using ethanol and an organic acid and; (d) the dietary fibers are separated from the polyphenols by precipitation of the dietary fibers in ethanol and; (e) the soluble dietary fibers are separated from the insoluble dietary fibers by redissolving the precipitated dietary fibers into water whereby the insoluble dietary fibers precipitate leaving the soluble dietary fibers in solution.
Type of AWCB	*olive waste*
Recovered high added compound	polyphenols and dietary fibers
Details/methodology applied	Centrifugation, solvent extraction

Patent No	EP 1773721 B1 20111005
Publication Date	5/10/2011 (Issue date)
Title	PROCESS FOR RECOVERING THE COMPONENTS OF OLIVE MILL WASTEWATER WITH MEMBRANE TECHNOLOGIES
Description/Abstract	A process for totally recovering the chemical components of olive mill wastewater (OMW) including, in sequence, the following operations: a) collecting the raw OMW after the olive milling process; b) adjusting the pH of the said OMW to within the range of 3-4.5; c) treating the OMW obtained from the preceding operation by means of enzymatic hydrolysis; d) separating out the particle and suspended components, resulting from the preceding operation, and a partially clarified liquid product; e) treating the said liquid product resulting from operation d) by tangential microfiltration (MF), and providing a retentate phase and a permeate phase; f) treating the permeate coming from the preceding operation by means of tangential nanofiltration (NF), and providing for a retentate phase and a permeate phase; g) treating the permeate coming from operation f) by means of reverse osmosis (RO), and providing a retentate phase rich in purified polyphenols and a permeate composed of purified water; the said solid phase resulting from operation d) and the said retentate phase resulting from operation e) being reusable as a substrate for compost production or for anaerobic fermentation processes, and the said retentate phase coming from operation f) being reusable for extracting the polyphenol compounds therefrom.
Type of AWCB	*olive mill waste water*
Recovered high added compound	polyphenols and purified water
Details/methodology applied	enzymatic hydrolysis, MF, NF, RO

Patent No	EP 1623960 B1 20091223
Publication Date	23/12/2009 (Publication date)
Title	Process for the recovery of tyrosol and hydroxytyrosol from oil mill wastewaters and catalytic oxidation method in order to convert tyrosol in hydroxytyrosol.
Description/Abstract	A process to treat the oil mill wastewaters (OMW) and especially for the preparation of Tyrosol and/or Hydroxytyrosol, which consists of: a) Rough Filtration (RF), Microfiltration (MF), Ultrafiltration (UF), Nanofiltration (NF) and Reverse Osmosis (RO) of the OMW; b) Chromatographic separation of Tyrosol, Hydroxytyrosol and other phenolic compounds from the concentrated RO; c) Oxidation of the so obtained Tyrosol to Hydroxytyrosol in the presence of methyl rhenium trioxide and of hydrogen peroxide in a protic solvent; d) Concentration and pulverization of the high molecular weight portion with the recovery of water and compounds with a high added value.
Type of AWCB	*OMW*
Recovered high added compound	tyrosol and/or hydroxytyrosol
Details/methodology applied	Filtration, MF, UF, NF, RO, chromatographic separation.

Patent No	EP 2338500 A1 20110629
Publication Date	29/6/2011 (publication date)
Title	Process for producing concentrated and refined actives from tissues and byproducts of Olea europaea with membrane technologies.
Description/Abstract	The invention concerns an integrated process affording the production of purified fractions, as powder or concentrated solution, consisting of different biologically active compounds and families of compounds, starting from olive tree tissues and wastes of the olive oil industry and olive tree cultures, in particular olive tree leaves and twigs (pruning wastes), residues from the oil production (pomace or husks) and pigmented olive pulp. The refined products obtainable comprise not only oleuropein, hydroxytyrosol and related compounds, but also verbascoside and red anthocyanoside pigments. The proposed process is based on the integration of hot or cold extraction from the various vegetal starting materials with separation techniques by membrane tangential filtration, specifically microfiltration (MF) or ultrafiltration (UF), optionally followed by nanofiltration (NF) and completed by reverse osmosis (OI). These operations are completed, where necessary, by refining treatments of the thus obtained fractions of UF retentate, NF retentate and OI retentate on chromatographic resins.
Type of AWCB	*olive tree tissues and wastes of the olive oil industry and olive tree cultures, in particular olive tree leaves and twigs (pruning wastes), residues from the oil production (pomace or husks) and pigmented olive pulp.*
Recovered high added compound	oleuropein, hydroxytyrosol and related compounds, but also verbascoside and red anthocyanoside pigments
Details/methodology applied	Hot or cold extraction from the various vegetal starting materials with separation techniques by membrane tangential filtration, specifically microfiltration (MF) or ultrafiltration (UF), optionally followed by nanofiltration (NF) and completed by reverse osmosis (RO). Chromatographic

Patent No	EP 2338500 A1 20110629
	resins.

Patent No	EP 2526785 A1 20121128, US 20120302515 A1
Publication Date	28/11/2012 (publication date)
Title	Process for producing a phytoextract from vegetation waters and olive oil pomaces.
Description/Abstract	There is described the process for obtaining a phytoextract from vegetation waters and pomaces coming from olive milling. Said process is based on combining physical-chemical and enzymatic pre-treatment methods, membrane tangential filtration and vacuum evaporation. The method allows an eco-sustainable and efficient extraction of the active ingredients involved.
Type of AWCB	*vegetation waters and pomaces coming from olive milling*
Recovered high added compound	polyphenolic compounds
Details/methodology applied	Physical-chemical and enzymatic pre-treatment methods, filtration, vacuum evaporation.

Patent No	EP 1910257 B1 20140101
Publication Date	1/01/2014 (Publication date)
Title	Method of obtaining a natural hydroxytyrosol-rich concentrate from olive tree residues and subproducts using clean technologies
Description/Abstract	A method of obtaining a natural hydroxytyrosol-rich concentrate from olive tree residues and subproducts, consisting of the following steps: (a) processing solid and semi-solid residues from the olive tree by extraction with water or hydroalcoholic mixtures, (b) either feeding the extract containing hydroxytyrosol and other bioactive compounds from the olive tree directly to a nanofiltration unit with a molecular weight cut-off lower than 300 Da or mixing the extract obtained in step (a) with vegetation waters of olive mills and centrifuging in order to remove particles and other suspended solids and feeding the obtained supernatant of the centrifuge to said nanofiltration unit, wherein said hydroxytyrosol and other bioactive compounds with low molecular weight are recovered in a permeate stream of said nanofiltration unit, and (c) feeding the permeate stream of said nanofiltration unit to the feed compartment of a reverse osmosis unit wherein the said hydroxytyrosol and other bioactive compounds are retained and concentrated in a retentate stream.
Type of AWCB	*olive tree residues and subproducts*
Recovered high added compound	hydroxytyrosol-rich concentrate
Details/methodology applied	solvent extraction, NF

Patent No	EP 2049458 B1 20131225
Publication Date	25/12/2013 (publication date)
Title	Process for the production of hydroxytyrosol containing extract from olives and solids containing residues of olive oil extraction
Description/Abstract	A process of producing an extract containing hydroxytyrosol from a starting material selected from olives and/or pomaces residues of olives after the extraction of olive oil, said process including acid hydrolysis of said starting materials and purification of the resulting f) eluting the products retained over said second chromatographic resin with water in the absence of any organic solvent solution, characterized incomprising the following steps: a) carrying out said acid hydrolysis of said starting materials in water at a temperature not exceeding 140°C, at a pressure within the range of atmospheric pressure to 0,138 MPa (20 psi) above the atmospheric pressure and at a pH within the range of 1.0 to 6.0; b) removing suspended solids from the hydrolysis water solution of step a) to obtain a clarified aqueous solution; c) loading the product (A) obtained from step b) in a chromatographic column of a resin selected from acid activated weakly basic anion exchange resins to retain hydroxytyrosol, d) eluting the products retained over said chromatographic resin with water, in the absence of any organic solvent; e) loading the solution (B) obtained from step d) in a second chromatographic column of a resin selected from adsorbent non-ionic resins, o retain hydroxytyrosol; and wherein the process is carried out without making use of organic polar solvents.
Type of AWCB	*olives and/or pomaces residues after the extraction of olive oil.*
Recovered high added compound	hydroxytyrosol
Details/methodology applied	acid hydrolysis

Patent No	EP 1953133 A1 20080806
Publication Date	6/8/2008
Title	Process and apparatus for the production of hydroxytyrosol from olive oil extraction residues
Description/Abstract	Hydroxytyrosol is extracted from a by-product of the olive oil extraction, by carrying out acid hydrolysis of said by-product at a temperature within the range of 105°C to 140°C and at a pH within the range of 1.0 to 6.0, at a pressure of 10 to 20 psi.
Type of AWCB	*by-product of the olive-oil extraction*
Recovered high added compound	hydroxytyrosol
Details/methodology applied	acid hydrolysis

Patent No	EP 1987868 A1 20081105
Publication Date	05/11/2008 (pubication date)
Title	Method for the industrial use of tyrosol and hydroxytyrosol contained in the solid by-products of industrial olive crushing
Description/Abstract	Method for the industrial use of tyrosol and hydroxytyrosol, characterized in that their extraction is performed from industrial solid by-products of olive milling with an output of tyrosol and hydroxytyrosol over 90%.
Type of AWCB	*industrial solid by-products of olive milling*
Recovered high added compound	tyrosol and hydroxytyrosol over 90%
Details/methodology applied	solvent extraction

Patent No	EP 2743248 A1 20140618
Publication Date	18/6/2014 (publication date)
Title	Method for obtaining hydroxytyrosol extract, mixture of hydroxytyrosol and 3,4-dihydroxyphenylglycol extract, and hydroxytyrosyl acetate extract, from by-products of the olive tree, and the purification thereof
Description/Abstract	The invention relates to a method for obtaining an extract comprising hydroxytyrosol, as an acetylated product or as a mixture with 3, 4-dihydroxyphenylglycol and the purification thereof, comprising at least one column chromatography of a hydroxytyrosol source such as by-products of the olive and the olive tree, using a mixture of at least two ionic resins, preferably an anionic resin with a cationic resin. Preferably, in a first phase, a phenyl-rich liquid is obtained as the raw material for the extraction and purification of phenolic compounds, a second phase enables a hydroxytyrosol (HT)-enriched extract and hydroxytyrosol with 3, 4 dihydroxyphenylglycol (DHFG) mixture to be obtained, and hydroxytyrosol acetate is produced, and, in the third phase, highly pure hydroxytyrosol, DHFG and the mixture thereof and HT acetate are obtained. Each phase comprises extraction, reaction, concentration, adsorption and desorption, using mixtures of ion exchange resins, adsorption in non-ionic resins and a polymer phenolic fraction, membranes of reverse osmosis and evaporators.
Type of AWCB	*olive pomace*
Recovered high added compound	HYDROXYTYROSOL EXTRACT, MIXTURE OF HYDROXYTYROSOL AND 3,4-DIHYDROXYPHENYLGLYCOL EXTRACT, AND HYDROXYTYROSYL ACETATE EXTRACT
Details/methodology applied	extraction, reaction, concentration, adsorption and desorption, using mixtures of ion exchange resins, adsorption in non-ionic resins and a polymer phenolic fraction, membranes of reverse osmosis and evaporators.

Patent No	United States Patent Application 20160296903 A1
Publication Date	13/10/2016 (publication date)
Title	Emulsifiers from olive solid waste
Description/Abstract	A process is described by which the solid waste of olive processing remaining after oil expression and husk oil extraction is dehydrated, treated with alcoholic solutions, the alcohol being removed, the solid residue subjected to aqueous extractions, the aqueous medium being separated from the remaining solids and concentrated. The said material is also described, being capable of emulsifying oil-in-water emulsions and provide stability to colloidal foods.
Type of AWCB	*solid waste of olive processing*
Recovered high added compound	emulsifiers
Details/methodology applied	extraction

Patent No	United States Patent Application 20150196498 A1
Publication Date	16/07/2015 (publication date)
Title	Hydroxytrosol containing extract obtained from olives and solids containing residues of olive oil extraction
Description/Abstract	Hydroxytyrosol extracted from olives and/or from the solid residues of olives after the extraction of olive oil, by acid hydrolysis and purification on resin columns eluted with water contains hydroxytyrosol and tyrosol, is free from sugars, has a residual content of Benzo[a]pyrene that is less than 2 microg/Kg (weight BaP/weight of extract as dry matter), containing a weight ratio of hydroxytyrosol to hydroxymethylfurfural of between 45:1 and 10000:1, and the content of hydroxytyrosol in the extract is at least 0.5% (w/w) with purity of at least 40% (by HPLC 280 nm).
Type of AWCB	*residues from olive oil extraction*
Recovered high added compound	hydroxytyrosol extract
Details/methodology applied	Acid hydrolysis and purification on resin columns.

Patent No	United States Patent Application 20050103711A1
Publication Date	19/5/2005
Title	Isolation of oleuropein aglycon from olive vegetation water
Description/Abstract	The present invention provides economical methods for collecting oleuropein aglycon from olive vegetation water, a routine byproduct in the manufacture of olive oil. The methods have the advantage of facilitating the collection of other valuable constituents of olive vegetation water, and furthermore render the olive vegetation water environmentally benign, and thus suitable for routine disposal.
Type of AWCB	*olive vegetation water*
Recovered high added compound	oleuropein aglycon
Details/methodology applied	solvent extraction

17.Apple fruit

Apple (*Malus domestica Borkh*.) is the most favoured fruit of millions of people and is a widely grown fruit in temperate regions of the globe (Shalini & Gupta, 2010). 70-75% of apples are consumed as fresh fruits while the remaining 25-30% are processed into other products such as apple juice concentrate (AJC), packed natural ready-to-serve (RTS) apple juice, apple cider, wine and vermouth, apple purees and jams and dried apple products (Shalini & Gupta, 2010). Solid apple pomace waste and apple pomace sludge (liquid waste) are the main by-products obtained after the crushing and pressing of apples during the juice process. Apple pomace represents approx. 25-30% of the original fruits and apple pomace sludge 5-10% being highly susceptible to biodegradation due to their high content of carbohydrates, other vital nutrients, high moisture content and high BOD_5 and COD values (Dhillon et al., 2013; Grigoras et al., 2013).

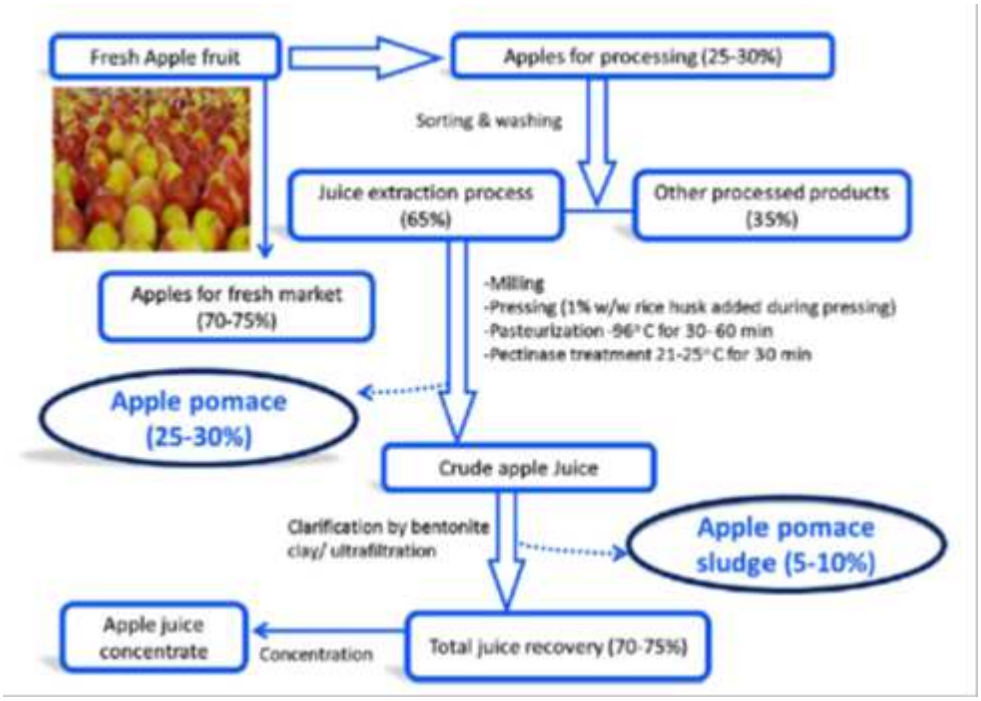

Figure 17.1: Diagram showing the apple processing steps and the majors by-products produced at the various stages (Dhillon et al., 2013).

Currently, the by-products from apple processing industry are treated in traditional ways, such as landfilling, incineration, composting, only a small proportion is utilized as low quality animal feed for ruminants, land spreading, added at soils as fertilizers, agro fuels or coal (Dhillon et al., 2013; Grigoras et al., 2013). However, these practices have adverse environmental impact (contaminated underground water, source of secondary pollution) being at the same time a real problem for manufacturers who have to manage extremely large volumes of waste generated daily (Grigoras et al., 2013). At this point it should be pointed out that both AP and APS exhibit advantages as a raw material for biotechnological products, including: (1) the high content of polysaccharides (mainly cellulose, starch and hemicelluloses), (2) the presence of mono-, di- and oligosaccharides, citric acid and malic acid, which can be metabolized by microorganisms and (3) high content of vitamins and other mineral ions which could limit the cost of nutrient supplementation for fermentation media (Dhillon et al., 2013).

17.1 Solid apple pomace (AP)

Apple pomace contains peel, flesh, stem, core, seeds and juice residues (Toor et al., 2015). A sample of apple pomace was reported to contain 54% pulp, 34% peel, 7% seeds, 4% seed core and 2% stem (Kołodziejczyk et al., 2007), however, apple pomace is an extremely variable product, probably due to large variations in the proportion of skins, pulp, core, seeds and juice in the by-product. Some physicochemical characteristics of apple pomace are summarized in Table 17.1 but it should be pointed out that the composition of apples themselves is variable and depends on the variety, maturity, season of harvest etc. Generally, fresh apple pomace contains 20-30% Dry Matter (DM) and pressed pomace contains 30-40% DM. Fresh apple pomace is bulky with density ranging between 400 and 1000 kg/m^3. Density and moisture content depend on processing methods and apple maturity (feedipedia, 2016; Toor et al., 2015). Apple pomace is generally poor in protein (3-8% DM) and rich in fibre and sugars. Crude fibre ranges from 5 to 50% DM, NDF from 23 to 56% DM, ADF from 11-55% DM and lignin from 15-24% DM. Sugar content is also variable: apple pomace is high in fructose (14 to 35% DM). Saccharose and glucose contents are lower but also variable (1-11% and 6-13% DM, respectively). The content of dietary fiber (DF) (pectins up to 25% DM) constitutes is on the average 50% of dry weight, whereas phenolics may vary from 1200 up to 10000 mg/kg dry weight (Dhillon et al., 2013; Kołodziejczyk et al., 2007).

Table 17.1: Summary of main physicochemical characteristics of solid apple pomace (AP) (Biemann, 1962; Dhillon et al., 2013; ECN, 2016; feedipedia, 2016; Kołodziejczyk et al., 2007; O'Shea et al., 2015; Oreopoulou & Russ, 2007; Shalini & Gupta, 2010).

PHYSICOCHEMICAL PROPERTIES	RANGE	COMMENTS
ENERGY		
Higher Heating Value (HHV) (MJ/kg)	17.2-23.2	
Fixed Carbon (%wt)^{db}	18.2	
Volatile Matter (%wt)^{db}	79	
Ash (%wt)^{db}	2.8	
Moisture (% wt)^{am}	66.4-78.2 (fresh), 5.7-9 (dehydrated)	
Carbon (%wt)^{db}	12.8-49.6	
Oxygen (%wt)^{db}	38.9-44.8	
Hydrogen (%wt)db	6.2-8.4	
Nitrogen (%wt)^{db}	0.4-1	
Sulfur (%wt)^{db}	0.05	
FODDER		
Dry matter (%wt)^{am}	21-30	Values from (feedipedia, 2016) are average values from a lot of samples.
Crude protein (%wt)^{db}	2.6-8	Values from (feedipedia, 2016) are average values from a lot of samples.
Crude fiber (%wt)^{db}	4.7-51.1	Values from (feedipedia, 2016) are average values from a lot of samples.
Neutral Detergent Fiber (NDF) (%wt)^{db}	23.4-56.4	Values from (feedipedia, 2016) are average values from a lot of samples.
Acid Detergent Fiber (ADF) (%wt)^{db}	11.4-55.2	Values from (feedipedia, 2016) are average values from a lot of samples.
Lignin (%wt)^{db}	15.3-23.5	Values from (feedipedia, 2016) are average values from a lot of samples.
Ether extract (%wt)^{db}	1-14.4	Values from (feedipedia, 2016) are average values from a lot of samples.

PHYSICOCHEMICAL PROPERTIES	RANGE	COMMENTS
Ash (%wt)[db]	0.4-6.2	Values from (feedipedia, 2016) are average values from a lot of samples.
Gross energy (%wt)[db]	17.2-23.2	Values from ref.19 are average values from a lot of samples.
FERTILIZER		
Nitrogen (g/kg)[db]	6.8-9.7	
Phosphorus (g/kg)[db]	0.1-1.4	Values from (feedipedia, 2016) are average values from a lot of samples.
Potassium (g/kg)[db]	4-10	Values from (feedipedia, 2016) are average values from a lot of samples.
Calcium (g/kg)[db]	0.3-2.6	Values from (feedipedia, 2016) are average values from a lot of samples.
Magnesium (g/kg)[db]	0.2-3.6	Values from (feedipedia, 2016) are average values from a lot of samples.
Sulfur (g/kg)[db]	0.07-0.6	
BIOACTIVE COMPOUNDS		
pectin (g/kg)[db]	35-250	
polyphenols (g/kg)[db]	1.2-10	

17.2 Apple pomace sludge (APS)

Apple pomace sludge (APS) is the liquid waste generated by apple processing industries. APS being also rich in carbohydrates and other vital nutrients and having high moisture content, biodegradable organic load [high biological oxidation demand (BOD) and chemical oxidation demand (COD) values] is highly susceptible to microbial attack. For instance, the BOD of APS is 72,000 mg/L and the BOD to COD ratio is high (0.6) and it starts fermenting directly on the filter press during juice extraction (Dhillon et al., 2013). Other physicochemical characteristics of APS are summarized in Table 17.2.

Table 17.2: Summary of main physicochemical characteristics of apple pomace sludge (APS) (Dhillon et al., 2013; Gassara et al., 2012).

PHYSICOCHEMICAL PROPERTIES	RANGE
WATER CHARACTERISTICS	
pH	3.3
Total Solids (mg/L)	115000-135000
Total Suspended Solids (mg/L)	41500
total carbon (g/L)	44.3-51.9
COD (mg/L)	120000
BOD_5 (mg/L)	72000
Total Nitrogen (TN) (mg/L)	2200-2940
total carbohydrates (g/L)	56.2-67.7
protein (g/L)	28.8-35.8
lipids (ether extract) (g/L)	5.1-6.2
Potassium (g/kg)[db]	6.8-8.0
Calcium (g/kg)[db]	0.9-1.1
Sulfur (g/kg)[db]	2.2-2.6
BIOACTIVE COMPOUNDS	
Citric acid (g/L)	40.4
Polyphenols (mg GAE/L)	383-720

17.3 Apple AWCB bioactive compounds patent and literature review

Apple pomace is being utilized for ***extraction of pectin*** since long (Shalini & Gupta, 2010) being the most reasonable utilization approach from both economic and ecological points of view (Schieber et al., 2001). Apple pomace has been shown to be a good source of polyphenols which are predominantly localized in the peels and are extracted into the juice to a minor extent. Major compounds isolated and identified include catechins, hydroxycinnamates, phloretin glycosides, quercetin glycosides, and procyanidins (Schieber et al., 2001). Dhillon et al. reviewed the compounds being recovered or produced by apple pomace including ***organic acids*** (citric, lactic acid)***, aroma compounds, bioethanol, enzymes*** (cellulases and hemicellulases, ligninolytic enzymes, amylases, pectinases, other enzymes)***, edible mushrooms, edible fibers, pectin, natural antioxidants, biopolymers*** (chitosan, xanthan gum), ***nutritional enrichment*** (culturing of industrially important microorganisms, animal/livestock feed, single cell protein, protein enrichment, fish feed, insect diets/biocontrol formulation preparations) among others (Dhillon et al., 2013).

Dhillon et al. summarized the various biotechnological compounds produced by using APS as raw material. APS has been utilized for the bioproduction of ***citric acid***. Higher bioproduction of citric acid with 40.372 g/L APS was achieved with optimum conditions of 25 g/L total solids (TS), 3% methanol as an inducer after 132 h fermentation time in a stirred fermenter (Dhillon et al., 2013). Finally, Gassara et al. studied the ***polyphenolic compound extraction*** (383–720 mg GAE/L) by liquid-state culture of Phanerochaete chrysosporium ATCC 24275 by employing apple pomace sludge and synthetic medium (Gassara et al., 2012).

The following tables summarize the patent review on recovery of various bioactive compounds from apple AWCB.

Patent No	EP1302251 B1
Publication Date	27/8/2008 (Issue date)
Title	Method for producing a vegetable flour using residues of agroindustrial processes, and method for producing papers and cardboards using said flour.
Description/Abstract	The present invention relates to a method for producing a vegetable flour that uses, as a raw material, vegetable materials that are residues of agroindustrial processes, particularly shells, pits and peels, to a method for producing papers and cardboards featuring particular tactile and visual characteristics that uses the same vegetable flour, and to the use of said flour as filler for plastics, rubbers, panels, pre-shaped components and the like.
Type of AWCB	*Residues of agroindustrial processes, particularly shells, pits and peels (nuts, hazelnuts, peanuts, pistachios, pine seeds, peaches, apricots, plums, prunes, olives, cherries, coffee, dates and the like), (bananas, pears, apples, peaches, apricots, grapes, tomatoes, fennels, artichokes, peas, beans and pineapple and the like).*
Recovered high added compound	Vegetable flour production and papers and cardboards.

Patent No	EP 1272254 B1 20060201
Publication Date	01/02/2006 (Issue date)
Title	Method for obtaining useful materials from the by-products of fruit and vegetable processing
Description/Abstract	Method for recovering useful substances from the by-products of fruit and vegetable processing, characterised in that when carrying out the recoveryprocess of pectin from the by-products using a selective adsorber as the first useful substance, the polyphenols contained in the by-products are separated off as a second useful substance and are recovered from the adsorber by means of subsequent desorption.
Type of AWCB	by-products arising during the production of juice from ripe fruits or vegetables are used, apple pomace or citrus pomace.
Recovered high added compound	pectin, polyphenols
Details/methodology applied	adsorption

Patent No	EP 3031819 A1 20160615
Publication Date	15/6/2016 (publication date)
Title	Method of extracting ceramide and/or pectin from whole apples or apple juice residue
Description/Abstract	The object of the invention is to provide a method of extracting useful ingredients: ceramide and/or pectin from whole apples and/or apple juice residues. In this context, the invention also provides a method of regenerating and recycling spent ethanol. These objects are achievable by a method of extracting useful ingredients: ceramide and pectin from whole apples and/or apple juice residues and a method of recovering and regenerating, or recycling the ethanol used for extraction.
Type of AWCB	*whole apples and/or apple juice residues.*
Recovered high added compound	ceramide (dietary fiber of apple?) and pectin
Details/methodology applied	solvent extraction

Patent No	EP 2518088 A1 20121031
Publication Date	31/10/2012 (publication date)
Title	Method for producing liquid pectin from apple pomace
Description/Abstract	The invention relates to pectin production and, more specifically, to methods for producing pectins with a high galacturonic acid content for the production of functional food products. The essence of the invention is that fresh, freshly pressed or dry raw plant material is used, and the hydrolysis and extraction of the pectic substances is carried out using water in the presence of 0.05-0.15% organic food acids at a temperature of 85-90 °C and with a solid to liquid phase ratio of 1:5-12. The hydrolysed mixture is separated in order to isolate pectin extract. The pectin extract is filtered and sent for vacuum concentration.
Type of AWCB	*apple pomace*
Recovered high added compound	pectins with high galacturonic acid content for functional food products
Details/methodology applied	hydrolysis and extraction

Patent No	EP 0824872 B1 20021009
Publication Date	09/10/2002 (publication date)
Title	Flavouring agents obtained from fruit pulp fibres
Description/Abstract	A process for preparing flavour precursors for meat flavours which comprises enzymatically hydrolysing citrus pulp, citrus pectin or apple pulp fibre with a pectolytic enzyme at a pH from 4 to 6, at a temperature from 40°C to 60°C for a period of time from 6 to 48 hours, inactivating the enzyme and drying the hydrolysate.
Type of AWCB	*citrus pulp, apple pulp fibre*
Recovered high added compound	flavour precursors for meat flavours
Details/methodology applied	enzymatic hydrolysis, and drying

Patent No	United States Patent 9101649
Publication Date	11/8/2015
Title	Phenolic compositions derived from apple skin and uses thereof
Description/Abstract	Described herein are phenolic compositions derived from apple skins. In particular, described herein are flavonoid-rich fractions derived from apple skin extract. The compositions are useful in the prevention and treatment of conditions associated with oxidative stress and/or inflammation, including certain neurodegenerative diseases. Methods of producing the compositions are also described.
Type of AWCB	*apple skin*
Recovered high added compound	flavonoid-rich fractions
Details/methodology applied	ethanol extraction

18.Citrus fruits

Orange is a citrus fruit consumed in high quantities all over the world in the natural and peeled forms and as a juice (Rezzadori et al., 2012). Citrus fruits are rich in water (85%), sugars (49% DM), pectins (20% DM) and low in protein (6.5% DM). However, the variability is important, as there are different species, many varieties, various collection stages and geographical origins: for instance, sugar content varies between 17% and 65% and pectins from 6 to 34% (feedipedia, 2016; Koppar & Pullammanappallil, 2013). Generally, all citrus fruits contain considerable amounts of lipids (oleic, linoleic, linolenic, palmitic, stearic acids, glycerol and aphytosterol), sugars (glucose, fructose, and sucrose), acids (primarily citric and malic). These also contain tartaric, benzoic, oxalic, and succinic), insoluble carbohydrates (cellulose, pectin), enzymes (pectinesterase, phosphatase, peroxidase), flavonoids (hesperidin, naringin), limonin, isolimonin, peel oil (d-limonene), volatile constituents (alcohols, aldehydes, ketones, esters, hydrocarbons, acids), pigments (carotenes, xanthophylls), vitamins (ascorbic acid, Vitamin B complex, carotenoids), and minerals (primarily calcium and potassium) (Sharma et al., 2017). Oranges are one of the most important commodities in terms of global agricultural production, ranked in 20th position in 2008 and representing around 10.5% of the world fruit production (Rezzadori et al., 2012). Approximately, more than 40% of the oranges produced globally are utilized in processing to make different commercial products, such as dehydrated citrus products or marmalades, jams, fresh juice and flavoring agents for beverages (Sharma et al., 2017). In addition to juice, orange production generates a broad range of other commodities including sweet orange oil (90% D-limonene), orange blossom, citrus honey, and marmalade. Approximately 40–60% of the processed fruit becomes citrus peel waste, which is composed of the peel, seeds and membrane residues resulting from juice extraction and approx. 0.5% are the liquid waste from processing industry, as shown in Figure 18.1 (feedipedia, 2016; Koppar & Pullammanappallil, 2013; Rezzadori et al., 2012; Santos et al., 2010). In general, orange residues have no economic value, even though their composition is rich in soluble sugars, cellulose, hemicellulose, pectin and essential oils that could form the basis of several industrial processes (Rezzadori et al., 2012). Possible applications include human consumption, fertilizer, animal feed, charcoal, adsorption of chemical compounds, bio-oil production and extraction of essential oils and pectin.

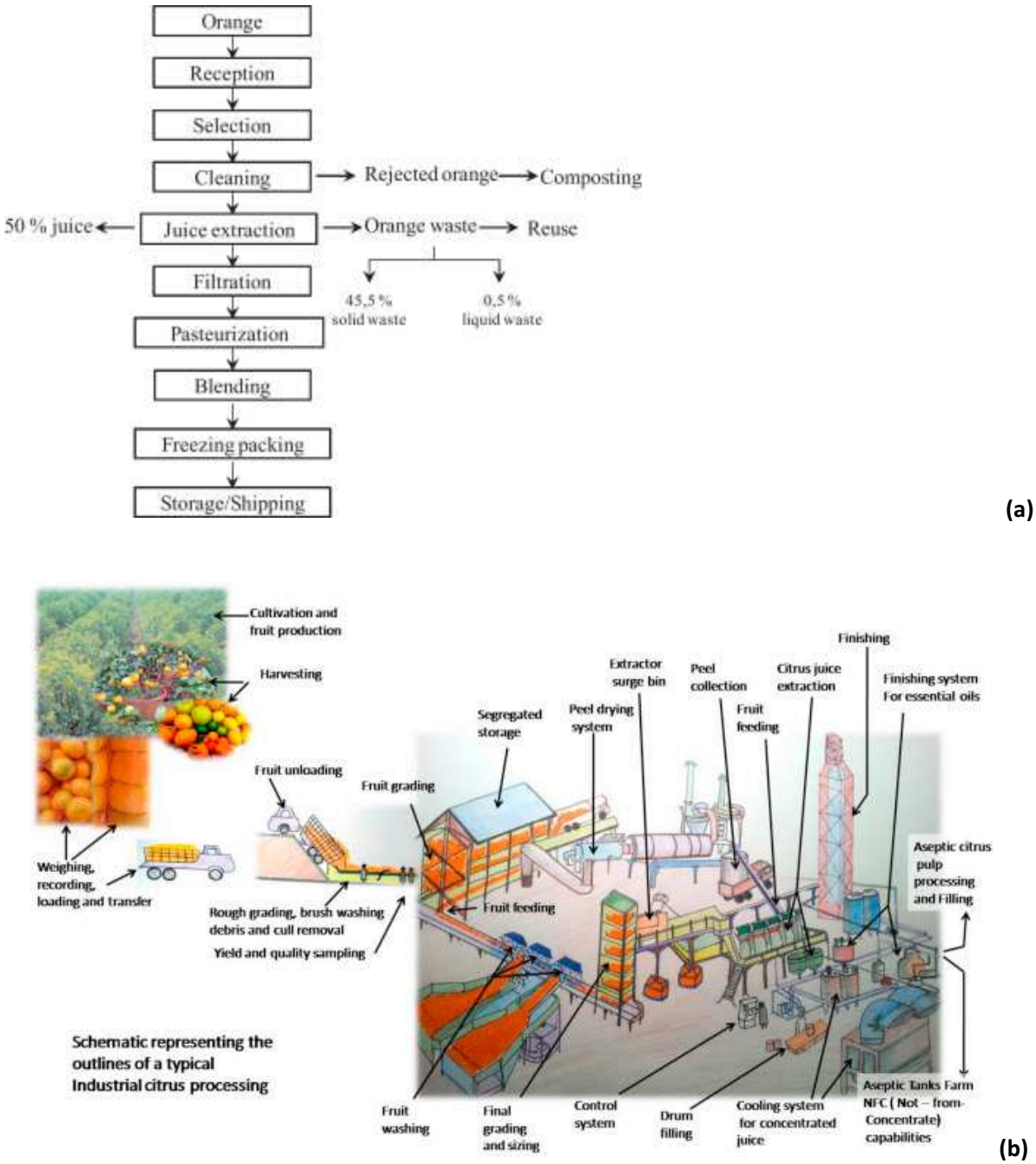

Figure 18.1: a) Diagram showing the orange juice processing with the major by-products (Rezzadori et al., 2012). b) Schematic representation of a typical industrial citrus processing (Sharma et al., 2017).

18.1 Orange (citrus) pulp/pomace

As already mentioned citrus pulp is the solid residue that remains after fresh fruits are squeezed for their juice and contains the peel (60-65%), internal/membrane tissues (30-35%) and seeds (0-10%). Citrus pulp is usually made from oranges but may also contain by-products of other citrus fruits, notably grapefruits and lemons. Physicochemical characteristic of citrus pulp/pomace are summarized in Table 18.1. These by-products are a source of fiber, dried pulp, essential oils, D-limonene, pectin, seed oil, ascorbic acid and flavonoids (main flavonoids in citrus species are hesperidin, narirutin, naringin and eriocitrin) (Sharma et al., 2017; Viuda-Martos et al., 2011). Large citrus processing plants mechanically press citrus pulp and peel to remove as much liquid as possible thereby generating press liquor. The pressed pulp is dried and sold as animal feed. The liquids (press

liquor and condensates from drier) are pumped to a waste heat evaporator, where D-limonene is volatilized leaving a molasses stream (Koppar & Pullammanappallil, 2013). The use of citrus pulp for animal feeding (as molasses) was found to be an effective way to decrease waste output. Currently, citrus pulp is used as a cereal substitute in ruminant feeds, due to its high energy content and good digestibility in ruminant species, for fibre (pectin) and for fuel production (Barros et al., 2012). Fresh pulp is often used locally to feed animals. Fresh citrus pulp has a natural acidity but it is still a perishable product due to its high content of water and soluble sugars. It may quickly sour, ferment and release sludge hazardous to the environment. Much of the pulp is dried (decreasing the water content from 80% down to 11%), as it is easier to haul and manage and can be stored year-round, and exported around the world. It has a higher nutritive value than fresh pulp. Drying is usually done at the fruit processing site to save on transportation costs (feedipedia, 2016; Koppar & Pullammanappallil, 2013). An alternative application of waste orange pulp is to convert it to a fertilizer by composting.

Table 18.1: Summary of main physicochemical characteristics of orange (citrus) pulp/pomace (Ángel Siles López et al., 2010; Assa et al., 2013; ECN, 2016; feedipedia, 2016; O'Shea et al., 2015; Sánchez Orozco et al., 2014; Sharma et al., 2017; Watanabe et al., 2010; Zhou et al., 2015).

PHYSICOCHEMICAL PROPERTIES	RANGE	COMMENTS
ENERGY		
Higher Heating Value (HHV) (MJ/kg)	17.1-18.4	
Lower Heating Value (LHV) (MJ/kg)	17.1	
Fixed Carbon (%wt)^{db}	18.3-19.9	
Volatile Matter (%wt)^{db}	77.1-77.9	
Ash (%wt)^{db}	2.2-4.6	
Moisture (% wt)^{am}	7.1-10.6 (dry), 83 (fresh)	
Carbon (%wt)^{db}	46.4-46.6	
Oxygen (%wt)^{db}	41.8-51.3	
Hydrogen (%wt)db	5.7-6.3	
Nitrogen (%wt)^{db}	1.1-1.5	
Sulfur (%wt)^{db}	0.05-0.06	
FODDER		
Dry matter (%wt)^{am}	23.3-34.2 (fresh), 88-89.1 (dried)	Values are average values from a lot of samples.
Crude protein (%wt)^{db}	5.8-6.7	Values are average values from a lot of samples.
Crude fiber (%wt)^{db}	12.9	Values are average values from a lot of samples.
Neutral Detergent Fiber (NDF) (%wt)^{db}	18.9-20.6	Values are average values from a lot of samples.
Acid Detergent Fiber (ADF) (%wt)^{db}	12.9-14.9	Values are average values from a lot of samples.
Lignin (%wt)^{db}	0.8	Values are average values from a lot of samples.
Ether extract (%wt)^{db}	2-3.3	Values are average values from a lot of samples.
Ash (%wt)^{db}	2-6.6	Values are average values from a lot of samples.

PHYSICOCHEMICAL PROPERTIES	RANGE	COMMENTS
Gross energy (%wt)[db]	17.2	Values are average values from a lot of samples.
FERTILIZER		
Phosphorus (g/kg)[db]	0.4-0.8	
Potassium (g/kg)[db]	14.9	
Calcium (g/kg)[db]	1.7-7.3	
Sulfur (g/kg)[db]	0.2	
BIOACTIVE COMPOUNDS		
Pectin (g/kg)[db]	425	
polyphenols (g GAE/kg)[db]	1.8-2.4	
starch (% wt)[db]	3.4-3.8	
organic acids (% wt)[db]	4.4	

18.2 Orange (citrus) wastewater

The citrus industry also generates significant amounts of wastewater. The wastewater typically contains condensate, wash water and press liquor. Note that condensate and press liquor are not generated if the pulp is not processed. The most common approach to treatment of wastewater is using lagoons or activated sludge process (Koppar & Pullammanappallil, 2013). Citrus wastewater, such as citrus pulp, has also high organic content, consisting of various soluble and insoluble carbohydrates, making these amenable and attractive for anaerobic digestion (Koppar & Pullammanappallil, 2013). The major physicochemical characteristics of citrus wastewater are summarized in Table 18.2.

Table 18.2: Summary of main physicochemical characteristics of citrus wastewater (Koppar & Pullammanappallil, 2013; Santos et al., 2010; Viuda-Martos et al., 2011).

PHYSICOCHEMICAL PROPERTIES	RANGE	COMMENTS
WATER CHARACTERISTICS		
pH	4.6-4.8 and 11.2	High pH value refers to processed citrus wastewater (derived from the pressing of orange peel)
Conductivity (mS/cm)	2.55	
Total Alkalinity (mg $CaCO_3$/L)	8360	citrus wastewater (derived from the pressing of orange peel)
Total Solids (mg/L)	151900	citrus wastewater (derived from the pressing of orange peel)
Fixed Solids (mg/L)	14160	citrus wastewater (derived from the pressing of orange peel)
Total Suspended Solid (mg/L)	20780	citrus wastewater (derived from the pressing of orange peel)
Fixed Suspended Solids (mg/L)	3200	citrus wastewater (derived from the pressing of orange peel)
TOC (mg/L)	52970	citrus wastewater (derived from the pressing of orange peel)
COD (mg/L)	147680	citrus wastewater (derived from the pressing of orange peel)
Total Kjeldahl Nitrogen (TKN) (mg/L)	62.8	

18.3 Orange (citrus) AWCB bioactive compounds patent and literature review

The direct utilization of orange peel is the simplest option for implementation, requiring little infrastructure or investment, whilst potentially greatly increasing the value of the waste material. Sharma et al. (Sharma et al., 2017) commented upon the environmental aspects of citrus waste reuse and its management schemes (Figure 18.2). The most common waste management methods for these citrus wastes are composting, anaerobic digestion, incineration, thermolysis and gasification. However, orange pulp contains many high value compounds, which if extracted employing state of the art technologies, could transform what is typically considered to be a problematic substrate to a high value commodity. Among these ***essential oils*** and ***pectin*** are the most attractive in terms of potential economic value (Ángel Siles López et al., 2010). Besides this, many other value added compounds or phytochemicals of commercial importance such as phenolic and flavonoids, fibers, limonoids and carotenoids can be efficiently extracted from the citrus wastes and utilized in several ways as reviewed by Sharma et al. (Sharma et al., 2017).

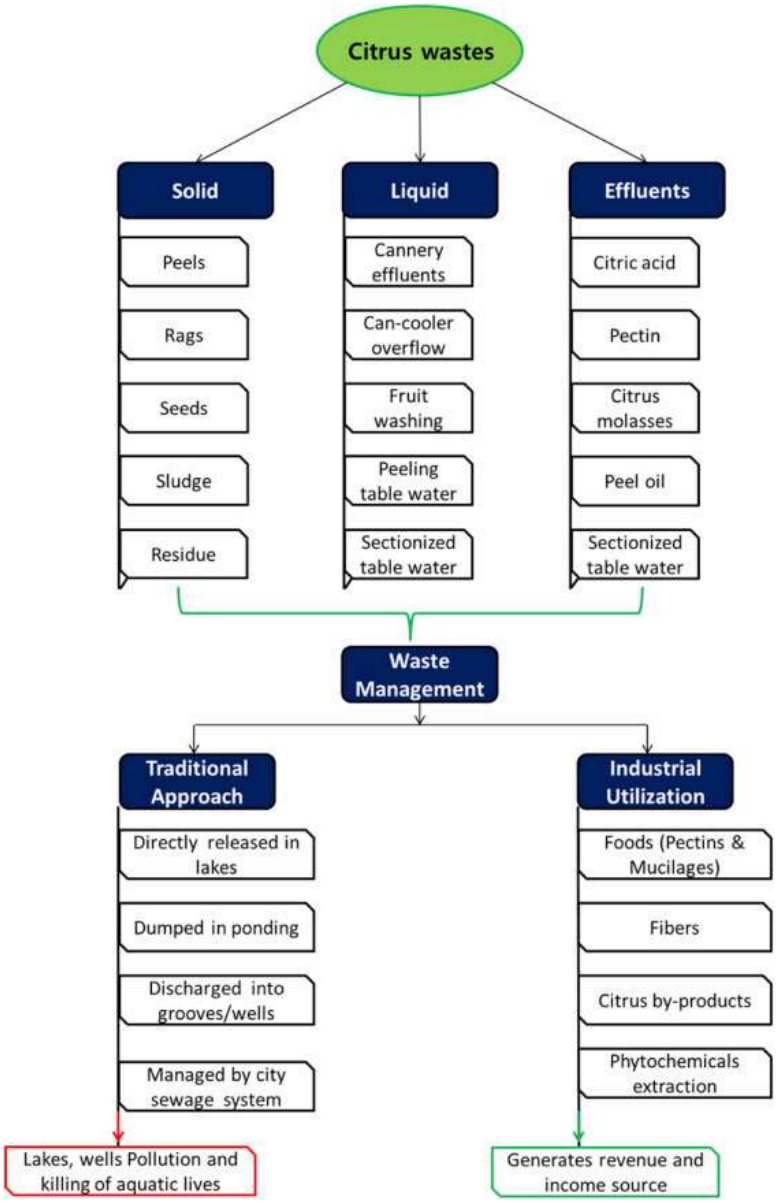

Figure 18.2: Environmental aspects of citrus waste reuse and its management (Sharma et al., 2017).

Additionally, Rezzadori et al. proposed six products which can be obtained from the solid fraction and four from the liquid fraction of the orange waste, including ***essential oils*** extraction by the (solid and liquid) orange residue (yield 1.6 g/kg of waste), ***dietary fibers*** recovery (yield 650 g/kg of waste), **soluble fiber/pectin** production (yield 43 g/kg waste), ***biogas*** production (43 m^3/t wet citrus waste), ***ethanol*** production (39.7 L/t wet citrus waste), ***limonene*** production (8.9 L/t wet citrus waste) (Rezzadori et al., 2012). Furthermore, during the EC-funded FP7 project NAMASTE-EU, new laboratory-scale protocols and processes were developed for the exploitation of citrus processing by-products and wheat bran surpluses via the production of ingredients useful for the formulation of new beverage and food products. Among the main results achieved in this project, there are the development and assessment of procedures for the selection, stabilization and the physical/biological treatment of citrus and wheat processing by-products, the separation and recovery of some bioactive molecules and ingredients and the development of procedures for assessing the quality of the obtained ingredients and for their exploitation in the preparation of new food products (Fava et al., 2013).

Finally, the following tables summarize a number of patents (applied or issued) regarding the recovery of high added value compounds from citrus industry.

Patent No	EP 2386338 A1 20111116
Publication Date	16/11/2011 (Publication date)
Title	Use of fruit skin extracts as corrosion inhibitors and process for producing same
Description/Abstract	The present invention relates to the use of fruit skin extracts as corrosion inhibitors, more particularly to the use of the skin of fruits such as mango, cashew, passion-fruit and orange, inter alia, more specifically as corrosion inhibitors for steel in an acid medium, preferably carbon steel 1020 in a 1 mole/L-1 hydrochloric acid medium, and also for various types of steel, metals such as copper and copper alloys, inter alia, in neutral and basic media, and to the process for producing same.
Type of AWCB	fruit skin of mango, cashew, passion-fruit and orange
Recovered high added compound	extracts as corrosion inhibitors
Details/methodology applied	solvent extraction

Patent No	United States Patent Application 20120135109 A1
Publication Date	31/5/2012
Title	Fiber obtained from fruit or vegetable byproducts
Description/Abstract	A fiber extracted from a fruit or vegetable byproduct is provided, the extracted fiber having a molecular weight of between about 5000 grams/mol (g/mol) and about 8000 g/mol, or a pectic oligosaccharide having a molecular weight of between about 300 g/mol and 2500 g/mol. The fiber may be extracted using physical methods or a combination of a physical method to break the fruit or vegetable byproduct cell walls and enzymatic hydrolysis. Also, a comestible containing the extracted fiber is provided. A method for producing a soluble fiber is further provided including reducing the particle size of a fruit or vegetable byproduct, subjecting the byproduct particles to a physical process to break cell walls of the particles, adding one or more enzymes, mixing or agitating the particles, and filtering the byproduct particles to provide a retentate and a permeate. The permeate contains the soluble fiber, which is optionally a prebiotic fiber.
Type of AWCB	orange peel, grapefruit peel, lemon peel, lime peel, or combinations thereof.
Recovered high added compound	fibers
Details/methodology applied	physical-chemical and enzymatic pre-treatment methods, filtration.

Patent No	EP 1784087 B1 20121010
Publication Date	10/10/2012 (Publication date)
Title	Process of extracting citrus fiber from citrus vesicles
Description/Abstract	A process of recovering citrus fiber from citrus vesicles, said citrus vesicles being separated from citrus juice, to obtain a food additive suitable for human consumption, the process comprising: (i) washing citrus vesicles with water and recovering water washed vesicles therefrom; (ii) an organic solvent extraction step comprising contacting the water washed vesicles with an organic solvent to obtain organic solvent washed vesicles; and (iii) desolventizing the organic solvent washed vesicles and recovering dried citrus fiber therefrom characterised in that said organic solvent extraction step is a single or multi-stage extraction wherein the retention time in each extraction stage is 5 minutes or less.
Type of AWCB	citrus juice
Recovered high added compound	citrus fiber
Details/methodology applied	solvent extraction

Patent No	EP 0824872 B1 20021009
Publication Date	09/10/2002 (publication date)
Title	Flavouring agents obtained from fruit pulp fibres
Description/Abstract	A process for preparing flavour precursors for meat flavours which comprises enzymatically hydrolysing citrus pulp, citrus pectin or apple pulp fibre with a pectolytic enzyme at a pH from 4 to 6, at a temperature from 40°C to 60°C for a period of time from 6 to 48 hours, inactivating the enzyme and drying the hydrolysate.
Type of AWCB	citrus pulp, apple pulp fibre
Recovered high added compound	flavour precursors for meat flavours
Details/methodology applied	enzymatic hydrolysis, and drying

Patent No	WO 2014094099 A1
Publication Date	26/6/2014 (publication date)
Title	Bioprocess for extracting silicon from the agro-industrial waste rice husk using the natural extractant citric acid, which is derived from waste from the citrus industry, for developing an organic silicate fertilizer
Description/Abstract	Bioprocess for extracting silicon from the agro-industrial waste rice husk using the natural extractant citric acid, which is derived from waste from the citrus industry, for developing an organic silicate fertilizer, particularly a bioprocess for extracting silicon from the agro-industrial waste rice husk using the natural extractant citric acid, which is derived from waste from the citrus industry, for developing an organic silicate fertilizer with the technological aim of providing an organic source of silicon from various agro-industrial wastes, through the extraction thereof by the processes of fermentation and decoction. The ideal process for extracting silicon has been defined in this first step, for providing silicon content in manure both when it is elaborated and after it has been sitting for three months, and also for lowering pH values and for increasing the concentrations of macro- and micronutrients. An increase in the use of said wastes has been observed due to the agro-industrial generation of large quantities thereof. In the second step of the invention, the process for elaborating the fertilizer was optimized, as well as the form of the wastes being altered.
Type of AWCB	agro-industrial waste rice husk, citric acid from the citrus industry
Recovered high added compound	organic silicate ferilizer

Patent No	US 20150065698 A1 + WO2013150262 A1
Publication Date	5/3/2015 (publication date)
Title	Microwave assisted citrus waste biorefinery
Description/Abstract	There is described a method of isolating one or more of pectin, d-limonene, a flavor compound, a flavonoid, a soluble monosaccharide, a decomposition product of a monosaccharide and cellulose, from citrus material wherein said method comprises the microwave assisted hydrothermal low temperature treatment of citrus material.
Type of AWCB	citrus waste
Recovered high added compound	pectin, d-limonene
Details/methodology applied	microwave assisted hydrothermal low temperature treatment of citrus material.

Patent No	EP 1272254 B1 20060201
Publication Date	01/02/2006 (Issue date)
Title	Method for obtaining useful materials from the by-products of fruit and vegetable processing
Description/Abstract	Method for recovering useful substances from the by-products of fruit and vegetable processing, characterised in that when carrying out the recoveryprocess of pectin from the by-products using a selective adsorber as the first useful substance, the polyphenols contained in the by-products are separated off as a second useful substance and are recovered from the adsorber by means of subsequent desorption.
Type of AWCB	by-products arising during the production of juice from ripe fruits or vegetables are used, apple pomace or citrus pomace
Recovered high added compound	pectin, polyphenols
Details/methodology applied	adsorption

19. Mandarin/tangerine fruits

The mandarin/tangerine tree is easily adaptable to diverse climates; it can be cultivated in desert, semitropical and subtropical climate conditions. Despite this adaptability, every variety needs specific climate conditions to obtain good quality fruit and an abundant production. Tangerine juice is often used to increase the color of orange juice in proportions of about 10% (Martí et al., 2011). Disposal of tangerine residues is problematic, as the juice producing industry is being grown rapidly in response to increasing health concerns. Several million tons of tangerines are in the market (Nitayapat et al., 2015). In this section, physicochemical characteristics of mandarin processing solid waste are only reported because no sufficient literature data were found on liquid waste of tangerine processing industry. On the other hand, commonly, in literature, waste from tangerine processing industry are referred to as citrus waste.

19.1 Tangerine processing solid waste

Fifty percent of the tangerines is discarded as solid wastes (including peel, core and frit) after the juice extraction process. Tangerine residues remain nutritious, having carbohydrates (e.g. lignocellulose and sugars), proteins, vitamins, minerals, antioxidants, etc. A summary of the main physicochemical characteristics of tangerine solid waste is provided in Table 19.1. At present, tangerine residues are diverted to landfill, and directly used as an ingredient of animal feeds or fertilizers as the main source of carbohydrate and carbon, respectively (Martí et al., 2011; Nitayapat et al., 2015).

Table 19.1: Summary of main physicochemical characteristics of tangerine wastes (Barros et al., 2012; Martí et al., 2011; Zhou et al., 2015).

PHYSICOCHEMICAL PROPERTIES	RANGE (PEELS)	RANGE (CORE)
ENERGY		
Higher Heating Value (HHV) (MJ/kg)	18.5	
Fixed Carbon (%wt)^{db}	20.6	
Volatile Matter (%wt)^{db}	76.5	
Ash (%wt)^{db}	2.9-4.1	3.4-3.5
Moisture (% wt)^{am}	73-81	70-82
Carbon (%wt)^{db}	47.3	
Oxygen (%wt)^{db}	42.6	
Hydrogen (%wt)^{db}	5.8	
Nitrogen (%wt)^{db}	1.4	
Sulfur (%wt)^{db}	0.08	
FODDER		
Crude fiber (%wt)^{db}	16-20	9-15
Neutral Detergent Fiber (NDF) (%wt)^{db}	17-30	11-21
Acid Detergent Fiber (ADF) (%wt)^{db}	16-26	14-26
FERTILIZER		
Nitrogen (g/kg)^{db}	13.9	
Sulfur (g/kg)^{db}	0.78	

19.2 Tangerine AWCB bioactive compounds patent and literature review

Edible fiber production, ***antioxidant extraction***, ***ethanol fermentation*** and ***citric acid production*** have been investigated as alternative utilization of waste from tangerine industry (Martí et al., 2011; Nitayapat et al., 2015).

20. Peach fruits

Peach is the third most important deciduous tree fruits worldwide, ranking after apples and pears (Wu et al., 2011). Peach [Prunus persica (L.) Batsch] has been reported to contain a variety of phenolics, such as chlorogenic acid, neochlorogenic acid, catechin, epicatechin and derivatives of cyaniding and quercetin. Composition and concentrations of these phytochemicals vary according to maturity, genotype, horticultural practices, geographic origin, postharvest storage conditions and processing procedure (Liu et al., 2015). Around 0.7 million metric tons of peaches are processed to natural juice and or canned in syrup in the EU (Oreopoulou & Russ, 2007). The main by-product from peaches processing industry is the pomace/pulp remaining after the production of juice. The pits of peaches, another major by-product, contain a kernel (like an almond) with bitter flavor.

20.1 Peach pomace/pulp

Depending on the ripeness of the peaches, approximately ten percent is lost as waste peach pulp (WPP) during the processing. Typically 1 kg of WPP contains 8.1 g sugar, 1.5 g protein, 0.3 g raw fat, 1.5 g potassium, 0.1 g calcium, 0.1 g phosphorus, 2.5 g cellulose and 0.3 g pectin (Argun & Dao, 2016b). Peach is produced with an annual global production rate of 3.34% and the total peach production in 2013 was about 21 million tonnes (Argun & Dao, 2016b). The following Table summarizes the main physicochemical characteristics of waste peach pomace/pulp.

Table 20.1: Summary of main physicochemical characteristics of waste peach pomace/pulp (Argun & Dao, 2016a; Arvelakis et al., 2005; Ashraf et al., 2011; Pagán et al., 2001).

PHYSICOCHEMICAL PROPERTIES	RANGE	COMMENTS
ENERGY		
Fixed Carbon (%wt)^{db}	18.1	Mixture of peach kernels + pulp
Volatile Matter (%wt)^{db}	81.3	Mixture of peach kernels + pulp
Ash (%wt)^{db}	0.5-0.7	Mixture of peach kernels + pulp
Moisture (% wt)^{am}	87.7 (pulp), 8.5 (kernels + pulp)	
Carbon (%wt)^{db}	52.0	
Oxygen (%wt)^{db}	40.7	
Hydrogen (%wt)db	5.8	
Nitrogen (%wt)^{db}	0.8	
Sulfur (%wt)^{db}	< 0.01	
FODDER		
Crude protein (%wt)^{db}	0.6	pulp
Crude fiber (%wt)^{db}	2.0	pulp
Ether extract (%wt)^{db}	0.2	pulp
Gross energy (%wt)^{db}	21.6	Mixture of peach kernels + pulp
FERTILIZER		
Potassium (g/kg)^{db}	2.3	Mixture of peach kernels + pulp
Calcium (g/kg)^{db}	0.4	Mixture of peach kernels + pulp
Magnesium (g/kg)^{db}	0.12	Mixture of peach kernels + pulp
BIOACTIVE COMPOUNDS		
polyphenols (mg GAE/100 g)	84.6	In mg/100 g fresh fruit
Pectin (g/100 g)^{db}	16	

20.2 Peach stones/pits/kernels

A significant part of the harvested peaches is processed resulting in a substantial amount of waste stones/pits containing the peach kernel. Peach kernels contain almost 50 wt% of oils (Wu et al., 2011). The main physicochemical characteristics of peach pits and kernels are summarized in Table 20.2.

Table 20.2: Summary of main physicochemical characteristics of peach pits/stones/kernels (Arvelakis et al., 2005; Ashraf et al., 2011; Jenkins & Ebeling, 1985a; Rahma & El-Aal, 1988; Saffe, 2014; Wu et al., 2011).

PHYSICOCHEMICAL PROPERTIES	RANGE	REMARKS
ENERGY		
Higher Heating Value (HHV) (MJ/kg)	20.8-21.4	Peach pits
Lower Heating Value (LHV) (MJ/kg)	19.6	Peach stones (kernels + pulp), peach seeds, peach pits
Fixed Carbon (%wt)^{db}	18.1-19.9	Peach stones (kernels + pulp), peach seeds, peach pits
Volatile Matter (%wt)^{db}	79.1-81.3	Peach stones (kernels + pulp), peach seeds, peach pits
Ash (%wt)^{db}	0.7-3.4	Peach stones (kernels + pulp), peach seeds, peach pits
Moisture (% wt)^{am}	7.0-8.5	Peach stones (kernels + pulp), peach seeds, peach pits
Carbon (%wt)^{db}	52-53	Peach stones (kernels + pulp), peach seeds, peach pits
Oxygen (%wt)^{db}	37.1-40.7	Peach stones (kernels + pulp), peach seeds, peach pits
Hydrogen (%wt)^{db}	5.8-5.9	Peach stones (kernels + pulp), peach seeds, peach pits
Nitrogen (%wt)^{db}	0.3-0.8	Peach stones (kernels + pulp), peach seeds, peach pits
Sulfur (%wt)^{db}	< 0.05	Peach stones (kernels + pulp), peach seeds, peach pits
FODDER		
Crude protein (%wt)^{db}	2.7 (seeds), 27.5 (whole peach kernels)	Peach seeds, whole peach kernels
Crude fiber (%wt)^{db}	1.9 (seeds), 3.0 (whole peach kernels)	Peach seeds, whole peach kernels
Ether extract (%wt)^{db}	37.7	Peach seeds
Ash (%wt)^{db}	3.4	whole peach kernels
Gross energy (%wt)^{db}	21.6	Peach stones (kernels + pulp)
FERTILIZER		
Phosphorus (g/kg)^{db}	0.02	Peach pits
Potassium (g/kg)^{db}	0.1-2.3	Peach stones (kernels + pulp), peach seeds, peach pits
Calcium (g/kg)^{db}	0.05-0.4	Peach pits, peach stone (kernels + pulp)
Magnesium (g/kg)^{db}	0.03-0.1	Peach pits, peach stone (kernels + pulp)
BIOACTIVE COMPOUNDS		
polyphenols (g GAE/kg)^{db}	7-8	In peach kernel oil
Oil yield (g/g DM)	0.25-0.38	Peach kernels (mainly oleic 66% and linoleic acid 26%)

20.3 Peaches AWCB bioactive compounds patent and literature review

The pomace/pulp remaining after the production of juice can be used for the recovery of ***pectin***. Pectin recovered from fresh peach pomace is highly methoxylated and has good gelling properties (Pagán & Ibarz, 1999; Schieber et al., 2001). Peach kernel oil has been widely used in the cosmetics industry as an ingredient in soaps, shampoos, lotions, creams, and shampoos because it is a light, penetrating oil, and absorbs easily and does not leave a greasy feeling. Peach kernel oil is nutritionally attractive and has an opportunity of producing high value products from the biowaste in peach industry due to their ***unsaturated fatty acid***, which play an important role in the regulation of a variety of physiological and biological functions, and ***antioxidant/polyphenolic*** constituents (Wu et al., 2011). The main fatty acids found in peach kernel oil are about 58-66% ***oleic*** acid and 26-32% ***linoleic acid*** (Wu et al., 2011). There are only few studies on the extraction of peach kernel oil and the fatty acid profile, polyphenolic compound, physicochemical properties and antioxidative properties of peach kernel oil are not well established yet (Wu et al., 2011).

Apart from the use of ***kernel oil*** in cosmetics, peeled kernels serve as a raw material for the production of ***persipan***. This requires debittering by hydrolysis of the cyanogenic glycosides. Grinding, soaking, and cooking reduce the cyanogenic glycosides content, but complete hydrolysis may be achieved by the use of b-glucosidase (Schieber et al., 2001). Peach (such as apricot) kernels also are good sources of protein containing approx. 28% protein; the main problem for their use in foods is that the peach kernel has slightly toxic effects when used excessively due to its content of hydrogen cyanide (prussic acid). Hydrogen cyanide is a chemical compound with extremely poisonous, because it binds irreversibly to the iron atom in hemoglobin, making it unavailable to transport the vital O_2 to the body's cells and tissues (Wu et al., 2011).

According to European patent EP1302251 B1, among to other residual agro-industrial waste, shells, pits and peels from peaches processing could be used for producing a vegetable flour and also for production of papers and cardboards from this flour.

Patent No	EP1302251 B1
Publication Date	27/8/2008
Title	Method for producing a vegetable flour using residues of agroindustrial processes, and method for producing papers and cardboards using said flour.
Type of AWCB	residues of agroindustrial processes, particularly shells, pits and peels (nuts, hazelnuts, peanuts, pistachios, pine seeds, peaches, apricots, plums, prunes, olives, cherries, coffee, dates and the like), (bananas, pears, apples, peaches, apricots, grapes, tomatoes, fennels, artichokes, peas, beans and pineapple and the like)
Recovered high added compound	papers and cardboards

VEGETABLES & ROOT CROPS

21.Potatoes

Potatoes are cultivated for food in more than 100 countries, sometimes as a staple food but usually as an alternative food. The starchy tubers are used as a vegetable and can be boiled, baked, fried (to make chips), dried and ground into flour to make biscuits, bread and other pastries. They can be cooked and frozen. Their very high-grade starch is appreciated for food and by the pharmaceutical industries.

Potatoes are also a very valuable source of feed for all classes of livestock. The tubers are relished by pigs and cattle. Sweet potatoes can be used on-farm or as an ingredient in commercial compound feeds. The economic value of the sweet potato as animal feed used to be debatable because producing them at 30% DM was as costly as importing grain at 89% DM (feedipedia, 2016). However, new varieties now produce more edible energy per ha per day than any other major food crop and 30% more starch/unit area than maize. Sweet potato tubers are used as an energy crop: the tubers can be fermented to produce alcohol, and the plant grows in areas where maize does not (Gupta et al., 2009; Lebot, 2009).

Potatoes are the world's fourth largest crop behind corn, rice, and wheat and have experienced a steady growth over the last two decades as a stable food crop and a major source of starch (FAO, 2016). According to data from the National Potato Council (NPC, 2016) the world's total potato production reached 385 million tn in 2014. A typical potato processing plant can generate 6–10% potato peel waste (PPW) from the peeling process (Mader et al., 2009), and other defect removal, trimming, and cutting processes can generate an additional 15% waste. This combined waste stream can pose a significant waste management effort, and therefore, knowing this waste's composition will facilitate its utilization into bio-products (Liang & McDonald, 2014).

PPW has been utilized in a variety of applications and traditionally has been used for local animal feed (Camire et al., 1997; Liang & McDonald, 2014). PPW is not suitable for non-ruminants without further treatment because it is too fibrous to be digested (Sepeleva & Galoburda, 2015), but as an inexpensive by-product it contains a large quantity of starch, nonstarch polysaccharides, lignin, polyphenols, protein and valuable base material for extraction of valuable products (such as natural antioxidants, dietary fibre, biopolymers, etc.) and fermentation processes (Al-Weshahy & Rao, 2012; Arapoglou et al., 2010; Sepeleva & Galoburda, 2015).

Figure 21.1: Potato tubers (left photo) and potato plant (right photo) (feedipedia, 2016).

21.1 Potato peels

Potatoes are usually peeled during processing and production losses in a form of potato peel waste (PPW) can vary from 15 to 40%, depending on the peeling method. Plants peel the potatoes as part of the production of crisps, instant potatoes and similar products. The produced waste is 90 kg per Mg of influent potatoes and is apportioned to 50 kg of potato skins, 30 kg starch and 10 kg inert material (Arapoglou et al., 2009).

Abrasion peeling is typical for chips production, whereas steam peeling is used for dehydrated and frozen potato products (Schieber & Saldaña, 2009). Steam peelers are compact and generate less product losses, but require high investment and operation costs. Because of that, steam peeling is reasonable when high quantities of product (from 8 to 20 t h^{-1}) have to be peeled in limited space and appearance of brown ring (also known as heat ring, or cooking ring) does not cause problems for final product. Brown ring occurs due to tissue damage and enzyme-catalyzed phenolic oxidation reaction. It is reported, that chemical peeling using NaOH could replace steam peeling to avoid heat-ring. Otherwise abrasion peeling is to be used (Camire et al., 1997; Sepeleva & Galoburda, 2015).

The method of peeling was found to be a key factor influencing the chemical composition of peels and its suitability for further utilization. Camire at el. (1997) compared the influence of peeling method on composition of potato peels. Abrasion, method of peeling used by potato chip manufacturers, results in more starch and less dietary fiber than the steam peeling method used in the production of dehydrated potatoes. Potato peels with either abrasion or steam peeling methods were extruded; at barrel temperatures of either 110 ^{o}C or 150 ^{o}C and fed moistures of either 30 or 35%. Extrusion was associated with an increase in total dietary fiber and lignin contents and a decrease in starch content in steam peels. Lignin content was found to decrease but total dietary fiber content was unaffected in extruded abrasion peels. Soluble nonstarch polysaccharides increased in both types of peeling because of extrusion (Camire et al., 1997).

The higher quantity of glucose recovered from the insoluble fiber fraction of extruded steam peels was reported to be the possible reason in the formation of resistant starch. On the other hand, manual peeling of potato produced peels with approximately 63%, on a dry weight basis of alcohol-insoluble fibers, which was separated into pectic substances, hemicellulose, cellulose, and lignin. These fractions consisted of 3.4% pectin, 2.2% cellulose, 14.7% protein, 66.8% starch, and 7.7% ash. The sugars in the alcohol-soluble fraction consisted of 1.4% total soluble sugars and 0.9% reducing sugars (Al-Weshahy & Rao, 2012).

The main physicochemical characteristics of potato peels are summarized in the table below.

Table 21.1: Summary of main physicochemical characteristics of potato peels (ECN, 2016; feedipedia, 2016; Gupta et al., 1993; Liang & McDonald, 2014; Mahmood et al., 1998).

PHYSICOCHEMICAL PROPERTIES	MEAN VALUE
ENERGY	
Higher Heating Value (HHV) (MJ/kg)	17.3
Volatile Matter (%wt)^{db}	92.3
Ash (%wt)^{db}	7.5
Moisture (% wt)^{am}	82.2
Carbon (%wt)^{db}	43.8
Oxygen (%wt)^{db}	46.2
Hydrogen (%wt)^{db}	6.0
Nitrogen (%wt)^{db}	2.5
Sulfur (%wt)^{db}	0.1
FODDER	
Dry matter (%wt)^{am}	17.8
Crude protein (%wt)^{db}	15.8

Crude fiber (%wt)[db]	3.4
Acid Detergent Fiber (ADF) (%wt)[db]	13.3
Lignin (%wt)[db]	21.6
Ether extract (%wt)[db]	0.7
Ash (%wt)[db]	7.9
Gross energy (MJ/Kg)	17.4
FERTILIZER	
Nitrogen (g/kg)[db]	21.4
Phosphorus (g/kg)[db]	3.1
Potassium (g/kg)db	32.2
Calcium (g/kg)[db]	8.4
Magnesium (g/kg)[db]	1.8
Sulfur (g/kg)[db]	0.2
VALUE-COMPOUNDS	
Starch (g/kg)[db]	533.9
Total sugars (g/kg)[db]	14.0

21.2 Potato wastewater

Large volumes of wastewater and organic wastes are generated in potato processing as result of the water used in washing, peeling, and additional processing operations. The treatment of this wastewater has been a challenge for the potato processing industry for many years. The wastewater effluent with high concentrations of potassium and Chemical Oxygen demand (COD) caused by the presence of starch, proteins, amino acids and sugars, imposes expensive treatment processes to the companies (Strætkvern & Schwarz, 2012). However, this waste effluent contains high amounts of valuable by-products (Dabestani et al., 2017).

An average sized potato processing plant producing French fries and dehydrated potatoes can create a waste load equivalent to that of a city of 200,000 people. About 230 million liters of water are required to process 13,600 tons of potatoes. This equals about 17 L of waste for every kilogram of potatoes produced. Raw potato processing wastewaters can contain up to 10,000 mg/L COD. Total suspended solids and volatile suspended solids can also reach 9700 and 9500 mg/L, respectively. Wastewater composition from potato processing plant depends on the processing method, to a large extent. In general, the following steps are applied in potato processing: washing the raw potatoes; peeling, which includes washing to remove softened tissue; trimming to remove defective portions; shaping, washing, and separation; heat treatment (optional); final processing or preservation; and packaging (Wang et al., 2006).

The potato composition used in potato processing operations determines the components of the resultant waste stream. Foreign components that may accompany the potato include dirt, caustic, fat, cleaning and preserving chemicals. Generally, the various waste streams are discharged from the potato plant after being combined as effluent. Processing involving several heat treatment steps such as blanching, cooking, caustic, and steam peeling, produces an effluent containing gelatinized starch and coagulated proteins. In contrast, potato chip processing and starch processing produce effluents that have unheated components (Pailthorp et al., 1987; Wang et al., 2006).

The main physicochemical characteristics of potato wastewater are summarized in the table below.

Table 21.2: Summary of main physicochemical characteristics of potato wastewater (Burgoon et al., 1999; Dabestani et al., 2017; Liang et al., 2015; Wang et al., 2006).

PHYSICOCHEMICAL PROPERTIES	MEAN VALUE
ENERGY	
Volatile Matter (%wt)^{db}	95.0
Ash (%wt)^{db}	4.8
Carbon (%wt)^{db}	42.2
Sulfur (%wt)^{db}	0.1
FODDER	
Ether extract (%wt)^{db}	2.3
WATER	
pH	6.4
Total Solids (mg/L)	128000.0
Total Suspended Solids (mg/L)	55175.0
COD (mg/L)	2800.0
BOD_5 (mg/L)	3000.0
Total Nitrogen (TN) (mg/L)	150.0
VALUE-COMPOUNDS	
Starch (g/kg)^{db}	180.5
Protein (g/kg)^{db}	113.3
Total sugars (g/kg)^{db}	30.0

21.3 Potato AWCB bioactive compounds patent and literature review

The composition of steam PPW was determined by Camire et al (Camire et al., 1997) and shown to contain starch (25%), nonstarch polysaccharide (30%), acid insoluble and acid soluble lignin (20%), protein (18%), lipids (1%), and ash (6%). The lipid fraction was shown to comprise long chain fatty acids, triglycerides, alcohols, sterols, sterol esters, and phenolics (Dobson et al., 2004). Suberin, a rubbery polyester material composed of polyaromatic and polyaliphatic domains, has been found in the cell walls of potatoes. Lignin, a three-dimensional polymer made up of phenylpropane units, has also been detected in the plant cell wall (Liang & McDonald, 2014).

Suberin and lignin fractions have been pressure extracted from PPW to obtain value added antioxidants and bioactive chemicals (Piletska et al., 2012; Wijngaard et al., 2012). While fermentation of PPW starch has been employed to generate alcohols and organic acids. Arapoglou et al. converted PPW by sequential enzymatic hydrolysis and fermentation using Saccharomyces cereviciae to yield ethanol (Arapoglou et al., 2010). Lactic acid has also been produced from PPW using pure cultures of *Lactobacillus var*. or *Rhizupus var*. (Afifi, 2011). Recently, PPW has been directly converted to primarily lactic acid, a useful chemical building block for the production of polylactic acid, using undefined mixed microbial culture fermentation (Liang & McDonald, 2014).

Many patents have been issued on recovery of the above bioactive compounds from tomato AWCB and are summarized in the following tables.

Patent No	CN 104000935 A
Issue Date	27/08/2014
Title	Method for extracting anti-oxidative phenolic acids from potato peel slag
Description/Abstract	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 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
Type of AWCB	Potato peel
Recovered high added compound	Anti-oxidative phenolic acids

Patent No	US 3891782 A
Issue Date	24/06/1975
Title	Method of extracting potato flour from waste peel and dehydrator waste
Description/Abstract	Potato flour is prepared from waste potato mash containing 25 to 30 percent or more specks by placing the mash on a drum dryer to produce a dry sheet of potato on the drying drum, adjusting or maintaining the moisture content of the sheet between about 10 and 15 percent, grinding the resulting sheet to a particle size adapted to allow separation of peel specks from the uncontaminated potato pulp and separating the thus dried pulp from the peel specks by screening.
Type of AWCB	Potato peel
Recovered high added compound	Potato flour

Patent No	US 6524639 B1
Issue Date	25/02/2003
Title	Composite food product comprising potato peel product
Description/Abstract	The present invention provides adhesive and binder compositions comprising a potato peel product characterized on a dry solids basis by at least 30% starch, at least 5% protein and at least 2% fibers.
Type of AWCB	Potato peel
Recovered high added compound	Composite food product

Patent No	CN 101617847 B
Issue Date	07/05/2012
Title	Production method of potato peel healthcare vinegar drink and product thereof
Description/Abstract	The invention belongs to the technical field of healthcare food production and relates to a production method of a healthcare vinegar drink of waste potato peel generated in a potato whole-powder production process, as well as a product thereof. Potato peel is rich in potassium (2600 mg/100 mg) and calcium (260 mg/100 mg) and contains a plurality of vitamins (Vb and Vc), antioxidation active matters and the like. Liquefaction, saccharification, cellulose hydrolysis and secondary fermentation with alcohol and acetic acid are carried out on the potato peel so as to obtain a potato peel healthcare vinegar with the acidity of 4.5 percent. The potassium content of the vinegar is as high as 520 mg/100 mg, and the calcium content is as high as 130 mg/100 mg. The healthcare vinegar can be used for seasoning during the cooking, can be mixed with medlar leach liquor, honey and the like for condensing the concentrated vinegar drink, and also can be mixed with the mediar leach liquor and honey to prepare the energy vinegar drink.
Type of AWCB	Potato peel
Recovered high added compound	Vitamins, antioxidant compounds

Patent No	US 2666080 A
Issue Date	12/01/1954
Title	Method of producing protein hydrolizate from potatoes and potato waste
Description/Abstract	The primary object of this invention is to provide a process of extracting virtually all of the amino acids from potatoes and raw potato waste wherein the resultant product is a solid or crystalline mixture of the amino acids in purified form and substantially free of acid, sugars, and undesirable cations. Another important object of this invention is to provide a process of producing a mixture of amino acids utilizing potatoes and raw potato waste as the source materials, which process is capable of being carried out eiiiciently and continuously to produce an exceptionally pure mixture of amino acids which results from the hydrol ysis or degradation of the protein fraction in the raw tuber including tuberin, a globulin protein which is also completely hydrolyzed in the process. Another important object of this invention is to provide a process of the character described in which the sequential operation can be effectively and properly controlled at each step so that the quality of the end product will be substantially uniform. And yet another object of this invention is to provide a purified amino acid product. which, besides having neutritional benefits, can also be employed to substantially improve the color and iiavor of potato slices fried in animal fat or fats, or vegetable oil or oils, hydrogenated or non-hydrogenated, for making potato chips.
Type of AWCB	Potato waste
Recovered high added compound	Protein hydrolizate

Patent No	US 5354818 A
Issue Date	11/10/1994
Title	Livestock feed from potato waste
Description/Abstract	A method of producing livestock feed from potato processing waste is disclosed that uses a starch-hydrolyzing enzyme, two fermenting yeasts, such as Saccharomyces cerevisiae and Candida utilis, and the yeast Saccharomycopsis fibuliger. The enzyme and yeasts are added in a particular sequence to comminuted potato waste after the potato particles have been heated and cooled to certain temperatures.
Type of AWCB	Potato waste
Recovered high added compound	Nutrients

Patent No	CN 103265647 A
Issue Date	28/08/2013
Title	Method for extracting pectin from waste potato residues
Description/Abstract	The invention discloses a method for extracting pectin from waste potato residues. The method comprises the steps of: mixing waste residues, bamboo charcoal powder, attapulgite and water, wherein the waste residues are obtained after potato starch is processed, the bamboo charcoal powder is equivalent to 3-5% of the weight of the waste residues, and the attapulgite is equivalent to 5-8% of the weight of the waste residues; inoculating lactic acid bacteria; controlling the temperature not to exceed 45 DEG C, and fermenting for 2-3 days; then, grinding to obtain a pulp, mixing the ground pulp, heating and boiling for 10-15min, then, cooling the pulp to 60-70 DEG C, and preserving the heat for 2-3h; and subsequently, carrying out secondary extraction. The bamboo carbon powder and the attapulgite are additionally provided and mixed in the fermentation link, so that the waste residues can be deconstructed favorably, pectin can be favorably separated out, and the yield of pectin can be increased; and in addition, the filter residues are secondarily extracted, so that the yield of pectin is further increased.
Type of AWCB	Potato waste
Recovered high added compound	Pectin

Patent No	US 7306739 B1
Issue Date	11/12/2007
Title	Potato wastewater treatment method using a starch-complexing emulsifier
Description/Abstract	A method comprising treating a potato wastewater stream containing suspended free starch particles with a potato starch-complexing emulsifier to form agglomerated starch particle-emulsifier complexes, and separating the complexes from the remainder of said wastewater stream. Also the separated starch complex suitable for human or animal consumption alone or in combination with other food ingredients. In various embodiments, the products comprise (a) at least about 2000 mg/100 g, BDS, glutamic acid; and/or (b) at least about 2500 mg/100 g, BDS, aspartic acid; and/or (c) at least about 10 g/100 g, BDS, total protein.
Type of AWCB	Potato wastewater
Recovered high added compound	Food ingredients

Patent No	CN 1915117 A
Issue Date	21/02/2007
Title	Method for preparing compound beverage of sweet potato from wastewater of sweet potato
Description/Abstract	A composite beverage with nutritive health-care function is prepared from sweet potato sewage, wolfberry fruit, white chrysanthemum flower, liquorice root, citric acid, white sugar and antiseptic through vacuum filtering, enzymolyzing, depositing, membrane separation, etc.
Type of AWCB	Potato wastewater
Recovered high added compound	Nutrients

22. Sugar Beet

Sugar beet (*Beta vulgaris*) is a plant whose root has a high sucrose content and which is one of the major feedstocks for the sugar industry. From 2007 to 2015, between 19 and 22% of the sugar produced in the world per year was obtained from sugar beet (ISO, 2016). World sugar production amounted to approximately 153.4 Mtn and 175.1 Mtn, in 2009 and 2015, respectively. At least 130 kg of sugar and 45-50 kg of dried sugar beet pulp can be obtained from 1 tn of sugar beet containing 16% sucrose (FAO, 2016; Özbaş & Özbaş, 2017).

The main by-products generated during industrial sugar extraction from sugar beet are beet pulp and molasses. In the sugar production process, sugar beet is processed by extracting sugar from sliced beet (also known as beet strips or cossettes) with hot water (70°C) to produce the so-called raw juice. This raw juice is purified to obtain the so-called thin juice, with an average sugar content of 16%. The thin juice is then concentrated in multiple steps, resulting in a thick juice with an average sugar content of 67%. The syrup left from the final crystallization stage is called molasses. The residue after juice extraction, known as wet/fresh sugar beet pulp, has a dry matter content of 10-15%. This high water content limits the use of wet/fresh beet pulp to the vicinity of the sugar factory both form a transport and storage point of view. In fact, less than 1% of the beet pulp produced is used as wet/fresh pulp - it is generally mechanically pressed to remove excess water, thereby raising the dry matter content to above 18 and up to 35% (in common practice to between 20% and 28%) and thus valorizing the wet/fresh pulp into so-called pressed pulp. This pressed pulp, though easier to transport, has relatively poor keeping qualities. If heaped and covered to exclude air, it can be stored up to two weeks. For longer storage, it must be ensiled. In practice, between 36 and 42% of the sugar beet pulp produced in the EU (expressed in dry matter) is used as pressed pulp, while the largest proportion (between 57 and 63%) is dried (to less than 12% moisture content) to form either **dried sugar beet pulp** or (when mixed with molasses) **dried molassed sugar beet pulp**. This dried pulp is mostly marketed in the form of pellets, but can also be supplied as shreds (CIBE, 2017b; CIBE, 2017a; feedipedia, 2016; Vučurović & Razmovski, 2012).

Molasses is traditionally used as feed supplement (CIBE, 2017b; CIBE, 2017a), but also increasingly as a feedstock to produce yeast, citric acid and bioethanol. For example, in Serbia 90% of ethanol production comes from this raw material nowadays. Sugar beet pulp (SBP) is the fibrous product left after the extraction of sugar from grown sugar beet. Due to its highly digestible fiber, SBP is valued as an excellent animal feed (or feed complement) as well as an energy source. Beet pulp has also been proposed as a cultivation substrate, for divalent cations complexation, as a source of polyols for the production of urethanes and polyurethanes and as a source of fiber in biodegradable composites or for paper manufacture (Vučurović & Razmovski, 2012).

Sugar beet by-products (SBBs) are among the most widely produced and comparatively underutilized agro-industrial AWCBs. SBBs are usually used as animal feed – indeed, in the "List of feed materials" of COMMISSION REGULATION (EU) No 68/2013 of 16 January 2013 on the Catalogue of feed materials, molasses is described as a syrupy **product** obtained during the manufacture of sugar from sugar beets, while SBPs are described as **products** of the manufacture of sugar consisting of slices of sugar beet that have had sugar extracted with water. However, these products can be (and in some cases are) utilized to produce clean energy and to offset the high costs of the energy required for extraction and production processes in the industry (Aboudi et al., 2016).

Several studies have shown that SBBs are a suitable material for biological treatment by means of anaerobic digestion (AD) giving the advantages of agro-food AWCBs to produce clean energy such as methane from biogas (Aboudi et al., 2015; Aboudi et al., 2016; Alkaya & Demirer, 2011; Montañés et al., 2015; Ohuchi et al., 2015; Suhartini et al., 2014). However, bioconversion of agro-food AWCBs is still having limitations due to the presence of ligno-cellulosic (biodegradability issue) and nitrogen deficiency despite high carbohydrate content (Anwar et al., 2014; Sawatdeenarunat et al., 2015). Co-digestion of agro-food AWCBs with nitrogen-rich livestock manures can solve this problem by

balancing the nutrient content in the anaerobic digester, providing the required buffering capacity and adding a variety of microorganisms coming from animal digestive tracts who are capable of degrading vegetal fibers (Aboudi et al., 2015).

Figure 22.1: Sugar beet roots (left image), sugar beet dried pulp pellets (middle photo) and sugar beet molasses (right photo) (feedipedia, 2016).

22.1 Sugar beet pulp

Sugar beet pulp (SBP) is a product recovered after sucrose extraction from sugar beet slices. It is compressed, dried and usually used for cattle feed due to its high content in digestible fiber (Almohammed et al., 2017). The chemical composition of SBP can be given as: 26–32% hemicelluloses, 22–24% cellulose, 21.5–23% uronic acids, ~1–2% lignin, ~7–8% protein, 7.5–12% ash and ~0.5% residual sucrose. SBP is especially rich in pectin (38–62%) but has a low lignin content. A typical sugar beet usually contains at least 16% sucrose and 5% fiber on a wet mass basis (Özbaş & Özbaş, 2017).

As an AWCB of the sugar production industry, SBP is generally used for feed formulation, with comparatively moderate commercial value. Therefore, many attempts have been made to make the best use of these AWCBs (Huang et al., 2017). Several alternative ways for the valorization of sugar beet pulp were recently proposed, based on a biorefinery concept (Günan Yücel & Aksu, 2015; Hamley-Bennett et al., 2016; Vučurović & Razmovski, 2012). Yapo et al. (2007) reported the promising potential of sugar beet pulp as a good source of pectin, owing to its high pectin content (25–30% dry weight basis) and its availability in large quantities (Yapo et al., 2007).

SBP has a high pectin content on dry basis and pectin extracted from SBP exhibits superior emulsifying properties compared to other sources (Ma et al., 2013). SBP pectin possesses better surface-active and emulsifying properties, mainly because of a higher amount of protein. The enzymatic modification decrease of the protein content from 1.56% to 0.13% without any other significant change in composition decreased the emulsifying activity and stabilizing ability. In addition, SBP pectin contains a large amount of soluble dietary fiber, which is crucial in functional and health foods and contains galacturonic acid, rhamnose, arabinose and galactose as main sugar constituents (Huang et al., 2017; Lv et al., 2013).

As SBP is evaluated as an AWCB, it is mainly used as a cheap and readily available carbohydrate source for the production of renewable energy, especially liquid fuels, such as bioethanol, methane, biofuels etc. Furthermore, sugar beet pulp constitutes an attractive and inexpensive substrate for biogas production. Conversion of 1 ton of sugar beet roots generates around 45-50 kg SBP dry weight. In EU countries alone, between 4.9 and 6.3 million tonnes of SBP dry weight are produced annually, with year-on-year variation depending on the quantity of beet processed into sugar. In 2007, the company AGRANA opened a biogas plant in Kaposvár, Hungary, with SBP as the principal feedstock (Agrana, 2007). In 2016/17, this biogas plant generated about 30 million m^3, sufficient for the site to cover approximately 80% of its primary energy requirement for the 2016/17 beet campaign, or about 60% of its total primary energy needs for beet processing and the refining of raw

sugar into white sugar for the 2016|17 financial year. About 8.3 million m^3 of the biogas produced at the facility (containing about 58.7% methane) were refined by the biogas upgrading plant installed in autumn 2015 into approximately 4.9 million m^3 of biomethane (100% methane) for feeding into the local natural gas grid. The biomethane injected into the grid was equivalent to the annual heating requirement of about 1,950 single-family homes (Agrana, 2017b).

In 2012, a biogas plant with the installed capacity of 2 MW, producing biogas from fresh and ensiled SBP (50×10^3 ton per a year), was opened in the sugar factory in Strzelin (Poland) (Ziemiński & Kowalska-Wentel, 2017). The biogas plant operates all year round and its technological raw material is beet pulp. The plant uses fresh beet pulp during the sugar beet processing campaign (October to January) and ensiled beet pulp during the remaining period of the year. The facility is designed for an annual output of approximately 9.9 million m^3 biogas, 17.5 million kWh electricity and 18.1 million kWh heat. Another biogas plant, using mainly beet pulp and designed for an annual output of approximately 7.3 million m^3 biogas, 13.7 million kWh electricity and 14.5 million kWh heat, was opened in Zygmuntowo (Glinojeck) in 2013 (GMI, 2014).

Table 22.1: Summary of main physicochemical characteristics of sugar beet pulp (Agrana, 2017a; Fedna, 2012; FeedBase, 2013; Potthast et al., 2011; Tereos; Trident, 2017; EBZ, 2017).

PHYSICOCHEMICAL PROPERTIES	MEAN VALUE
ENERGY	
Ash (%wt)^{db}	7.4
Moisture (% wt)^{am}	74.8
Organic matter (N free) (%wt)^{db}	85.0
FODDER	
Dry matter (%wt)^{am}	89.5
Crude protein (%wt)^{db}	9.0
Crude fat (%wt)^{db}	0.55
Crude fiber (%wt)^{db}	18.4
FERTILIZER	
Phosphorus (g/kg)^{db}	0.8
Potassium (g/kg)db	4.5
Calcium (g/kg)^{db}	4.9
Sodium (g/kg)^{db}	0.5
Magnesium (g/kg)^{db}	2.1
BIOACTIVE COMPOUNDS	
Sucrose (%wt)^{db}	14.7

22.2 Sugar beet molasses

Sugar-beet molasses is a thick concentrated liquid syrup, a product obtained during the processing of sugar beet into sugar. In general, beet molasses contains approximately 50% saccharose, 1% rafinose, and 0.25% glucose and fructose by dry weight. The non-sugar content includes many important micronutrients such as minerals and vitamins. Potassium, calcium, sodium, magnesium and iron are present in appreciable amounts in beet molasses. It is important to mention that the minerals in molasses are dissolved and thus readily available for uptake. Molasses also contains B vitamins and does not contain fat, fiber or cholesterol. Minor constituents of beet molasses include proteins, betain, glutamine acid, purine and pirimidine bases, organic acids, pectin, and melanoidins. The composition of molasses is determined by numerous factors such as the quality of raw material and the processing practices (Filipčev et al., 2010).

Although molasses is mainly used as a supplement for livestock feed and as a source of carbon in fermentation processes, for example in for the production of ethanol, by tradition it also serves as a sweetener and colorant substitute in cakes. Molasses is considered to be generally recognized as safe (GRAS) by the U.S. Food and Drug Administration, and people believe molasses has health benefits beyond its special taste and flavor due to it being rich in minerals. In addition, several studies evidenced that molasses is a rich source of phenolic compounds (Guimarães et al., 2007; Payet et al., 2006) having possible roles in the prevention of several chronic diseases involving oxidative stress (Scalbert et al., 2005; Valli et al., 2012; Yao et al., 2004). Also, it has been reported that extracts from cane molasses possess significant antioxidative activity coupled with interesting physiological functions that include anti-inflammatory, vaccine adjuvant and infection resistant features as well as protective effect against DNA oxidative damage (Filipčev et al., 2010; Guimarães et al., 2007; Takara et al., 2007).

These results suggest that sugar beet molasses contain various compounds with beneficial effects for health. Therefore, it is not odd that sugar molasses has been highly recommended by nutritionists for daily administration to protect health. Unlike sugar cane molasses, sugar beet molasses is rarely used for human consumption, mainly because of its unpleasant taste and odor, although there are parts of world, such as some parts of Central Europe and Turkey where people are used to consume sugar beet molasses. In Germany, concentrated non-extracted syrup from sugar beet (Zuckerrübensirup) is commonly used as a sweetener (Filipčev et al., 2010).

Maillard browning carbohydrate–amino acid condensation products, formed during sugar production, also occur in very high concentration in molasses and range from low organic compounds to complex aromatic polymers. They are strongly involved in the color and aroma of molasses, and they have been reported to have antioxidant activities. In the light of the recommendation of increasing the intake of antioxidant-rich foods, the substitution of sugar with molasses could represent a potential extra source of antioxidants (Cooper et al., 2007; Kitts et al., 2012; Valli et al., 2012; Yilmaz & Toledo, 2005).

Table 22.2: Summary of main physicochemical characteristics of sugar beet molasses (Agrana, 2017a; Fedna, 2012; FeedBase, 2013; Nordzucker, 2017; Potthast et al., 2011; Tereos; Trident, 2017; EBZ, 2017).

PHYSICOCHEMICAL PROPERTIES	MEAN VALUE
ENERGY	
Ash (%wt)^{db}	10.8
Moisture (% wt)^{am}	24.3
Carbon (%wt)^{db}	39.7
FODDER	
Crude protein (%wt)^{db}	12.0
Crude fat (%wt)^{db}	2.7
FERTILIZER	
Phosphorus (g/kg)^{db}	0.5
Potassium (g/kg)db	49.1
Calcium (g/kg)^{db}	3.1
Sodium (g/kg)^{db}	8.7
Magnesium (g/kg)^{db}	0.7
BIOACTIVE COMPOUNDS	
Total Sugar (%wt)^{db}	50.0
Vitamin B (%wt)^{db}	0.1
Sucrose (g/kg)^{db}	530.3

22.3 Sugar beet AWCB bioactive compounds patent and literature review

Sugar beet is grown commercially for sugar production but also, albeit to a much smaller extent, for bioethanol and biogas production. One AWCB of sugar manufacture, sugar beet pulp (SBP), is the fibrous material remaining after sugar extraction from sugar beet. SBP is generally considered as animal feed due to its ligno-cellulosic content. Due to the comparatively high drying costs and relatively low protein content, alternative usages have to be investigated to try to make better use of the large amount of this product, notwithstanding the fact that the EU is a SBP deficit region and hence a net SBP importer. Comprehensive studies have been carried out in respect to the conversion of SBP to biomass, as an alternative, environmentally friendly fuel. SBP can be considered as a renewable energy resource and its conversion seems to be of great technological importance (Özbaş & Özbaş, 2017).

Sugar beet molasses on the other hand, is among the most important raw materials for fermentation industries. More specifically, it is utilized for the production of baker's yeast, citric acid, organic acids, amino acids, antibiotics, and enzymes (Yilmaztekin et al., 2008). Regarding molasses' bioactivity in *in vivo* or *ex vivo* systems, there is few data available in the literature. Sugar molasses have been reported to have immunomodulatory activity in human whole blood cell cultures (Rahiman & Pool, 2010), to raise HDL cholesterol level in rats (Schlegelmilch et al., 2005), and to have inhibitory effects on mutation and nitric oxide production in lipopolysaccharide-stimulated macrophages (Wang et al., 2011). Valli et al. (2012) studied the effectiveness of molasses in the counteraction of the oxidative damage in cultured cells (Valli et al., 2012).

Many patents have been issued on recovery of valuable bioactive compounds from sugar beet AWCBs and are summarized in the following tables.

Patent No	CA 2301220 A1, DE69824868D1, DE69824868T2, EP1012349A1, EP1012349B1, US6506897, WO1999010542A1
Issue Date	26/08/1998
Title	Method of preparing l-arabinose from sugar beet pulp
Description/Abstract	The invention relates to a method of preparing crystalline L-arabinose by extraction of sugar beet pulp, from which sugar has been extracted, in a strong alkaline solution, by hydrolysis of the obtained crude araban with a strong acid at an elevated temperature, by neutralization and filtration of the obtained solution, by chromatographic separation of the L-arabinose fraction, by purification of the obtained L-arabinose solution by means of cation and anion exchangers and adsorbent resins, and by recovering the pure L-arabinose as a crystalline product.
Type of AWCB	Sugar beet pulp
Recovered high added compound	L-arabinose

Patent No	US 2626706 A, DE860594C
Issue Date	27/01/1953
Title	Process for the extraction of pectin from sugar beet pulp
Description/Abstract	This invention relates to a process for extracting pectin from sugar-beet waste materials, more particularly from sugar-beet pulp. It will increase the by-product value of the beet pulp and will provide a-new source of material from which pectin can be prepared. It has been found that pectin can be efficiently removed from sugar-beet waste materials, such as sugar-beet pulp.
Type of AWCB	Sugar beet pulp
Recovered high added compound	Pectin

Patent No	CN 103783273 A
Issue Date	14/05/2014
Title	Method for producing mycoprotein feed from sugar beet pulp
Description/Abstract	The invention relates to a method for producing mycoprotein feed from sugar beet pulp. The method comprises the following steps of 1, carrying out raw material treatment by crushing sugar beet pulp and adding 10-15% of wheat bran into the crushed sugar beet pulp, 2, adjusting water content of the sugar beet pulp to 40-50% and adjusting a pH value of the sugar beet pulp to 7, 3, inoculating the treated sugar beet pulp with 2-3% of a fermentation strain, carrying out stirring to obtain a uniform mixture, and carrying out fermentation at a temperature of 28-30 DEG C for 20-30h, and 4, drying the fermented mycoprotein, and carrying out crushing to obtain the mycoprotein feed. After sugar beet pulp crushing, a boiling process is carried out. The fermentation strain comprises 50% of geotrichum candidum and 50% of candida. The method utilizes fermentation of the sugar beet pulp obtained by sugar preparation to realize feed preparation and thus the problem of high treatment difficulty of sugar beet pulp in the factory is solved, pollution on the environment is avoided, a sugar beet added value is increased and feed production methods are increased. The method has low equipment and condition requirements, has simple processes and is convenient and practical.
Type of AWCB	Sugar beet pulp
Recovered high added compound	Mycoprotein

Patent No	WO 1988009622 A1, EP0365590A1, EP0365590A4, US4992288
Issue Date	15/12/1988
Title	Method of removing oxalic acid and/or sulfite from sugarbeets
Description/Abstract	A method for reducing the amount of oxalic acid and/or sulfites in a sugarbeet comprising the steps of slicing the surgarbeet into cossettes and contacting the cossettes with an oxidizing compound such as hydrogen peroxide.
Type of AWCB	Sugar beet pulp
Recovered high added compound	Oxalic acid

Patent No	US 4816078 A, DE3702653A1, DE3702653C2, EP0276702A2, EP0276702A3, EP0276702B1
Issue Date	28/03/1989
Title	Process for production of crystalline L-arabinose
Description/Abstract	The invention concerns a process for production of L-arabionose in crystalline form. Starting material are extracted sugar beet pulp or other L-araban containing plant materials. These are heated in an autoclave as an aqueous suspension in the presence of Ca(OH)2. The so obtained solution is chromatographed on a cationic exchanger in the Ca-form. The araban containing fraction is hydrolyzed after adding H2 SO4, neutralized and rechromatographed on a cationic exchanger in Ca-form. After concentrating the arabinose containing fractions L-arabinose is obtained in form of crystals by cooling crystallization.
Type of AWCB	Sugar beet pulp
Recovered high added compound	L-arabinose

Patent No	US 2842591 A
Issue Date	08/07/1958
Title	Process of treating sugar beet molasses to recover barium saccharate and glutamic acid
Description/Abstract	This invention relates to the processing of sugar beet molasses, and more particularly, to the removal of sugar values from sugar beet molasses in such a manner that the nitrogenous volumes contained in the molasses are preserved. Precipitation of sugar values in sugar beet molasses as barium saccharate, acidulation of the barium saccharate to free the sugar and recover the same by crystallization is a well known commercial process. The conditions of precipitation, the weight ratio of barium oxide to sugar contained in the molasses, the temperature of the molasses during precipitation and the processing of the waste Water are usually all adjusted and designed to recover the highest possible economic yield of crystal sugar per unit weight of molasses treated. Nitrogenous values originally contained in the beet molasses are recovered by subsequently hydrolyzing the barium process filtrate to convert the glutamine and/ or pyrrolidone-carboxylic acid content to glutamic acid. Hydrolysis is accomplished either through the use of strong alkalis, such as caustic soda, or strong acids, such as hydrochloric acid. Glutamic acid may be crystallized from the hydrolyzate at its isoelectric point. Another object of this invention is to provide a process for recovering sugar from sugar beet molasses while simultaneously substantially completely converting glutamic acid precursors to glutamic acid in a manner to avoid destruction of glutamic acid values and to afford efficient recovery of barium for reuse.
Type of AWCB	Sugar beet molasses
Recovered high added compound	Barium saccharate and glutamic acid

Patent No	US 8211675 B2, EP1870474A1, EP2038422A1, EP2038422B1, US20100062503, WO2008000699A1
Issue Date	03/07/2012
Title	Lactic acid production from concentrated raw sugar beet juice
Description/Abstract	The present invention is in the field of the preparation of lactic acid by means of fermentation on industrial scale wherein a concentrated raw beet juice having a Brix of at least 60 is used as fermentation substrate. After dilution to the desired initial sugar concentration and addition of nutrients, the juice is fermented to lactic acid and/or lactate by means of a lactic acid-producing microorganism. Said concentrated raw beet juice is prepared by: washing and cutting sugar beet and extracting the cossettes in water, removing the beet pulp from the resulting raw beet juice, and heat treating the raw beet juice at a temperature between 50 and 90 degrees Celsius, and concentrating the raw beet juice to at least 60 Brix. It was found that concentrated beet juice having a Brix of at least 60 is storage-stable, is not very sensitive to infections, and can be used as fermentation substrate for lactic acid production on industrial scale with the same yield, chemical purity, optical purity, clarity and taste as lactic acid obtained from fermenting white sugar.
Type of AWCB	Sugar beet molasses
Recovered high added compound	Lactic acid

Patent No	US 4359430 A
Issue Date	16/11/1982
Title	Betaine recovery process
Description/Abstract	Betaine is recovered from natural sources such as beet molasses, rest molasses and vinasse by diluting the molasses to 25-50% solids, introducing the molasses to the top of a chromatographic column containing a salt of a polystyrene sulfonate cation exchange resin cross-coupled with from about 2 to about 12 weight percent of divinylbenzene, eluting with water and collecting a fraction of betaine from the downstream side of the resin. When successive feeds with predetermined intervals are made, the feeds may be partly overlapped. The betaine from the preceding feed is then eluted by the dilute molasses from the following feed. The betaine fraction is evaporated under vacuum and the betaine crystallized as anhydrous crystals or as betaine monohydrate.
Type of AWCB	Sugar beet molasses
Recovered high added compound	Betaine

Patent No	US 20040082776 A1, DE10241116A1, EP1396497A1
Issue Date	29/04/2004
Title	Process for recovery of uridine from molasses
Description/Abstract	The disclosure concerns a process for the recovery of uridine from molasses by means of chromatographic processes, whereby uridine is enriched to a high yield and high purity and in particular that uracil is separated from uridine.
Type of AWCB	Sugar beet molasses
Recovered high added compound	uridine

Patent No	WO 2007071729 A2, CA2634371A1, CN101346475A, EP1963539A2, EP1963539B1, EP1963540A2, US7763116, US20070169772, US20080299287, WO2007071727A2, WO2007071727A3, WO2007071729A3
Issue Date	28/01/2007
Title	A process for the recovery of a brown food-grade sugar product from a sugar beet solution
Description/Abstract	The invention relates to a process for the recovery of a brown food-grade sugar product from sugar beet solutions, which can be obtained from various beet sugar process streams, such as thin juice, thick juice and molasses. The process comprises providing a sugar beet solution, which contains malodorous volatiles as a result of one or more purification processes; subjecting said sugar beet solution to electrodialysis to provide an electrodialyzed liquid, wherefrom malodorous volatiles are at least partly removed; and recovering from said electrodialyzed liquid a product selected from liquid and solid brown sugar products of food-grade and combinations thereof. The invention also relates to food-grade beet sugar products derived from a sugar beet solution. These products are suitable for substituting the corresponding cane sugar derived products. In a further aspect the invention relates to the use of electrodialysis for removing malodorous volatile components from a sugar beet solution.
Type of AWCB	Sugar beet molasses
Recovered high added compound	Food-grade sugar

Patent No	EP 1839497 A2, EP1839497A3, US20070224320
Issue Date	03/10/2007
Title	Betaine dry product for use in animal feeds
Description/Abstract	A method of producing a betaine -rich animal feed product, comprising the steps of: providing a betaine-rich aqueous solution by chromatographic separation of sugar beet molasses; providing a dried sugar beet pulp by drying sugar beet pulp at a temperature below 400°C; mixing the aqueous solution and the dried sugar beet pulp to effect absorption of the aqueous solution by the sugar beet pulp; followed by drying the sugar beet pulp and aqueous solution. Also provided are betaine containing dry products obtainable by the above process.
Type of AWCB	Sugar beet molasses/pulp
Recovered high added compound	Betaine

23.Onions

Onions (*Allium cepa L.*) is a major crop in many European countries. Lately, there has been an increase in demand for processed onions which has led to an increase in waste production. Accordingly, it has been estimated that 500,000 tons of onion solid wastes (OSW) are generated on an annual basis, as a result of unintended or deliberate processing losses (Choi et al., 2015; EUROSTAT, 2015a). The waste includes the brown skin, the outer layers, roots and stalks, as well as onions that are not large enough for commercial use. This waste represents an environmental problem, since onion wastes are not suitable for fodder in high concentrations, due to the onions characteristic aroma, and neither as an organic fertilizer because of the rapid development of phytopathogenic agents. Therefore, a possible solution could be to use onion wastes as a source of food ingredients, since onion are rich in several groups of plant compounds, such as dietary fibre (DF), fructooligosaccharides (FOS), flavonoid and alk(en)yl cystein sulphoxides (ACSOs), that have perceived benefits to human health (Benítez et al., 2011; Choi et al., 2015; Griffiths et al., 2002). Onion composition is variable and depends on cultivar, stage of maturation, environment, agronomic conditions, storage time and bulb section (Abayomi & Terry, 2009; Downes et al., 2010). Water makes up the majority (80–95%) of the fresh weight of onion. Up to 65% or more of the dry weight may be in the form of nonstructural carbohydrates (NSC) which include glucose, fructose, sucrose and FOS. Moreover, onion is known for its flavonoid content, contributing considerably to its dietary intake in many countries (Benítez et al., 2011).

Previous investigations revealed that OSW is significantly richer in polyphenols compared with the edible part, with differentiated and peculiar polyphenolic composition (Ly et al., 2005; Ramos et al., 2006). Several of the OSW constituents were proven to possess anti-platelet (Furusawa et al., 2003), antioxidant (Park et al., 2007), antimicrobial (Lanzotti et al., 2013) and other biological properties (Štajner et al., 2006). Therefore, OSW may be regarded as a unique source of distinct phytochemicals, which could be exploited for the production of health-care and health-promoting commodities (Katsampa et al., 2015).

Onion is known to be rich in quercetin, a flavonoid belonging to an important class of natural compounds, which are widely used to treat several diseases, such as cancers of the prostate, breast, ovaries, colon, rectum and kidney (Hertog & Hollman, 1996; Jang et al., 2013; Jin et al., 2011).

Quercetin exists in onion peel mainly in the form of aglycone, as quercetin glucosides are hydrolysed during peel formation. The total quercetin (TQ) content in onion solid wastes (OSW) was evaluated to range between 0.5 and 20 g/kg depending on waste origin (Jang et al., 2013). Thus, the extraction methods of these valuable components from OSW should be worth investigating from an economic point of view and environmental benefit. In recent years, several extraction methods have been reported to obtain quercetin from onions, including conventional solvent extraction (Wach et al., 2007), ultrasound-assisted extraction (Jang et al., 2013), and microwave assisted extraction (Kumar et al., 2014).

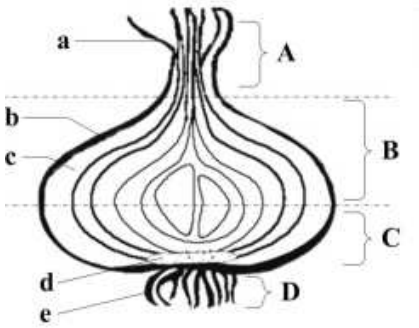

Figure 23.1: I. Diagrammatic illustration of the parts of the onion bulb: neck dry tissue (a), outermost scale/skin (b), fleshy scale (c), root cap (d), outer root (e); neck area (A), shoulder/upper half of the onion bulb (B), and lower half of the onion bulb (C), and root area (D) (Wang et al., 2012).

23.1 Onion peels/skin

The retrieval of helpful bioactive substances from the onion skin has been attended as the way to utilize onion solid wastes. Thus, the extraction methods of valuable components from the waste of onion should be worth enough to pursuit I economic point of view and environmental benefit (Jin et al., 2011).

Onion wastes can be used as a potential source for value- added products and food ingredients. Also, due to increasing customer demand for food supplement and health-related compounds, these processed and stabilized onion wastes can be used as an alternative for synthetic food supplements. Recently, researches on natural compounds have been gaining popularity. Several studies showed that valorized onion by-products are important sources of natural antioxidants. Onion wastes are also a source for compounds, such as dietary fiber (DF), FOS, flavonoids and S-alk(en)yl-L-cysteine sulfoxide (ACSOs). All these compounds are demonstrated to possess great health benefits (Griffiths et al., 2002). The valuable phytochemicals in onion waste residues can be used for pharmaceutical, food and cosmetics industries. Several studies have been carried out to gain knowledge of the dietary fiber component, the sulfur content of skin and top–bottom of onion waste, as well as regarding the nutritive mineral elements and fatty acid profile (Sharma et al., 2016).

The main physicochemical characteristics of onion peel/skin are summarized in the table below.

Table 23.1: Summary of main physicochemical characteristics of onion peels (Abdullah & Chin, 2010; Benítez et al., 2011; ECN, 2016; Gupta et al., 1993; Jang et al., 2013; Jin et al., 2011; Kiassos et al., 2009; Salak et al., 2013; Tobias et al., 2010).

PHYSICOCHEMICAL PROPERTIES	MEAN VALUE
ENERGY	
Higher Heating Value (HHV) (MJ/kg)	16.2
Lower Heating Value (LHV) (MJ/kg)	14.7
Fixed Carbon (%wt)^{db}	16.2
Volatile Matter (%wt)^{db}	69.7
Ash (%wt)^{db}	10.1
Moisture (% wt)^{am}	12.4
Carbon (%wt)^{db}	44.3
Oxygen (%wt)^{db}	31.6
Hydrogen (%wt)^{db}	5.3
Nitrogen (%wt)^{db}	0.7
Sulfur (%wt)^{db}	0.5
FODDER	
Dry matter (%wt)^{am}	87.6
Crude protein (%wt)^{db}	4.0
Crude fiber (%wt)^{db}	8.6
Neutral Detergent Fiber (NDF) (%wt)^{db}	13.8
Ether extract (%wt)^{db}	0.1
Ash (%wt)^{db}	14.1
Gross energy (MJ/Kg)	16.9
FERTILIZER	
Nitrogen (g/kg)^{db}	5.7
Phosphorus (g/kg)^{db}	0.6
Potassium (g/kg)db	7.8
Calcium (g/kg)^{db}	31.6
Magnesium (g/kg)^{db}	1.9

PHYSICOCHEMICAL PROPERTIES	MEAN VALUE
Sulfur (g/kg)[db]	1.6
VALUE-COMPOUNDS	
Polyphenols (g/kg)[db]	14.5
Quercetin (g/kg)[db]	9.2

23.2 Onion AWCB bioactive compounds patent and literature review

Exploitation of onion waste as a source of functional compounds and its application as a food ingredient is a promising field, which requires interdisciplinary research of food technologists, food chemists, nutritionists and toxicologists. To achieve this goal, several important factors should be considered, including sufficient dedicated internal resources, identification of best alternatives for waste streams and application of proper analytical tools for valorisation. Complete usage of onion waste practices can be a good example set for organizations to realize that reducing waste would be practical. Moreover, certain requirements must be achieved in order to reuse the waste economically and effectively. First, an adequate source of recyclable materials, such as continuous supply of onion waste along with well-established systems for extraction of the value-added compounds from the same. Second, ready and accessible facilities or analytical methods for complete characterisation and quantification of micronutrients and other functional compounds from onion waste. Third, the usage and maintenance of product quality from the onion waste is a significant barrier in the food processing industry where shelf life, tamper resistance and food safety are the issues of paramount concern. Also, natural and anthropogenic toxins, such as, prooxidant and polycyclic aromatic hydrocarbons should be excluded by efficient quality control systems. Forth, active participation of the food and allied industries, regarding sustainable production and waste management are those that are needed to be faced. Fifth, future investigations on the bioactivity, bioavailability and toxicology of phytochemicals from onion waste along with their stability and interactions with other food ingredients should be carried out carefully both in vitro and in vivo studies. Also, potential demand for the recycled onion waste needs to exist. Recycling will not be complete unless each and every component, including technical and economical-feasibility challenges, product quality and health safety is in place

Many patents have been issued on recovery of valuable bioactive compounds from onion AWCB and are summarized in the following tables.

Patent No	CN 101791095 B, CN101791095A
Issue Date	25/07/2012
Title	Comprehensive utilization method of wasted onion peels
Description/Abstract	The invention relates to a comprehensive utilization method of wasted onion peels. The method comprises the following steps: firstly, sorting and rinsing onion peels and then performing dewatering through vibration to obtain dewatered onion peels; secondly, feeding the dewatered onion peels into a vacuum freeze dryer so as to freeze dry the onion peels until the water content of the freeze-dried object is less than 7 percent to obtain the freeze-dried onion peels; thirdly, crushing the freeze-dried onion peels to obtain the onion peel powder; and finally packaging the onion peel powder to obtain the onion peel powder product. The comprehensive utilization method produces the onion peel powder by combining vacuum freeze drying technology and jet milling technology and therefore ensures that the thermally sensitive nutritive material is not decomposed or lost, maintains the nutritive materials in the onion skin and peel, reduces the production cost and ensures the product quality..
Type of AWCB	Onion peels
Recovered high added compound	Nutritive materials

Patent No	CN 102342504 A, CN102342504B
Issue Date	10/10/2012
Title	Bio-fermentation onion skin extractum and production method thereof
Description/Abstract	The invention discloses a bio-fermentation onion skin extractum and a production method thereof. The production method is characterized by comprising the following steps of: mixing 87 to 96 weight percent of onion skin powder, 2 to 5 weight percent of lactic acid bacteria fermenting agent and 2 to 8 weight percent of yeast fermenting agent; standing and culturing the mixture with water moisture of between 60 and 65 percent at temperature of between 33 and 36 DEG C for 10 to 18 hours to obtain fermented onion skin powder; heating the fermented onion skin powder to temperature of between 60 and100 DEG C, refluxing, extracting, filtering, reducing pressure, drying and smashing, thus obtaining the bio-fermentation onion skin extractum. The bio-fermentation onion skin extractum produced by using the method is applicable to patients with hypertension, hyperlipidemia and diabetes mellitus and can be used as burdening of foods, such as bread, desserts, beverage and the like; the onion skin extractum is fermented by probiotic bacteria, so active ingredients of onion skin can be promoted, the quality of the product is improved, and the resource utilization rate is increased effectively; and the product with extremely high application value can be obtained, the environmental pollution is avoided, the cost is reduced and the resources are saved.
Type of AWCB	Onion skin / Onion Peels
Recovered high added compound	Nutrients, vitamins,

Patent No	CN 101671371 B
Issue Date	15/10/2009
Title	Method for extracting flavonoid compound from onion skins
Description/Abstract	The invention relates to a method for extracting flavonoid compound from onion skins by combining a zymohydrolysis method and a supercritical fluid extraction method, belonging to the technical field of comprehensive utilization of crop products and relating to a functional food deep process technology. The method mainly comprises the following procedures: taking an onion skin as the raw materialand carrying out vacuum drying or vacuum cooling drying firstly until the water content rate of the onion skin is about 10 percent; pulverizing the dried onion skin until the grain diameter is 40-60 meshes; taking the onion powder as the raw material and extracting the flavonoid compound by adopting the combination of the biological zymohydrolysis method and the supercritical fluid extraction method, i.e. preparing the flavonoid compound with high yield and pureness by adopting a zymohydrolysis process by complex enzyme firstly and adopting supercritical CO2 fluid to extract the zymolyte later.
Type of AWCB	Onion skins
Recovered high added compound	Flavonoid compounds

Patent No	US8187643 B2
Issue Date	29/05/2012
Title	Shampoo formulation for treatment of hair loss and method of use
Description/Abstract	A shampoo formulation comprising a shampoo, bicarbonate soda, and onion skins used alone or in combination with a conditioner comprising acetic acid for the treatment of hair loss and promotion of hair growth.
Type of AWCB	Onion skins
Recovered high added compound	The present invention is directed toward shampoo formulations for preventing hair loss and stimulating hair growth. The formulation is a mixture of shampoo, bicarbonate soda and onion skins used in combination with a conditioner containing acetic acid. The use of the shampoo formulation is used similar to that of a typical shampoo and conditioner.

Patent No	CN103520449 A

Patent No	CN103520449 A
Issue Date	22/01/2014
Title	Preparation method and application of onionskin flavones
Description/Abstract	The invention discloses a preparation method of onionskin flavones. The preparation method comprises the following steps: step one, carrying out extraction, separation and purification of onionskin total flavones: 1) taking 3 kg of onionskins, adding 40-60 L of distilled water, heating to 67-70 DEG C, holding for 2-8 h, filtering, and pouring out the supernatant to obtain a filter residue; 2) adding 40-60 L of a 70% ethanol into the filter residue obtained in the step 1), heating to 67-70 DEG C, holding for 2-8 h, filtering, and thus obtaining a supernatant and a residue; 3) concentrating the supernatant obtained in the step 2), and drying to obtain an onionskin flavones primary product; and 4) drying the residue obtained in the step 2) to obtain an onion dietary fiber. The preparation method improves the bioavailability of the onionskin flavones; through establishment of a hyperlipidemia model, an anti-obesity effect and the mechanism of the onionskin flavones are studied, finally a micro-capsule technology is adopted, an anti-obesity onionskin flavones microcapsule health-care food is prepared, and thus the stability and the application scope are further improved.
Type of AWCB	Onion skins
Recovered high added compound	Flavonoids, Onion dietary fiber

24.Cabbages

Cabbage is a leafy green or purple biennial plant, grown as an annual vegetable crop for its dense-leaved heads. It is a kind of necessary vegetable in daily life because of containing a variety of vitamin C and vitamin E. Its production is increasing almost every year. The spoilage of large quantity of vegetables occurs due to seasonal glut coupled with inadequate and non-technological post-harvest handling, transportation, storage and lack of processing facilities (Basak et al., 2014).

It is estimated that up to 30% of the total production, approximately one million tons, is discarded as waste. The waste consists of the outer part of cabbage, which is usually removed before sale. Waste is produced during harvest, transport, and at the wholesale markets. Large amounts of waste are also generated from kimchi factories during the trimming process. Sometimes, cabbages are abandoned in the field, due to overproduction and an inefficient marketing system. Since cabbage waste contains more than 90% water and decomposes readily, many unpleasant environmental consequences arise when it is abandoned in fields or near factories. Unlike food waste or other organic solid wastes, cabbage waste, which consists of homogenous materials containing adequate nutrients, can be used as a substrate for culturing microorganisms, without significant modification (Choi & Park, 2003).

Cabbage is highly perishable vegetable because of its higher moisture content and for prolonging its self-life, requires immediate processing by removal of high amount of moisture (Basak et al., 2014; Yang et al., 2013b). It contains high concentration of globulin protein and rich in calcium, phosphorus, sulphur, iron, ascorbic acid and other water-soluble vitamins. Considering its high nutrient profile, very low cost and easy availability throughout the year, cabbage wastes could be utilized as fodder lowering the cost of animal diets (Nath et al., 2013).

It is worth-mentioning that cabbage leaves are used by some women to help reduce breast swelling and relieve the pain and discomfort that breast engorgement or weaning a baby from breastfeeding can cause. Researchers do not know if there is a property within the cabbage itself that helps to decrease the pain and swelling, or if the swelling goes down because the cabbage leaves are acting as cold compresses. Either way, studies show that if your breastfeeding and you put cold cabbage leaves directly on your breasts, it's not only soothing, but it can be soothing can help lessen your breast pain and swelling (Lawrence & Lawrence, 2011; Yu, 2011).

Figure 24.1: Cabbage heads at harvest time (left) and cross-section of the Chinese cabbage leaves (L1, outer leaves; L2, mid-leaves; L3, inner leaves) (right) (Kang et al., 2010; Seong et al., 2016).

24.1 Cabbage leaves

Cabbage and cauliflower (brassica oleracea) are the commonly used vegetables all over the world. Consumers preference for a particular part of cabbage varies among recipes considering the appearance, taste, and texture. In some foods, the outer greenish leaves are used for soups with soybean paste, whereas the yellowish inner leaves are used as vegetable outer rolls for grilled pork, beef, chicken, and seafood dishes. With respect to its health benefits, the dietary antioxidants in cabbage have been extensively studied for their ability to prevent reactive oxygen species (ROS), which mediate aging and oxidative damage-inducing pathological disorders such as inflammation and atherosclerosis (Huxley & Neil, 2003; Ji et al., 2011). In addition, several antioxidant phenolic compounds including flavonoids were investigated and identified in whole cabbage leaves (Harbaum et al., 2007; Kim et al., 2004; Roy et al., 2007). Because cabbage leaves have different color, texture, taste, and availability depending on their parts, the different antioxidant capacities should be investigated to utilize as fresh-cut products and health-benefit materials (Seong et al., 2016).

From farms to dining tables, travelling this path huge amount of agro, market and kitchen wastes are produced by these two vegetables. On an average, 30–50% of wastes produce from cabbages and cauliflowers as stems and leaves while process for selling in farm and in markets and for the process of cooking in kitchen (Choi et al., 2002). Twenty million tonnes of food wastes produce each year in Australia, and 10% of food waste is recycled and the other 90% is sent to landfill. Cabbage and cauliflower wastes contain more water and therefore readily decompose and create unpleasant environmental consequences (Hossain et al., 2014; Ngu & Ledin, 2005).

Fresh cauliflower and cabbage leaves with stems are a rich source of proteins, soluble sugars, both macro- and micro- elements and have good digestibility and dry matter intake. These can be fed either as such, after drying or ensiling with cereal straws, without affecting the palatability, nutrient utilization, health or performance of livestock (Wadhwa et al., 2013).

The main physicochemical characteristics of cabbage leaves are summarized in the table below.

Table 24.1: Summary of main physicochemical characteristics of cabbage leaves (Gupta et al., 1993; Nath et al., 2013; Tobias et al., 2010; Wadhwa et al., 2006; Wang et al., 2010).

PHYSICOCHEMICAL PROPERTIES	MEAN VALUE
ENERGY	
Higher Heating Value (HHV) (MJ/kg)	1.0
Ash (%wt)[db]	9.6
Moisture (% wt)[am]	92.2
Carbon (%wt)[db]	4.4
Nitrogen (%wt)[db]	1.5
FODDER	
Dry matter (%wt)[am]	9.4
Crude protein (%wt)[db]	13.7
Crude fiber (%wt)[db]	6.5
Neutral Detergent Fiber (NDF) (%wt)[db]	20.9
Ether extract (%wt)[db]	5.0
Gross energy (MJ/Kg)	1.0
FERTILIZER	
Nitrogen (g/kg)[db]	2.0
Phosphorus (g/kg)[db]	0.3
Potassium (g/kg)db	1.7
Calcium (g/kg)[db]	0.4

PHYSICOCHEMICAL PROPERTIES	MEAN VALUE
Magnesium (g/kg)[db]	0.1
VALUE-COMPOUNDS	
Vitamin C (g/kg)[db]	0.1

25.Carrots

The carrot (*Daucus carota L.*) is an annual or biennial herb with a thick fleshy taproot, which is the primary organ of agricultural importance. Carrot roots are usually orange, but there are also white, black, yellow, red and purple varieties. The roots range in length from 5 cm to more than 50 cm and are generally conical. However, there is tremendous diversity in root shapes and sizes. The leaves are alternate and compound and organized as a rosette. Carrot roots are an important food product. Depending on the variety, carrots are sold fresh or processed: pre-packed, boiled and canned, frozen, diced and sliced, etc. (Bradeen & Simon, 2007).

There is a long tradition of feeding carrots to livestock but their use in animal feeding is marginal nowadays. Feed carrots are usually cull (grade-out) or surplus carrots obtained during periods of overproduction. They are typically fed fresh and are available whole or chopped, unwashed or washed (Morel d'Arleux, 1990). Carrots can also be ensiled. Dehydrated carrots are popular treats for horses and pets. Other carrot products that are occasionally fed to livestock include the tops resulting from harvesting, and various by-products of carrot processing (juice, aromas).

Carrots are fragile vegetables and their production can be wasteful. In France, for instance, more than half of the carrots produced for canning are discarded. Using grade-out and surplus carrots in animal feeding may reduce the environmental cost associated with their disposal (Goby & Gidenne, 2008).

Carrots are among the most popular root vegetables and have been identified as the main dietary sources of α- and β-carotene in most European countries (O'Neill et al., 2001). The predominant carotenoid identified in carrot cultivars is β-carotene (Alasalvar et al., 2001). Carrots also contain substantial amounts of vitamin C and phenolic compounds, with chlorogenic acid being the most abundant phenolic compound identified in carrot cultivars (Kenny & O'Beirne, 2010; Kreutzmann et al., 2008).

After processing, carrot residues, e.g. peels, pomace, are usually discarded or used as animal feed. However, carrot by-products still contain high contents of beneficial substances, especially bioactive compounds with antioxidant activities, carotenoids and phenolic compounds (Prakash et al., 2004; Zhang & Hamauzu, 2004). Finding a way to utilize these residues or transforming them into value added products are therefore of interest.

Figure 25.1: Carrot roots (left photo) and carrot plant (right photo) (feedipedia, 2016).

25.1 Carrot peels/skin

After processing, many types of carrot residues, e.g. peels and pomace, are separated. These by-products are typically used only as an ingredient of an animal feed or even discarded in many cases. Phenolic content and profile varies significantly among the different carrot tissues (peel, cortical parenchyma and vascular tissue), where peels provide about 50% of the carrots' total phenolic amount (Alegria et al., 2016). Chantaro et al. (2008) reported that carrot peels still contained a relatively large amount of b-carotene, around 20.45 mg/100 g (d.b.), whereas the recommended b-carotene in a dietary allowance for a typical adult is 4.8 mg (Chantaro et al., 2008). These results imply that it is worthwhile to search for an appropriate means to extract b-carotene from carrot residues.

The main physicochemical characteristics of carrot peels/skins are summarized in Table 25.1.

Table 25.1: Summary of main physicochemical characteristics of carrot peels (Alegria et al., 2016; Bezerra et al., 2005; Chantaro et al., 2008; feedipedia, 2016; Tobias et al., 2010).

PHYSICOCHEMICAL PROPERTIES	MEAN VALUE
ENERGY	
Higher Heating Value (HHV) (MJ/kg)	15.7
Ash (%wt)^{db}	8.1
Moisture (% wt)^{am}	88.5
Nitrogen (%wt)^{db}	1.6
Sulfur (%wt)^{db}	0.2
FODDER	
Dry matter (%wt)^{am}	11.5
Crude protein (%wt)^{db}	9.1
Crude fiber (%wt)^{db}	9.5
Neutral Detergent Fiber (NDF) (%wt)^{db}	16.0
Acid Detergent Fiber (ADF) (%wt)^{db}	9.9
Lignin (%wt)^{db}	1.0
Ether extract (%wt)^{db}	1.3
Ash (%wt)^{db}	8.1
Gross energy (MJ/Kg)	10.5
FERTILIZER	
Nitrogen (g/kg)^{db}	15.6
Phosphorus (g/kg)^{db}	3.2
Potassium (g/kg)db	26.1
Calcium (g/kg)^{db}	3.8
Magnesium (g/kg)^{db}	1.2
Sulfur (g/kg)^{db}	0.6
VALUE-COMPOUNDS	
Starch (g/kg)^{db}	8.3
Polyphenols (g/kg)^{db}	3.0
Total sugars (g/kg)^{db}	39.2
β-Carotene (g/kg)^{db}	0.2

25.2 Carrot leaves

Many vegetable leaves, including those of carrot are wasted. Carrot leaves are very rich in both nutrients such as vitamin C, β-carotene, fibers and several minerals such as Na, P, K, Ca, Mg, Mn, Zn, and Fe. They have a pleasant taste and characteristics suitable for processing. They may be used as a

raw basis for the preparation of several foods. The use of the by-products of the vegetable industry has presented technological viability, and they have been used for the formulation of cream soups made of dehydrated vegetable stalks.

Carrot leaves, like others green leafy vegetables, are a good source of essential fatty acids (e.g. alpha-linolenic). Additionally, they have omega-3 and omega-6 fatty acids, which are scarce in nature. Omega-3 (alpha-linolenic acid - LNA - 18:3n-3) and omega-6 (linoleic acid - AL - 18:2n-6) are considered essential but cannot be synthesized by mammals, and therefore must be obtained through diet (Almeida et al., 2009).

The main physicochemical characteristics of carrot leaves are summarized in Table 25.2.

Table 25.2: Summary of main physicochemical characteristics of carrot leaves (feedipedia, 2016; Gowda et al., 2004; Krishna, 1985).

PHYSICOCHEMICAL PROPERTIES	MEAN VALUE
ENERGY	
Higher Heating Value (HHV) (MJ/kg)	16.1
Ash (%wt)^{db}	17.4
Moisture (% wt)^{am}	83.6
Nitrogen (%wt)^{db}	1.9
FODDER	
Dry matter (%wt)^{am}	72.1
Crude protein (%wt)^{db}	3.9
Crude fiber (%wt)^{db}	16.7
Ether extract (%wt)^{db}	2.3
Ash (%wt)^{db}	5.8
Gross energy (MJ/Kg)	5.4
FERTILIZER	
Nitrogen (g/kg)^{db}	6.2
Phosphorus (g/kg)^{db}	4.5
Calcium (g/kg)^{db}	20.1
Magnesium (g/kg)^{db}	2.3
VALUE-COMPOUNDS	
Starch (g/kg)^{db}	14.3
Total sugars (g/kg)^{db}	38.8
β-Carotene (g/kg)^{db}	0.5

25.3 Carrot AWCB bioactive compounds patent and literature review

As many fruits and vegetables, carrots are seasonal and perishable, and difficult to preserve as a raw material. Therefore, they are processed into various products such as juice, concentrate and jam (Kamiloglu et al., 2016; Khandare et al.). As a result of processing, large amounts of by-products including peel and pomace are generated. By-products of carrot processing represent a major disposal problem for the industry concerned, however they are also promising sources of bioactive compounds. There are a few patents issued on recovery of bioactive compounds from carrot AWCB and are summarized in the following tables.

Patent No	US 7138152 B2, US7527820, US20040131748, US20070071861, WO2004043163A2, WO2004043163A3
Issue Date	21/11/2006
Title	Process for extracting carotenoids from fruit and vegetable processing waste
Description/Abstract	A process of extracting carotenoids from a source of fruit or vegetable processing waste including the steps of: admixing the source, a first organic solvent and a surfactant to form a slurry, whereby surface tension in tissue cell structure of the source is decreased, enhancing penetration of the surfactant into the tissue cell structure so that the carotenoids and the surfactant may form a combination; treating the slurry with a second organic solvent which solubilizes the combination; separating the treated slurry into a liquid fraction and a solid fraction; and separating a first portion from the liquid fraction, the first portion including a solution of the second organic solvent and the combination.
Type of AWCB	Carrot peels, carrot skins
Recovered high added compound	Carotenoids

Patent No	WO1994013743 A1
Issue Date	23/01/1994
Title	Method for isolation of vegetable oleoresins producible by hexane extraction
Description/Abstract	The vegetable oleoresins are produced by extraction of vegetable starting products comprising the oleoresins with a mixture of water and an organic acid immiscible with water. In this manner the use of hexane or other environmentally dangerous solvents is avoided, and also, the yield of oleoresins is improved.
Type of AWCB	Carrot waste
Recovered high added compound	Oleoresins

26.Cauliflowers

Cauliflower is originated over 2000 years ago in the gardens of Asia Minor and the Mediterranean. The word cauliflower comes from latin word caulis means stalk and floris means flower. The botanical name of cauliflower is *Brassica oleraceal* var. Botrytis. Cauliflower is nutritious, the verstality of this plant is reflected by the fact that not only the curd but also leaves are used as a vegetable. Typically, only the head (the white curd) is eaten. The cauliflower head is composed of a white inflorescence meristem. Cauliflower heads resemble those in broccoli, which differs in having flower buds. *Brassica oleracea* also includes broccoli, brussels sprouts, cabbage, collard greens, and kale, though they are of different cultivar groups.

Cauliflower is well known to contain various nutrients, such as vitamin C, glucosinolates, carotenoid and leaf protein (Volden, Bengtsson, & Wicklund, 2009). The cultivation and consumption of cauliflower have increased rapidly over the last few years. Except for increasing production of cauliflower curd (the sole edible part of cauliflower), tons of cauliflower by-products (stems and leaves) are also generated during the harvest every year. However, people have no way of disposing of cauliflower by-products except by stockpiling or landfill, which would lead to environmental pollution due to their abundant organic matter and moisture contents. Consequently, effective and economic strategies and approaches to process these cauliflower by-products are urgently needed (Xu et al.).

Cauliflower waste (CW) constitutes about 48–58% of the total weight of cauliflower and on dry matter basis consists of 85.5% organic matter, 16.6% cellulose, 14.9% crude protein, 8.4% hemicellulose, 17% total sugars, 3.9% reducing sugars, 6.25% phenolics, 14% ash; the main minerals present are 9.83% Ca, 6.12% Mg, 4.26% Na, 28.74% K and 0.62% S. Disposal of this nutritionally rich CW in municipal bins results in rotting, which creates foul smell thereby adding to the environmental problems and jeopardizes public health. Due to its nutritional value, this waste can be utilized as an important substrate for production of industrially important products such as bioethanol or enzymes (Dhillon et al., 2007).

Figure 26.1: Cauliflower head (left) and leaves (right) (Featherstone, 2016).

26.1 Cauliflower leaves

Cauliflower leaves are the main by-product of cauliflower cultivation. Cauliflower leaves which are normally wasted can be cooked like any other green leafy vegetable and can be used as a valuable source of micronutrients as they are rich in calcium, iron and phosphorus and also source of natural antioxidants the use of which may help in preventing degenerative diseases (Mogra et al., 2012).

Regarding the byproduct proportion, leaves constitute about 50% of the total; the rest is mainly stem. These residues are responsible for important environmental problems in the industries (2) and

diminishing their environmental impact has been the subject of an increasing concern in recent years (Llorach et al., 2003). The main physicochemical characteristics of cabbage leaves are summarized in Table 26.1.

Table 26.1: Summary of main physicochemical characteristics of cauliflower leaves (Dhillon et al., 2007; Gupta et al., 1993; Podsędek, 2007; Stella Mary et al., 2016; Tobias et al., 2010; Wadhwa et al., 2006).

PHYSICOCHEMICAL PROPERTIES	MEAN VALUE
ENERGY	
Fixed Carbon (%wt)[db]	39.0
Volatile Matter (%wt)[db]	51.0
Ash (%wt)[db]	16.4
Moisture (% wt)[am]	9.0
Carbon (%wt)[db]	31.8
Oxygen (%wt)[db]	59.4
Hydrogen (%wt)[db]	3.2
Nitrogen (%wt)[db]	3.7
Sulfur (%wt)[db]	1.1
FODDER	
Dry matter (%wt)[am]	91.0
Crude protein (%wt)[db]	22.9
Crude fiber (%wt)[db]	11.9
Neutral Detergent Fiber (NDF) (%wt)[db]	98.0
Acid Detergent Fiber (ADF) (%wt)[db]	58.0
Lignin (%wt)[db]	8.0
Ether extract (%wt)[db]	5.0
Ash (%wt)[db]	9.4
FERTILIZER	
Nitrogen (g/kg)[db]	36.7
Potassium (g/kg)db	28.7
Calcium (g/kg)[db]	9.8
Magnesium (g/kg)[db]	6.1
Sulfur (g/kg)[db]	7.4
VALUE-COMPOUNDS	
Ascorbic acid (g/kg)[db]	0.5
Polyphenols (g/kg)[db]	6.3
Total soluble sugars (g/kg)[db]	17.0

26.2 Cauliflower AWCB bioactive compounds patent and literature review

Cauliflower is an important vegetable grown all over the world, and has a wide variety of uses, directly as vegetable or as an ingredient in salads, soups etc. It has the highest waste index, i.e. ratio of non-edible to edible portion after harvesting and thus generates a large amount of organic solid waste, which creates a foul odour on decomposition. Although, Wadhwa et al. (2005) have reported that cauliflower waste has good protein (16.1%), cellulose (16%) and hemicellulose content (8%), it has not been put to any commercial use and is simply left in the municipal bins for rotting (Oberoi et al., 2007; Wadhwa et al., 2006).

It is considered as a rich source of dietary fibre and it possess both antioxidant and anticarcinogenic properties. Phenolic compounds and vitamin C are the major antioxidants of brassica vegetables, due to their high content and high antioxidant activity (Podsędek, 2007). Lipid-soluble antioxidants (carotenoids and vitamin E) are responsible for up to 20% of the brassica total antioxidant activity. The level of non-starch polysaccharide (NPS) in the upper cauliflower stem is similar to that of the

floret and both are rich in pectic polysaccharides, while the cauliflower lower stem is rich in NPS due mainly to cellulose and xylan deposition (Femenia et al., 1998; Stojceska et al., 2008). The table below lists one patent on the recovery of nutrients from cauliflower wastes.

Patent No	CN 102100301 B
Issue Date	13/02/2013
Title	Feed containing cauliflower waste and production method thereof
Description/Abstract	The present invention relates to a cauliflower waste feed and preparation containing the feed comprises the following components and parts by weight content: cauliflower waste 75 to 80, 20 to 25 crop production by-product, cut the cauliflower waste after drying, crops After the production of by-product cutting spray broth, mixing and compacting said material sealed in polyethylene plastic bags, 3-5 months after the product bag which can be used as feed. Compared with the prior art, the long-term preservation, not moldy, wide range, palatability, and contain microbial secondary metabolites.
Type of AWCB	Cauliflower waste
Recovered high added compound	Nutrients

Reference list

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