Chapter 2

Chapter Title: Waste Biomass suitable as feedstock for biofuels production

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Abstract

Research and technology development in the field of residual biomass exploitation for the production of biofuels is advancing. Non-food waste could form an excellent feedstock for biofuel generation. Residual biomass of food or first generation biofuels industries forms an ideal feedstock for fuel production forming simultaneously an environmentally friendlier solution for their disposal. A number of challenges are associated with waste-biomass exploitation as collection, transportation and their management can dramatically affect the economics of the processes. The economics can however be improved if added value products are extracted prior to their treatment for biofuels. Furthermore, technological challenges related to feedstock quality and quantity variations have to be resolved. In this section, promising biomass for the characterization and the potential exploitation of which, substantial research is already in place is presented. The relevant biomass is, or has the potential to be abundant and its exploitation in the near future is realistic and possible.

Keywords: Citrus peels, waste valorization, agricultural waste, grape mark, lignocellulosic biomass, oil production residual biomass

2.1 Introduction

2.1.1 The need for biofuels

Babu (2008) defines **biomass** as a term used to describe all Earth's living matter. It is a general term for material derived from growing plants or from animal manure (which is effectively a processed form of plant material), while, according to Jessup (2009), **biofuels** are solid, liquid, or gaseous energy sources derived from renewable biomass sources. On the other hand, in article 2 of the European Community Directive "On the promotion of the use of biofuels" specific definitions of a narrower spectrum are given. As such, the term "biomass" is used to express the biodegradable fraction of products, waste and residues from agriculture (including vegetal and animal substances), forestry and related industries, as well as the biodegradable fraction of industrial and municipal waste. The term 'biofuels' is exclusively referred to liquid or gaseous fuel for transport, i.e. the directive focuses in fuels

which can partially replace fossil-origin fuels employed in transport. It describes specific characteristics of “bioethanol”, ‘biodiesel’, ‘biogas’, ‘biomethanol’, ‘biodimethylether’, ‘bio-ethyl-tert-butyl-ether’, ‘bio-methyl-tert-butyl-ether’, ‘synthetic biofuels’, ‘biohydrogen’, ‘pure vegetable oil’ which are the referred biofuels, which naturally originate from processed biomass. (EU,2003). In this work, the broader definitions are preferred, although a great deal of the chapter focuses on biomass which can provide liquid and gas biofuels.

Biomass has always been used for the production of energy. Chemicals and pharmaceutical products have been obtained from biomass; biomass has been burnt to produce energy since fire was harnessed. Since the energy crisis of 1973, considerable interest was developed in biomass use towards meeting the energy needs of the world. Furthermore, the interest to valorization of biomass was awakened as the awareness of the finite nature of fossil liquid and gaseous hydrocarbons and their ultimate depletion rose. There was much argument over when this would occur. Goldstein (2019). However, in the mind of the society the search for alternative energy sources had begun.

A drop in oil prices in the 1990s kept bioenergy markets apart from the production. But the reliance on fuel supplies from a few major producers and the need to reduce greenhouse emissions imposed the search for renewable sources of energy; valorization of biomass was a good option. Special attention was given to the replacement of transport fuels as their numbers were steadily rising. Karp and Halford (2010). The European Union in particular in 2008 decided that by 2020, one fifth of the totally consumed energy should be obtained from a renewable energy reservoir. Great weight was also given to the energy consumed for transportation. As such, biofuels was expected and resolved to comprise at least a 10% of the energy used in that sector by the end of the second decade of the 21st century. Rechberger and Lötjönen (2009). Renewable forests and field crops appeared to be attractive and suitable sources of biomass in processes aiming at generating biofuels. Moreover, it was expected that the existing technology could function efficiently and that it was a feasible solution towards meeting set targets of gradual fossil fuel replacement. And in fact, by the end of the first decade of the 21st century a high production of biofuels was reached in North and South America. Brazil, Argentina and United States produced and consumed large amounts of bioethanol. A very high percent of liquid biofuels mainly in the form of bioethanol was also employed in Australia, China and Canada. Europe was predominantly producing and utilizing biodiesel. Azadi *et al.* (2017).

Appropriate for biofuel production biomass includes in principle, food-crops containing sugars and starch or crops which have high oil content; those can be converted to appropriate fuels via a sequence of transformation and reaction paths. Biomass of lignocellulosic content is also a very good candidate. It can be either obtained as the side or

waste product of other processes, like agricultural and forestry residues. It can also be obtained via purposefully cultivated plants in the form of the so called energy crops. Additional sources for biofuel production form: used and waste oils, other organic wastes, algae (micro or macro-algae, encountered or grown in open or pond waters or in photobioreactors). Stafford *et al.* (2017). Every year, the plants on earth produce and store in themselves up to four times the energy needed by the humanity per annum. Guo *et al.* (2015). As such, a shrewd, systems-approach planning for the valorization of the available biomass can substantially reduce our dependency on fossil fuels. However, to reach such a goal, a number of parameters have to be accounted for prior investment in new processes expands. The aim of producing replacement fuels has to be harmonically enlaced with objectives such as CO₂ reduction, independence from a few energy providers in the world, that fossil fuels replacement does not impact on food production and availability, that deforestation is not a consequence, *etc.* In other words, the urge for biofuel production will not be shifting the problems associated with energy elsewhere, thus forming alternative types and kind of dependencies. Moreover, new, fit-for-the-purpose technologies have to be developed and the industrial size production of large quantities of desired commodities may have to be questioned and probably partially shifted or be replaced by smaller, specialized-goods production. Alternative methods of production mobile, transformable, of extendable or shrinkable capacities may need to be invented and evolve. Alternative products of a functionality similar to the one offered by existing commodities, or entities with completely new properties and potential uses may also arise as side or by-products of the alternative energy production processes.

The selection of good or adequately suitable feedstocks for biofuels production is a question with multiple answers. And many of the answers which have been given so far have created more important questions. Much progress is being made however, thanks to the substantial research already conducted and continuously expanding. In the search of such feedstocks, one has to wind through a multi-stage and multi-scale labyrinthine pathway in order to first identify the primary qualities required to be possessed by the feedstock, to subsequently devise the processes which have the potential to provide expected outputs and to finally implement a multi objective optimization process in order to guarantee the viability of the venture. There is a multiplicity of issues which have to be addressed and the primary ones lie in the definition of the problem which is to be solved. The top-to-bottom approach is traditionally implemented by the chemical engineers during the process conceptual design. The problem is relatively static; well defined raw materials and desired products; the engineer searches for the best route to arrive from the starting to the end point. Biomass valorization and the production of biofuels from biomass form an unprecedented opportunity for the implementation and development of the-top-to-bottom, bottom-to-top coupled

method, described in detail by Pham&El Halwagi (2012). The method can be also coupled with the atomic targeting and design. El-Halwagi (2017). Furthermore, in their book Sengupta and Pike (2012) present how different chemicals including biofuels can be obtained from waste biomass. They focus on processes which can contribute towards a sustainable economy. They present the advances of chemistry and technologies which can be used towards biomass valorization and how non-renewable feedstocks can be replaced by renewable ones.

Furthermore, given the dynamics and the volatility of the market in the globalized world an embedded flexibility in the kind of the products, the methods of production and the capacity may counterbalance any costs which may affect the economics and the viability of the process. Thus, space should be sought for versatile designs to replace traditional rigid requirements where stability of the selected feedstock and product prices are the key factors governing the process economics.

2.1.2. Problem definition

Until the end of the first decade of the 21st century the raw materials for biofuel production were carefully selected and they were obtained through cultivations dedicated to that very purpose. The associated with this objective agricultural cultivation involved starchy, sugary and oily plants which would otherwise have been used for the production of food. Moreover, the employed for their growth land, would have normally been occupied for the production of vegetables for feeding people. This had its impact on agricultural products, rising their prices, deforestation of the tropics due to the expansion of food and non-food crop cultivation to those areas. Thus, the apparent solution of the energy problem, was causing a number of new problems. As such, the net result was not moving the situation forward; the energy availability problem was just transformed to another entity. However, the technologies which have been developed, the research which has been conducted and the wisdom which has been acquired have not gone awry. They can always be implemented in the valorization of biomass of a different origin, such as waste and residual biomass and perennial grasses. Such an application will provide additional economic and environmental benefits. Naturally, the exploitation of these alternative sources of biomass will not be straightforward as the collection of the waste biomass, the variability of its composition, its potential degradation before treatment, discontinuity in availability, pose different technological challenges. However, sustainability is a parameter which has always to be taken into consideration. Cyclic economy is also gaining ground in the engineering thinking and objectives for the future development. As such, the value of bioenergy, instead of being measured merely in terms of the quantity of the replaced fossil fuels, it should be holistically assessed and the impact that it has on the food production, on the forests and the potential deforestation, on

the spent water resources and their pollution, on its effects on the wildlife, the soils, the society should be “measured” and accounted for. Union of Concerned Scientists (2012).

Furthermore, the initial approach of employing corn, and other reach in sugars and starch crops, traditionally used to cover needs of human and animal food, is proven incapable to reach the required needs for bioethanol as transport fuel. Sarkar *et al.* (2012). On the other hand, there is a great quantity of organic wastes produced and accumulated via human activities (city, kitchen, agricultural, animal-farm wastes, wastes of lignocellulosic origin like forest residues or residual ligocellulosic mass from other processes) which can be exploited for the production of biofuels via a number of appropriately designed processes. Stephen and Periyasamy (2018). Between those, excellent quality lignocellulosic waste biomass can be accumulated from the residuals of crops production (wheat, corn, barley, rye, oats, and other), from a number of different agricultural activities as well as from the residual biomass of food industry branches which employ processing of freshly collected fruits and vegetables, like the juice industry for instance. These option of plant-origin waste biomass also consists an environmentally friendlier way of disposal. Rivas-Cantu *et al.* (2013).

2.1.3. The biomass pool

The waste biomass which can be used for biofuels production range from anything which can be burnt, serving the purpose of producing thermal energy as a solid fuel, to more sophisticated specialized waste, which can provide high efficiency and high quality liquid biofuels. Waste biomass which can be used for the production of biofuels can be:

1. Waste biomass which is generated as a by-product or residual product following agricultural activities for the production of food. Typical examples are branches of fruit-trees after pruning, fruit tree leaves, husks of legumes and their stems and leaves, wild vegetation trimmings, corn residues, like rice, wheat, barley, oat, rye, millet straws, sorghum stalks, cassava peels and stalks, yam straws, nut shells.
2. Forest material which involves branches and leaves of forest trees, willow, poplar, bamboo, canes, sawdusts, firewood, woodchips
3. Uncontrolled growth wild type vegetation like perennial grasses and shrubs such as switchgrass, miscanthus, jatropha, algae, micro- and macro-algae and vascular land plants
4. Waste Energy Cane. Energy cane refers to high biomass sugarcane
5. Natural cosmetics industries waste biomass like seeds, roots, stems and peels of fruits and vegetables

6. Food industry waste: remains of plant or animal origin, fish remains, bones, skins, fermentations waste biomass, frying oils and other fats, corn-cobs, coffee and other beverages of plant origin waste biomass, sugarcane and sugar beet waste, kernels and shells of nuts, *etc.*
7. Waste from human activities, city and general waste, plastics, paper, waste food, waste tires, greenhouses plastic sheets, crop protection plastic nets.
8. Other organic waste like animal and poultry manure, energy industry waste of oil or lignocellulosic origin

Figure 1. Sugar canes: Truncated photo from <https://www.pexels.com/search/agricultural%20waste/>.

Such biomass feedstocks can be used to produce biofuels via a number of treatment methods. The methods of treatment and their value as biofuel feedstocks depends on their chemical composition and on their content on cellulosic compounds, sugars and carbohydrates and their content in oils. However, a great variety of those also contain small quantities of compounds which have valuable properties as natural medicinal, food or cosmetic agents. Furthermore, their potential use as biofuel feedstock often solves the problem of their disposal as a waste.

There are different ways that this biomass can be treated so as to provide valuable products. The main methods of biofuel production is employing processes, like anaerobic fermentation, pyrolysis and co-pyrolysis, gasification, transesterification, fermentation, acid or base hydrolysis, solvent extraction supercritical or not, simple mechanical processes of grinding and pelletizing, simple thermal treatment such as drying, direct biomass combustion, or combinations of the above.

The chemical composition of the biomass is a very important factor when seeking for the most appropriate methods of treatment which could potentially be employed. However, the uniformity of biomass in terms of composition, the variation of its availability during the year, the potential need of collection, transportation and storage are factors which define the kind of the process which will make its exploitation economically viable and the quantity and quality of the products which can be obtained. As such, before selecting a specific type of biomass, questions like the following ones have to be answered:

What secondary biomass is already available? Is the selected biomass accessible? In which quantities? Which are their qualities (characteristics)? How is its distribution through time? Which is its spatial distribution? How long can it be stored for before degrading or suffering an alteration of its composition? In which form should it be stored? Does it need to be transported? How easy will that be? Can transport fuels be obtained? Can they be used locally? Is their quality better or worse than that of the fossil fuels (i.e. what is their nitrogen and/or sulphur content?).

Furthermore, the importance of its valorization as a biofuel has to be assessed in additional terms which involve safety, environment and society. For example, does its use for biofuel production solve any other problems? Does it result in a substantial reduction of the environmental impact that it would otherwise provoke as waste? Does it contribute towards local or national energy independence? Does it reduce the energy footprint by reducing transportation of fossil fuels in the area? Does it produce a safer alternative to employed energy sources? Does it contribute to the economic development of the area without shifting problems to other places of the world? Does it help the preservation of biodiversity?

In a preliminary evaluation of the biomass valorization the geography and the population of the area of the industrial process are of crucial importance for this type of enterprise and the collection and transportation of residual biomass can constitute an important expense while the long term storage of biomass is of crucial importance for its quality. As such, mobile units of treatment or multiple establishments of small units versus one large facility may be worth considering. Moreover, the potential of extraction of high added value compounds prior to biorefining may substantially increase the financial potential of the process. This often implies that the biomass under question has already been well and reliably characterized. In the following paragraphs a number of promising feedstocks is presented. Amongst the huge multitude of potential feedstocks a few selected biomasses are discussed. Their primary common characteristic is their relative abundance and a substantial amount of completed research on their characteristics. The reason for the selection of each specific biomass is explained in the relevant sections.

Figure 2: *Equisetum*: A plant with important medicinal and pesticide properties, abundantly encountered in wet soils. Potential biofuels precursor following extraction of added value compounds.

2.2. Kinds of Feedstock

A number of potential feedstocks are presented in the following sections. Each feedstock is accompanied by a description which intends to answer as many of the above questions as possible.

2.2.1 Spent coffee grounds

According to the ECF (2016), a few billions of coffee cups are consumed daily all over the world thus making it the most extensively preferred beverage worldwide: USA consumed about one and a half million ton of coffee each year for the period 2011-2013. Mexico two hundred thousand ton, Brazil over one million ton, while EU consumes about two and a half million ton of coffee; however, it imports around three million ton, from which part is re-exported. The production of coffee in 2015 was approx. nine million ton; from each kilogram of coffee 0.91 kg of solid waste is produced, thus the importance of a further valorization of this residue becomes obvious. As Murthy & Naidu, (2012) confirm, coffee is a very popular drink and as such its trade is extensive. In fact, as they state, it is the first but the petro-oil in use in the world.

In a comprehensive review, Campos-Vega *et al.* (2015), report a detailed catalog of compounds which can be exploited by spent coffee grounds, as the cited in the review research articles suggest. In the mentioned review, it is proposed to use spent coffee grounds in order to extract several added value products. More specifically they state that the residual mass after the initial coffee extraction contains numerous organics like different

kinds of polysaccharides and fatty acids, which can be extracted following further treatment. As presented in their review, research is being conducted towards biofuel generation from the exploitation of coffee residues. Moreover, its capacity as a source of sugars, as absorbent of pollutants and in particular heavy metals and as a primary source for the production of activated carbons are also being investigated.

At least 10-15 % lipids, measured on a dry basis, have been found to remain on the used coffee grounds. Different coffee residual biomass samples have been analysed and an approximate 90% of lipids was found to remain in the solid residue after coffee extraction. Spent coffee biomass oil consists mainly of triglycerides and small amounts of diglycerides, free fatty acids, terpenes, sterols and tocopherols. Therefore, it represents an important source of raw material for a variety of products inclusive biofuels. Cholakov *et al.* (2013) applied extraction methods on spent coffee grounds to evaluate their potential as source of biofuels and activated carbon absorbents. Their results were promising in both aspects but not conclusive, so they recommended the need for further research. Coelho and co-workers examined the influence of three co-solvents, namely ethanol, isopropanol and ethyl lactate, on the yield and composition of the oil extracted from the above SCGs. The highest yield (12.4 %) was obtained at $T = 333.2\text{ K}$ with 5 % ethyl lactate as a co-solvent. Georgina *et al.* (2018).

A great proportion of the overall, worldwide spent coffee waste biomass production is generated at the industrial sites where instant coffee is manufactured. Therefore, a further treatment for added value compounds, for biofuels or any additional application will be free of costs of collection and transportation of the raw material, and their management. The weight that these costs carry in processes which target the valorization of waste biomass constitute a major issue; they can be such that they can actually make or break the respective processes Lervolino *et al* (2018). Consequently, expansion of existing instant coffee industries so as to incorporate processes for the extraction of added value compounds from the remains of the spent coffee may be a worth considering venture.

2.2.2 Lignocellulose biomass

Sindhu *et al.*, 2016 present an overview of lignocellulosic biomass, which is high in cellulose, hemicellulose, lignin and as such it can serve as an excellent source for biofuel generation. And of course, an important virtue of this type of biomass is that it is renewable. Second generation lignocellulosic biomass in particular, in addition to being an excellent candidate for bioethanol production, is an amply available and low cost feedstock, which is often accumulated in places favoring its treatment and as such, minimalizing the otherwise high

costs of transport and collection process as analyzed in the aforementioned section for spent coffee grounds. Such biomass can be the straw of cereals cultivated for human or animal consumption, i.e. field residues or process residues such as residual biomass produced during the collection of wheat, rye, barley, oats, corn and other cereals, which are traditionally used for animal feed, as natural absorbent of water and as insulation material in certain constructions. The collection of cereals takes place in the summer months and as such this type of biomass can be collected in a dry form and can be transported to biorefineries simultaneously with the collection of the edible crop. Such an option reduces the management needs associated with the residual biomass collection. Husks of legumes, rice and corns can be also used in a similar way and for their collection the same methods can be applied. Additional source of lignocellulosic origin is the bagasse disposed of bioethanol production units, which with further treatment can produce additional biofuels. Moreover, they are readily available in the sites of bioethanol production and unless they are further treated for further added value products generation, they form a waste which has to be disposed of according to environmental requirements at additional costs.

Figure 3. Hay residues *Truncated photo by Petar Starčević*
(<https://www.pexels.com/photo/hay-field-under-clear-sky-2389122/>).

According to Eurostat Cereals in EU is a product aiming to be used as food or food derivatives by humans and/or animals. Cereals are extensively produced in Europe and all over the world. During 2015 cereals and rice production in Europe reached around three hundred and twenty million ton, half of which were different kinds of wheat and an approximate 20% was barley. (KFE,2017). In addition to cereals Europe cultivates plants with oil generating seeds, such as turnip-rape, rape, soya, sunflower the production of which was approximately 30 million ton in 2016 with rapeseeds being the two thirds of that quantity, sunflower approaching one third, while soya production which was only two and a half million ton at the time has an increasing tendency (EAF&F 2017a). These seeds are primarily used for oil or/and bioethanol production. Therefore, the waste biomass produced after the

treatment of those seeds could always be further utilized for the extraction or formation of value added products, while appropriate further treatment can provide additional biofuels.

According to Zabed *et al.* 2016 the world availability of such biomass is approximately three to four billion ton per year while 2-5 ton of such biomass could produce approximately 1-2 m³ of ethanol. In their review amongst others they provide the content of cereals of different origin (i.e. from rice or wheat, or barley or oat) in cellulose, hemicellulose and lignin as measured by Saini *et al.* (2015), Ludueña *et al.* (2011), (rice husk) and Sánchez (2009) (oat and rye straw).

Bioethanol production has well advanced over the last decade. The processes for its production were designed so as to employ primary biomass produced for that very purpose. As such, the raw materials composition and properties were assumed to be adequately similar. However, the biomass properties are subject to numerous conditions such as variety of the crop, season, temperature variations during growth, soil properties, irrigation frequency, fertilizer kind and quantities used. Additionally, as these were industrial size continuous processes, the constant supply of biomass of the same quantity and composition is of key importance for their efficient operation which also ensures good and within the required specification product quality. Abraham *et al.* (2016). Second generation biomass and generally waste biomass of a varying origin and composition will require inventive actions and the design of processes versatile enough to adapt to the expected variations. This may be proven a very challenging task. Abraham *et al.* 2016, discuss the potential of rice straw as second generation source of biofuel so that this waste of a high annual volume can be exploited. While this type of biomass can be used for the production of bioethanol, the solid waste of the process can be further treated for the production of other type of biofuels. The formation of biopolymers can also be feasible from this feedstock. According to Saini *et al.* (2015) the annual universal production of rice residues is over 700 ton. Useful waste biomass from rice straw consists of the rice stems, the leaf-sheaths and their blades. Much research has been conducted on this waste biomass and data on its composition are available in the literature.

Wheat straw is the residue of harvested wheat with an estimated annual yield of 1–3 ton per acre. Talebnia *et al.* 2010, report research on wheat straw as biofuel source. This raw material, as many others of its kind, mainly contains cellulose (of very highly attached to each other strains), hemicellulose and lignin in mass proportions of around one third to 40% for the former, one fifth to one forth hemicellulose, and 15-20% for the latter, as well as a smaller proportion of extractives. This kind of biomass-resources is encountered in ample quantities everywhere in the world. Those remains of agricultural produce after all useful food parts have been collected can be exploited for direct bioethanol production without the

need for any additional investment. United States alone generates over 400 Mt of biomass which comes from agricultural wastes usable for bioethanol production, while an additional amount of approximately 0.4 billion ton of energy crops is also available (Saini *et al.* 2015).

The production of corn, wheat, rice and sugar cane can provide the majority of agricultural waste biomass which with appropriate management and can form a precious raw material for biofuel production. (Kim and Dale 2004).

While the production of biofuels and more that of bioethanol is more straightforward when dedicated for that purpose crops are used as their composition is more or less the same, when a variety of waste biomass is employed instead, the existing cannot be directly fed with this alternative feedstock. An effective way to resolve this shortcoming is the implementation of appropriate pretreatment stages. Such stages can for instance increase the biomass content in fermentable sugars. Alternatively, new fermentation technologies can be developed so as to ensure viability and efficiency of the production process. Sarkar *et al.* (2012).

Corn waste biomass, which consists of stalks and leaves, the empty cobs and the husks, is a much promising biomass for bioethanol production, because of its quantity (1 g per kilogram of produced corn-grins or about four ton of waste biomass per acre according to Kim and Dale, 2004) and its composition. Sarkar *et al.* (2012).

A study conducted by Ayeni and Daramola 2017 considered the exploitation of corn waste biomass for the production of biofuels and other products of everyday use. For that purpose they utilized different pretreatment methods involving between others alkaline hydrolysis with or without hydrogen peroxide and dilute acid hydrolysis. They used these processes in order to characterize the corn-cob, to enhance the cellulose, to remove the lignin, to solubilize the hemicellulose and overall to evaluate the economics of the aforementioned exploitation of this type of biomass on the basis of the above separations and characterisations and they proposed methods which they demonstrated that can ensure process viability. Ayeni and Daramola (2017). Shariff *et al.* (2016) have also conducted research on corn cob residual biomass and in other kinds of feedstocks like palm wastes, rice husk, wheat straw, wood sawdust, corn cob (which is abundant in Malaysia throughout the year) for the slow pyrolysis process. Corn cob waste biomass was characterized for its content in cellulose, hemicelluloses and lignin the mass fractions of which were found to be approximately 0.46, 0.4 and over 0.11, respectively. Shariff *et al.* (2016). Corn cob has low content of nitrogen and sulfur and a high proportion of volatile matter thus was demonstrated that slow pyrolysis is a suitable method for its valorization.

Bagasse from a multiplicity of processes can form an excellent feedstock for the generation of biofuels, simultaneously solving the environmental issues associated with their disposal or cutting costs from their further treatment. According to Sánchez 2009, the estimated at the time quantity of bagasse from all over the world was over a third of a million ton. Similarly, perennial biomass can be exploited for the same objective. Mantziaris *et al.* (2017). However, for both categories of these biomasses, the variation in quantity, quality (composition of feedstock) and availability of feedstock are posing new technological challenges imposing the need for versatile and inventive approaches for their valorization. At the same time however, they can act as a make-up feedstock to counterbalance seasonal and compositional variations of biomass.

Figure 4: *Perennial plants*

In summary, lignocellulosic residual biomass is abundant in the planet, it is of low cost and often a waste which has to be environmentally disposed of, concentrated and accessible. It has a composition which is suitable for biofuel production, much research has been conducted already and available for its treatment technology does exist.

2.2.3 Palm, Olive, Coconut, Avocado and Argan oil production residues

Edible oil production from trees serves the biofuel biomass supply in different ways. One is that the oil production trees have a considerable life span and as such they are providing yearly biomass from prunnings and leaves. The trees producing oily fruits have a smaller but non-negligible content of oils in their leaves and branches; as such, the valorization of residual biomass from trimmings towards biodiesel production in particular, is appropriate. They are evergreen trees and as such they produce a continuous leave supply. Their leaves have valuable compounds, the extraction of which can be considered as means of improvement of the economics of processes, thus valorizing their residual biomass for

biofuel. And of course, the used cooking oil resulting at a later stage is an excellent biodiesel source, too.

For some of those, the residual biomass has been already well characterized and their exploitation technologies are developed or are in the process of development. Moreover, the need for oil production from all aforementioned plant-fruits is in increasing demand and as such, plantations are rapidly increasing. Therefore, the future and present abundance of this type of biomass is also an important factor for which this type of feedstock is worth considering.

2.2.3.1. Olive oil production residues The olive tree is a very long living tree. It is not uncommon to find trees as old as a few or even several ages, while the existence of trees over a thousand years old can also be found. They are evergreen trees and their fruit, the olive, is either mildly treated and its flesh is eaten or is crashed to provide its juice, the olive oil. The great majority of the universal olive oil production comes from trees grown around the Mediterranean. (Christoforou, & Fokaides 2016). The recent global olive oil production sums up to approximately two million ton. Olive oil production involves mechanical separation of the fruit from the leaves that are gathered together with the fruit during its collection, the mechanical crashing of the olives, the separation of the oil from the solid mass with or without the addition of water as a means of an assisting extraction solvent and the subsequent separation of the olive oil from the solid (olive-mill solid wastes) and the liquid wastewaters. Depending on the method of treatment, and whether there has been addition of water during treatment or not, subsequent wastewaters can be removed separately or together with the solid residue. Both those waste streams are produced in very large quantities and their pollution potential is high. Christoforou & Fokaides (2016) present a comprehensible review of techniques employed for the olive-mill solid-waste to energy utilization. The treatment and disposal of olive mill wastewaters however, forms a much greater problem, the solution of which is a really pressing necessity. The applied techniques have not given satisfactory results. Haddad *et al* (2017). In addition to the above, olive leaves, olive tree branches from pruning and bark can be utilized towards that direction. Although extensive research has been done on the reduction of the pollution caused by olive mill wastewaters, substantially less work has been conducted towards the valorisation of the solid and liquid wastes associated with the olive oil production. There are however studies on added value products from olive leaves; important effects of olive leaves as antihypertensive, anticarcinogenic, antiinflammatory, hypoglycemic, antimicrobial and hypocholesterolemic. (Talhaoui *et al* 2014). Additional medicinal properties have been reported. Extracts of olive leaves can also serve as cosmetic precursors and also as food preservatives.

Figure 5: Typical olive trees before pruning (left). Leave-load of the tree before trimming (top left). Typical branch-load of the tree before trimming (bottom left). Typical pruned trees on the right.

Altogether, every year a great amount and variety of waste biomass is generated from the olive cultivation (eg. pruning of branches) and the olive treatment processes to obtain edible olives and olive oil. These residues involve olive leaves, olive branches from pruning, olive-mill wastewaters and olive mill solid-wastes. The latter two, as mentioned above form an undesirable and difficult to treat waste. The leaves of the former two are occasionally used as animal food. Branches are usually burned on site as they are difficult to be moved and transported. (Talhaoui *et al.* 2015). In addition to being in the pruned branches, olive leaves, are collected in large amounts in the olive mills. This is because leaves are also falling during the collection of the olives. Leaves collected together with the olives are approximately one third of the volume or one tenth of the weight of the collected olives which are taken to the olive mill (Herrero *et al.*, 2011). The leaves are separated from the olives by suction, immediately before milling. Erbay & Icier (2010) analyzed olive leaves and found that they contained oil (about 7 %), carbohydrates about 30%, protein, fiber, ash and water. In a subsequent study, Erbay & Icier (2010), characterized olive leaves and provided a list of typical compounds which can be found and can also be extracted from the leaves. These compounds is worth knowing and considering for improving the economics of a facility which aims at using olive cultivation waste biomass for the production of biofuels and explained in the introduction. As Velazquez Martí *et al.* (2011) and Talhaoui *et al.* (2015) report in their

review, the leaves from a typical olive tree pruning amount to about 25% w/w of the trimmings; the thin branches constitute approximately half of the total weight of the pruned biomass and the thicker branches or wood the remaining 25%. Naturally, this is only an example and the proportions vary depending on a number of factors such as the variety of olives, the kind of cultivation and the protocols followed, the size and the age of the trees, the local pruning practice. However, rainfall during the year may also be an important factor. The pruning of olive trees can produce around 10 ton per hectare of residual biomass depending on the country, the variety, the morphology of the area, as well as the local climate conditions and cultivation practices. However, these figures can substantially change as pruning frequency and extent can be substantially altered because of the transition of the farming activities to complementary ones (i.e. to complement agricultural activities with animal pasture or with involvement in tourism). Velazquez-Martí, *et al.* 2011 give a comprehensible and detailed quantification of the pruning residual biomass as a function of tree kind and conditions.

Olive bark and branches possess properties similar to the ones of the leaves and as such they can be used for the extraction of valuable compounds. After the extraction of such compounds, the solid waste can be further treated for biofuel production. (Cara *et al.* 2007, Ballesteros *et al.* 2011, Romero *et al.* 2010, Sequeiros & Labidi 2017,); the waste leaves can be also used for the same purpose.

Therefore, olive oil production wastes have the potential to be utilized for biofuel production. Their production can be combined with that of olive oil and that of valuable products from olive leaves. There are multiple methods to employ in order to minimize costs, increase profitability and minimise environmental impact on the way towards a cyclic economy and sustainability. For example, Lervolino *et al.* (2018) have integrated olive wood waste supply chain with a thermo-catalytic reforming process in which biofuels are produced and optimally distributed. They have assessed the environmental gains of the venture using carbon dioxide equivalency as an indicator and they identified the conditions under which such a process can be self-sustained and eco-friendly. Haddad *et al.*, 2017 are proposing a new method for olive-mill wastewaters valorization. Their method involved mixing olive-mill wastewaters with sawdust to produce biofuels and to transform a polluting entity to valuable products.

2.2.3.2. Biomass Wastes from Palm Oil production

The palm oil production comes mainly from Indonesia and Malaysia in particular. Smaller quantities are produced in West Africa and in Latin America. The tree life span is 25-30

years, they are harvested every 10 days and they are pruned twice a year; the waste biomass from pruning is often left to decay and fertilize the soil of the farm.

According to the Department for Environment, Food and Rural Affairs of UK (2012) palm oil is the most used vegetable oil in the world and it has a great number of uses in addition to being inexpensive. Moreover, the palm tree is a very efficient producer of oil, although its lifespan does not expand beyond 30 years. DEFRA(2012)

Palm oil is extracted from the flesh of the fruits of the oil palm tree. The quantity of palm oil which can be produced from the flesh corresponds to approximately one third of the mass of the fruit. The stone of the fruit is crashed and pressed to produce the palm kernel oil. Those two oils are usually refined and further processed to produce a number of derivatives for a number of different applications in the food sector (biscuits, margarine, bakery products, frying-oil) also in the production of biodiesel, animal foods, soaps, cosmetics. Its use as a first-generation biofuel also advances with increasing rate.

Similarly to olive oil production, after the extraction of the palm oil there is a substantial amount of biomass left, the management of which is very problematic. Consequently, a great effort is put towards its valorization via the production of fuels. However, most of this waste mass is continuously produced and therefore abundantly available and also concentrated at the place of oil production. Therefore, the economics of a subsequent treatment will not be burdened by the costs of collection; moreover, if additional treatment is planned in the same area via an extension of the oil production facility, transport costs will be also negligible.

The energy content of those wastes can be exploited following different treatments employing a number of existing technologies, ranging from direct combustion, combustion to electricity generation, pyrolysis, esterification, torrefaction, gasification, up to anaerobic digestion and fermentation. Research is being advancing in biomass characterization, factors affecting economic viability, optimal existing technologies and improved methods of treatment, economics, life cycle analysis, and other. (IISD 2014)

Lee *et al.* (2017) investigated the slow pyrolysis products obtained by relevant with palm oil production wastes (palm kernel shell, empty fruit bunch and palm oil sludge) as feedstock. Their findings implied that the former two had higher lignin contents; more over they appealed as precursors for biochars while they were displaying a promising potential for biofuel generation

As mentioned above, Malaysia is a leading country as palm oil producer. Chiew and Shimada (2013) have applied a life cycle analysis, in order to make a comparison on biofuel production using different technologies and a waste biomass consisting of empty bunches of

palm-oil fruits as feedstock. The research also involved other potential uses of this waste. They found that the option of biofuel for combined heat and power production was the best.

In a later study, Kurnia *et al* (2016) compare and discuss developed and in the process of development technologies which are used for the valorization of palm-oil wastes towards biofuel production. They have furthermore discussed the challenges that future research and development has to address. They classify the biomass treatment and conversion methods as thermochemical, biological or physical, each category having their pros and cons. The thermochemical processes are more suitable for large scale applications, although they are more energy intensive as compared to the other two categories. The studies comparing the different technologies back up their arguments by means of relevant LCA studies via which the sustainability aspects of the different scenarios are evaluated. In the whole process of palm-oil generation, the plantation stage appears to carry a heavy environmental weight. However, in terms of costs and on the basis of economics, biofuels from the treatment of palm-oil waste do not appear attractive, especially when the cost of fossil fuels is dropping or stays at the levels of 2016. Therefore, aspects which affect the economics of waste treatment such as transport and distribution of biofuels, design of conversion methods, have to be improved. Better improved metrics for a more representative evaluation of the environmental impact of the processes via life cycle analysis have to be devised. It is worth mentioning here though, that the plantation costs and environmental impact have to be considered in connection with the life span of the tree life. Palm oils become productive four years after they are planted and they are productive for twenty to thirty years. Trees with a longer life span may form a better alternative towards edible oil production and subsequent exploitation of their residual biomass. As such, if a comparison was to be made, olive trees are superior to palms, although they grow in different geographical areas.

The aforementioned findings regarding the methods of exploitation of energy, using palm oil waste biomass are also supported by a review conducted by Sukiran *et al* (2017). According to them, the hygroscopic nature, the low calorific value and the high quantity of oxygen and moisture contained in those wastes restricts their potential as fuels. As such, they propose to enhance the properties of those wastes towards the formation of fuels employing torrefaction processes; they present an overview of factors associated with such a treatment. They also show characterization results of these waste biomasses. They discuss different views resulting from previous research (which is also projected to the present) on oil palm solid wastes torrefaction; potential applications related to the yield obtained via those methods of treatment were shown. Moreover, discussion was conducted around the potentials and the evolution of methods for the valorization of palm oil wastes. They conclude that the torrefaction technology can form an excellent method of biomass valorization towards

energy production. Finally, they evaluate the relevant costs of the technique and they characterize it as as a potentially feasible and economically viable.

Asibey *et al.* (2018) have conducted research on the valorization of waste biomass in Ghana towards the production of electricity. They acknowledge the impact which waste collection and management has on the economics of waste valorization, but also the health risks from the untreated waste, especially in African cities. Palm oil waste biomass is an excellent feedstock for the production of electricity according to their research; it is also a better source or raw material for combustion compared to the rest of the waste produced by the local agro-industry. The volumes of waste biomass produced in the process of palm oil production are very large and have already been used for the generation of electricity as a means of energy sources for the needs of the relevant industrial processes; the potential of such a valorization in sub-Saharan Africa is great. However, in their view, there is a hurdle which is owed to the existing local policies, which have to be reconsidered together with the country current institutional arrangements so as to take advantage of this potential. Their work also refers to the need to give consideration to maintaining biodiversity and to increase the safety of the processes. Asibey *et al.* (2018). Obviously, the appropriateness of biomass for biofuel production strongly depends on the area, the alternative energy resources of the local community, the variety of potential feedstocks, and as such, valorization of palm oil wastes in Africa is unlikely to have the same efficacy as in Malaysia or Indonesia or in South East Asia in general. Consequently, studies which deal with the economics of such processes, especially when based on life cycle analyses, have to refer to the local conditions, because owing to the different prices and costs of labor, all such findings are area specific.

A study conducted in Malaysia by Hansen and Nygaard (2014) examined the operational status and the evolution of a number of plants which were using or were planning to use palm-oil waste biomass for the production of energy; the study examined both completed plants and plants in the progress of construction. Amongst a continuing increase of construction of such plants, thirty nine were advancing towards full operation. Plants accounted for in the study involved plants producing electricity either as stand alone or in connection with others. The produced electricity was then directly used by the industries of the area, by plants connected to the national grid, and by combined power and heat generation plants. During 1990-2010, substantial pressure was exerted from the international community because the industry of palm-oil production was expanding in a way that could provoke serious environmental problems in the future. As a consequence Malaysia was forced to adopt environmentally friendlier practices including the valorization of palm oil effluents and waste biomass. A simultaneous fossil-fuel price rising encouraged

energy-intensive industries like those of cement and rubber-glove, refineries, power generators to use energy produced by sources like palm oil waste biomass to meet their respective needs. However, as in the case of Ghana, progress on waste mass valorization had been hindered, amongst others, by problems in the implementation of energy policy, costs rises, obstacles in networks formation.

In addition to palm-oil waste, date palm residues can be utilized for biofuel production. Bensidhom *et al.* (2018) have studied this type of lignocellulosic biomass, which is extremely abundant in Tunisia. For that purpose, they used a fixed-bed reactor to pyrolyze the respective biomass, i.e. date palm wood, leaves, empty bunches of fruit and similar remains; they produced bio-oil in yield 17-26, biochar (with yield up to 37%) and syngas with a yield in over 40%. They characterized the respective biofuels and found that they have a great potential to function as alternatives to usual fossil fuels. This biomass however, before being exploited for biofuel production needs to be aggregated and transported to appropriate places for the respective treatment.

2.2.3.3. Biomass Wastes from Coconut Oil production

Besides palm oil waste biomass, coconut oil residues are also an available source for biofuel production and the pros and cons of the management of its valorization have analogies with those of palm oil, as the issues of transportation and aggregation of biomass residues are of a similar kind, while at the same time, they are produced in similar areas. In Malaysia for example, coconut is extensively cultivated; however, after the extraction of coconut milk the residual biomass is usually used as fertilizer or as animal feed or it is left to decay. Research on the characterization of this biomass has been conducted by several researchers and a brief account is given below.

Abigor *et al.* (2000) studied biofuel production by catalytic (PS30 lipase) transesterification of palm-stone oil and coconut oil and examined the effect of tert-butanol, 1-butanol, n-propanol and iso-propanol in the overall outcome. They characterized the oils and reported the efficiency of the reaction in each case. They found that they could produce fuel of a quality consistent with biodiesel specifications.

Biodiesel fulfilling the requirements of quality was also produced by Thushari and Babel 2018, in a high efficiency process which employed methanol and a catalyst produced by coconut meal waste in an open reflux reactor.

Sulaiman *et al.* (2003) considered the valorization of coconut waste by means of a reactive extraction method recovering coconut milk from the coconut solid waste in order to produce biodiesel. Different temperatures, potassium hydroxide concentration and agitation speeds were employed in their experimental study. They then employed response surface

methodology to identify the range of optimum conditions (reported in their work) with a yield of approximately 90% towards biodiesel.

In a subsequent study, Talha and Sulaiman (2018) produced biodiesel using solid coconut waste and a CaO-waste derived catalyst, in a packed bed reactor; they conducted an in situ transesterification reaction obtaining biodiesel yield 95% at 61 °C with 2.3% w/w % catalyst loading and methanol. The mass of methanol was 12 times that of the solid.

A refinery waste-coconut-oil employed as raw material, was treated with ethanol, with and without water, for the production of biodiesel, by Oliveira *et al.* (2018). The conversion at which they reached was over 99% on a molar basis. They found that when water adsorption was simultaneously conducted with the esterification, a lower molar quantity of alcohol was needed, thus improving the process costs and mass economy.

2.2.3.4. Biomass Wastes from Avocado Oil production

The consumption of avocado is very high and it has been increasing worldwide in recent years. Avocado is eaten raw, but it is also extensively used in large quantities in the food industry. It is also used in the cosmetics production.

The seeds are high in starch and polyphenols. Avocado seeds were characterized in terms of thermal and physical properties as well as chemical composition and technologies for their valorization as fuel are shown by Domínguez *et al.* (2014). Avocado is in fact, a fruit which is extensively traded in the world and its world-wide production was estimated to be nearly five million ton in 2014, which corresponded to an increase of 140% from 1995 to 2015. A great amount of valuable biomass is the residual products (skin, stone) of guacamole manufacturing. This industry generates a large amount of such waste biomass products which are good for energy production, because they possess high calorific value. Perea-Moreno *et al.* (2016). Durak and Aysu, (2014) studied experimentally, by means of slow pyrolysis, the potential of avocado stones for biofuel production. Avocado stones were used in a fixed-bed plug-flow reactor with and without catalyst; bio char, oil and gas were obtained. Potassium hydroxide and alumina were used as individual catalysts, at three temperatures ranging from 400 to 600°C. In addition to those, the same group also produced bio-oil from the same biomass, employing individually ethanol and acetone with potassium hydroxide and zinc chloride as individual catalysts, as well as without catalyst. Avocado stones were put in an autoclave and were subjected to supercritical treatment using ethanol or acetone as solvents. The processes were conducted under high pressure, at temperatures 250 °C, 270 °C and 290 °C with or without the aforementioned catalysts. The highest conversion (liquid+gaseous products) of nearly 77 % was obtained at 290 °C

with acetone via a ZnCl_2 10% catalytic process. (Aysu and Durak, 2014). Furthermore, Díaz-Muñoz *et al.* (2016) and Bazzo *et al.* (2015) have also researched valorization of avocado stones towards absorbents and adsorbents formation. Perea-Moreno *et al.* (2016) described avocado stones enthalpy of combustion properties. Their calorific value assimilated that of olive stones and almond shells and concluded that the avocado stones may be used as a solid fuel for heating.

Rachimoellah *et al.* (2009) investigated the capacity of oil from avocado seeds to produce biodiesel. They conducted a series of measurements at different temperatures, with different alcohols by changing their molar ratios to the employed quantity of oil; they also modified the method of removing impurities from the end product. They used sodium hydroxide as a catalyst 1% w/w%. They found that at 60 °C, using six times more alcohol than oil and subsequent product dry washing process a biodiesel 85% in methylester was formed.

2.2.3.5. Biomass Wastes from Argan Oil production

Argan oil is produced in small quantities at present and its main production is centered at the country of its origin, i.e. Morocco. However, as its properties are gaining increasing recognition and publicity, its production in large scale is advancing fast. The argan oil exports from Morocco have dramatically increased the last 20 years; the importers employ it for a number of uses, cosmetics production being the most common one. As Charrouf and Guillaume (2008) report, argan oil is an advanced product with excellent, valuable dietary compounds. For that reason the interest on it has been increasing and there is a continuous rise and expansion of the extent of plantations and of the trees producing this oil, both in Morocco and in other countries where the respective trees can grow. In a subsequent publication of theirs, Charrouf and Guillaume (2018) report on the progress of an admirable project which holistically addresses production, social, environmental and other issues associated with sustainable processes. In their work the seven stages through which argan-oil production has to go are explained. Argan oil is produced via inefficient production methods which however do not harm its physicochemical properties. More efficient processes are currently in the progress of development, while their application and industrial implementation is also advancing.

As mentioned, argan oil production and argan-oil tree plantations are rapidly expanding. Given the experience from other oils presented in this section, where the problem of the waste first became significant and then consideration was given to the development of methods for their management, it would be prudent to consider valorization of its waste biomass prior to the industrialization of its production so that integrated, energy independent, self-sustained argan oil production units can be developed. Such units can make allowance

to incorporate the production of added value products and the valorization of their waste in their original design of the process. Naturally, intensive research is required in this field as the characteristics of the materials involved are far from well known.

2.2.4 Citrus

Citrus is the most important fruit crop in the world with a production estimated at approx. 90 million tons in 2014. According to the Food and Agriculture Organization of the United Nations (FAO), in 2012, the production of orange, lemon and grapefruit worldwide was around 95 million ton. Nearly 26% of citrus fruits are used for the production of juice. The biomass residues from the juice production is estimated to be fifteen million ton, and it consists of seeds, peels, and pulp. Citrus peel is rich in antioxidants and multiple other valuable compounds with anti-inflammatory, anti-cancer, anti-proliferative, and anti-viral and other activities which may contribute to the prevention of disease (Mhiri *et al.* 2017), (Geraci *et al.*, 2017). The largest share of citrus juice production is orange juice, followed by grapefruit, lemon and lime. Other citrus fruit such as mandarins, tangerines, pomelos are produced and traded in much smaller quantities. (CBI). The food industry is expanding very fast. Especially in the most developed countries, where the time spent for food preparation by families and individuals is continuously shrinking. Consequently, the food industry is expected to generate much more by products, which in many cases is merely waste biomass of plant origin, like fruit skins, vegetable stems, fruit stones and seeds, pomace, nut shells, etc. Amongst those, the citrus juice industry is producing a great deal of waste biomass very high in added value compounds. Sharma *et al* (2016).

The orange (*Citrus sinensis*) is a very common and highly consumed crop. It is part of the citrus family, and it is one of the highest worldwide crops produced. The production of concentrate for the juice industry is one of the primary applications. The orange peel is a part of the residual biomass generated by the processing of citrus. The quantity of orange-juice production residuals is estimated at around sixteen million ton per year. (Ayala *et al.*, 2017).

Oranges are extensively cultivated in America (Florida and California in the United States, Mexico, Brazil) in Asia (China, India, Pakistan, Iran, Mediterranean countries) as well as in all European, Asian and African Mediterranean countries. (Siles- López, 2010). More than 50 % of the world orange production is generated in the American continent, where Mexico makes a significant contribution. The Mexican orange production was over four million ton in 2013, which represents over 6 % of the worldwide orange production. Mexico accounts for 5 % of the world grapefruit production and about 15 % of the lime-lemon global production. In Mexico, the citrus waste generation consists of approx. 750 thousand ton of orange, 70 thousand ton of grapefruit, and around 350 thousand ton of lemon and lime (Ayala *et al.*,

2017). According to the 2007 data of the Statistical Database of the Food and Agriculture Organization of the United Nations, Brazil produces over approx. 28% of the world orange-production; it is followed by USA which produces over 10% while Europe is in the third place with a production just under 10%. Over fifty percent of the processed fruit becomes waste. This waste biomass consists mainly of citrus peel (flavedo and albedo), seeds, membranes of the segments and the crushed endocarp. The peel can be used for extracting added value products for preserves, to produce marmalade for food or the peels are even used to produce animal food. However, in many cases it is just treated as a problematic waste and it has been often just been dumped to deserted areas close to the juice industries. In such cases, their decomposition resulted in a serious pollution threat for the underground water, a health and safety threat due to uncontrolled methane production and a visual sore and odor-repellant for the area. However, the valuable properties of the citrus peels and seeds have given drive to research and technologies development aiming at ways of valorization of this waste in multiple ways and towards a great diversion of applications ranging from the extraction of pharmaceuticals, food preservatives and flavoring agents to cosmetics and biofuels production. Of course, in order to develop such alternative valorization methods a good knowledge of their composition is required; Siles-Lopez *et al.* (2010) report in their article publications, which provide information and characterization data of different varieties of citrus fruits. According to those in citrus peel, sugars, cellulose, hemicellulose, starches, lignin, organic acids and proteins are contained in proportions which depend on variety, climate conditions, soil and other. Moreover, in this study, Siles-Lopez *et al.* (2010) report how to produce methane from citrus industry waste biomass; they also state associated with such a production problems. Erukainure *et al.*, 2016 highlight that the use of orange peel waste can be utilized for the extraction of high purity essential oils to decrease the purchase of high-cost raw materials using water as a solvent. Orange and citrus peels in general can be used to produce numerous quality added-value products the production of which can compensate for the costs of less profitable or even non-viable synergistic processes aiming at waste exploitation or at environmentally oriented transformation processes. For example, Raga & Lopes (2003), studied the chemical composition of a five-fold sweet orange oil obtained via vacuum distillation. They found that the quantitative composition of the obtained products demonstrated that by appropriate adjustment of the conditions of the fractionator, high quality oils could be obtained.

John *et al.* (2017) conducted a detailed literature survey on bioethanol production using citrus waste. They provide the composition of lignocellulose biomass of different feedstock used for bioethanol production and compare it with that of citrus-peel waste which contains low lignin and high carbohydrates (fructose, sucrose, cellulose, hemicellulose and pectin), and as such it can favor bioethanol production. Citrus peels contain polysaccharides and

soluble sugars. They found that it is possible to make citrus-peel waste more susceptible to saccharification with enzymatic treatment. They employed pretreatment methods to reduce the formation of compounds restricting its effectiveness. The pretreatment was involving dilute acid hydrolysis and steam explosion. A great incentive for the valorization of citrus peel waste comes from the understanding that extraction of added value products prior to biofuel production can greatly improve the economics of the venture, so scale up efforts are under way. Extraction of D-lemonene as an added value product can also facilitate the bioethanol production via saccharification because D-lemonene exerts inhibition on the enzymatic fermentation. The economics of the saccharification can be improved by acting on the selection of enzyme type, function or method of application. Options can be the immobilization of the enzymes for example, the use of cell-recycle reactors, co-culture fermentation and other. John *et al.*, (2017).

Bicu *et al.*, (2011) worked with cellulose extraction from orange peel, the pulping of which was achieved employing sodium sulfite and sodium metabisulfite. They evaluated how the addition of the pulping precursor, the reaction residence-time and the temperature affected the result. They found conditions at which good quality cellulose could be recovered with over 40% w/w yield. The obtained cellulose was good for a number of uses, such as water absorbents or fillers, including availability of cellulose as raw material for production of further derivatives.

Lanfranchi, (2012) conducted an evaluation of the economics of different methods of production of energy using the citrus waste biomass which resulted after removing the juice of the fruits, *i.e.* what has been reported before as juice production residual biomass such as peel, seeds, membranes of the segments, residual juice and pulp. Solid fuel can be produced via drying of the waste and produce solid pellets for combustion. However, as previous experience has shown, it has to be done via very well designed processes and employ only the less moist parts of this residual. This biomass has occasionally been used as a fuel. But it was highly uneconomical. This is because its content in water is very high (more than 90%). In these applications, the residual biomass, as a whole, was dried before it was burnt. However, this incurred high energy costs. As a result, it ended-up being a very inefficient energy source, which required the disposition of more energy for its drying than the energy provided by its combustion. The biofuels (bio-ethanol and bio-gas) production from those wastes is a much better option.

Rivas-Cantu *et al.* (2013) have conducted a study to present the best at the time technologies which can be employed for the valorization of citrus waste biomass towards the production of energy, using laboratory data obtained from the pretreatment and enzymatic hydrolysis of industrial waste. Their work involves results obtained from an extensive study

and long experience on the relevant work. They examined the production of sugars and value-added compounds. They also studied how different methods of pretreatment, including mechanical and chemical methods could be used to increase the yields towards the most valuable sugars. The key processing steps of the waste were the following: Shredding and grinding below 1.25 cm particles to form a suspension in water -which was partially hydrolyzed by steam-, flash distillation or centrifugation for fermentation-inhibitor limonene removal, enzymatic hydrolysis of the resulting slurry under a controlled temperature and pH range, fermentation, or simultaneous saccharification and fermentation to produce ethanol and finally distillation to separate the produced biofuel from the waste. They also report problems associated with the implementation of this technology. Such technologies have not yet found their way to an efficient large scale, although much progress is being made.

In summary, citrus peel waste can form an excellent second generation non-food lignocellulose feedstock for biofuel production. Prior to its utilization as a biofuel raw-material it can provide other added value products following extractive processes. All citrus wastes are good for those applications but orange peel has a higher concentration of carbohydrates and as such it can provide the desired products at higher yields Joshi, *et al.* (2015).

2.2.5 Grapes mark

According to the literature review conducted by Brunerova *et al.* 2017 the vineyards of the world extend to approximately 8 billion hectares of land. The residual biomass from grapes and wine production consists of pruning and trimming the vines producing an average of 5 kg per waste biomass per vine and later from the pomace, left over after the grapes are crushed for the production of wine.

Corbin *et al.* 2015, report on the further usage of grape pomace which is either further fermented and distilled for the production of alcoholic drinks in the form of grapa, or is used as animal feed, as a raw material for added value products like antioxidants or it can be used as a promising source for biofuel (bioethanol or biogas) production. According to them the pomace contains a high portion of water soluble compound which upon fermentation can provide ethanol equal to approximately 25% of the pomace waste or to be subjected to acid-pretreatment followed by enzymatic hydrolysis to produce 0.4 litre of ethanol per kg of pomace.

The environmental impact of the burying of untreated grape pomace is highlighted by Mendes *et al.* 2013, water contamination and soil erosion being amongst the most important ones. In their review they report on the composition of the residual biomass following wine production. High concentrations of phenolic compounds hinder the natural degradation of

this waste biomass; extraction of such compounds however, is something we should aim at, because they are very valuable and they can found diverse applications such as for the formation of food supplements or cosmetics or for other uses in the pharmaceutical industry, as adhesives or as compounds whose range of application can expand if the necessary research is conducted. In their study Mendes *et al.* 2013 focus on the grape skins and in particular to red ones; after having assessed their composition, they evaluated their chemical structure with attention to the main macromolecular constituents; the target was to develop strategies for their valorization towards formation of compounds for bio-composite applications and insulation materials. Typical composition identified was: cellulose, hemicelluloses, proteins, tannins, sugars, aliphatic compounds and ash in approximate percentages of, 21, 12, 19, 14, 12, 14 and 8%, respectively, a great proportion of which are water soluble. Following this analysis, they considered it plausible to employ a multistage process for the treatment of grape skins; they proposed pre-extraction of polar compounds, subsequent polar compounds extraction with hot water and finally valorization of grape skin solid part as bio-composite.

In their work “Extraction and purification of high added value compounds from by-products of the winemaking chain using alternative/ nonconventional processes/ technologies” Yammine *et al.* (2018), considered the valorization of winery waste products. Their literature review, provided quantitative data (approx. 65 Mt world production of grapes in 2014 around 50 Mt of which were used for wine production and an estimated maximum of over 15 Mt of valuable waste biomass is left over) which can be used for the production of multiple value-added products. The authors also compared different technologies for the extraction methods, but their comparison could not provide any solid results. Yammine *et al.* (2018)

Prado *et al.* 2012 and Coelho *et al.* (2018) studied the supercritical fluid extraction of grape seeds. The collated literature review of Prado *et al.* (2012) highlighted the benefits of grape seeds for food supplement and their antimicrobial activity, which resulted in the commercialization of relevant applications. The researchers focus on the extraction of those valuable compounds by means of supercritical carbon dioxide, but they do not focus on any further treatment of the waste biomass from this process. Grapes employed in wine production are crashed and the produced pomace is left to ferment. The fermented pomace is subsequently subjected to distillation. The batch or semi-batch distillation of those fermented residues provides pisco, a grapa like alcoholic drink.

Farías-Campomanes *et al.* 2013 conducted an experimental study for the process of extraction of polyphenolic compounds from such fermented grape bagasse. Bagasse of this type contains approximately 50% of seeds, while the remaining 50% is equally shared between grape stems and skins. They employed supercritical carbon dioxide extraction with

ethanol and water to enhance extraction of polar compounds and they found that it is viable to establish an industrial supercritical fluid extraction plant to recover phenolic compounds from grape bagasse. They find that this is viable even for small scale production units.

Sanahuja-Parejo *et al.* (in press) have produced bio-oil via the co-pyrolysis of polystyrene and grape seeds achieving high conversions and good oil properties *i.e.* with a higher pH value than the acidic bio-oils obtained from lignocellulosic mass, a lower content of phenols and oxygen and an increased quantity of aromatics, owing to the hydrogen-donor contribution of polystyrene in the process.

Xu *et al.* (2009) subjected winery waste into pyrolytic treatment in a bubbling fluidized bed reactor. The calorific value of the produced gases and bio-oil were evaluated and optimum conditions for the process were identified in order to ensure a positive net energy operation. Using self-produced biogas and bio-oil to cover the thermal needs of the pyrolysis they achieved a sustainable bio-oil production.

Zhang *et al.* (2017) designed and compared two methods of valorization of grape pomace towards energy uses; combustion for electricity and pyrolysis for biofuels, *i.e.* for bio-oil and bio-gas. They found that the latter had a better positive impact on wineries in terms of economics as well as environmental aspects. According to this study, small scale wineries (<50 ton annual wine production) appeared to obtain a high economic advantage by composting of this biomass, as opposed to the large scale ones, which did not benefited substantially from the addition of such processes for the pomace valorization.

Miralles *et al.* 2008 studied the Grape Stalks Waste as Low Cost Biosorbents: their work established that grape stalk waste is an efficient sorbent in the removal of cadmium (II), lead (II), nickel (II), and copper (II). The results obtained showed that grape stalks can be used as sorbing material for those metal ions.

2.2.6 Waste oil and cooking oil

This type of waste is found in great abundance. It is very harmful for the soil and the aquatic environment if disposed of. At the same time, it forms an important source of energy. Its importance from an economic point of view becomes preponderant for countries which import edible oil, Hajjari *et al.* (2017). The treatment that it requires to be transformed to useful fuel is relatively limited. Therefore there is ample scope in its large scale transformation to biodiesel. The key difficulties in its valorization are primarily associated with its collection and the substantial variability of its composition, which depends on a number of factors. A great quantity of biodiesel is already being generated by means of processing waste oil and cooking oil in smaller and larger scale using different oils and extensive research is conducted in order to enhance its transformation to good quality

biodiesel. Piker *et al.* (2016) have tested the efficacy of catalytic biodiesel production at ambient temperature using appropriately treated waste egg-shells for the formation of the employed catalyst. The study was conducted in small scale using different alcohol to oil proportions, stirring conditions, treatment length, and catalyst cycles. In all cases promising results were obtained. Atabani *et al.* (2019) have combined waste cooking oil with spend coffee grounds and higher alcohols to achieve good quality biodiesels with very good cold properties. Along the same lines Thushari *et al.* (2019), Developed and characterized catalysts formed from coconut husk. Subsequently they employed these catalysts to converting waste coconut oil to biodiesel. Using catalyst, methanol and oil in approximate 10:12:1 weight proportions they obtained over 75% conversion of good quality, within standards, biodiesel. They studied the effect of increasing temperature, catalyst content and reaction time and achieved an optimum 90% conversion to biodiesel. Chicken fat and waste cooking oil were catalytically transformed to good quality biodiesel in a house made system by Soegiantoro *et al.* (2019). Different temperatures, catalyst and alcohol types were tested and efficiency reached 91% under optimal conditions while the cost per unit product was lower than the commercial biodiesel price.

As reported earlier, the collection of waste cooking oil is one of the important problems associated with its valorization. In a comprehensive work Hajjari *et al.* (2017) provide an effective and practical method for the solution of this problem. Sheinbaum *et al.* (2015) on the other hand, conducted a dual purpose study in Mexico-city. One aspect of the study was focusing on the methods and obstacles faced during waste-cooking oil collection and the other on the emissions produced by its use in public transport bus diesel-engines. They found that the collection and disposal had a great variation, while the use of biodiesel resulted in reduced emissions only in the case in which the exhaust gas of the buses were employing recirculation system.

In conclusion, waste cooking oil is a promising feedstock for biodiesel production, but research on this topic in imperative and versatile methods of its valorization still need to be invented.

2.2.7. Additional sources

Silva *et al.* (2016) and Souza *et al.* (2016) have studied the production of biodiesel using the non-edible acidic Macauba (*Acrocomia aculeata*) oil with very promising results. City waste or food waste can be subjected to anaerobic digestion for the production of biogas. However, a substantial amount of residual mass is to be further treated and valorised. (e.g Yang *et al* 2016).

In addition to the above reported residual biomass biofuel feedstock, a multiplicity of other sources do exist. For example wastes such as husks and kernels of seeds, which have a high calorific value and can be used as solid biofuels via direct burning. However, they can also be utilized as adsorbents of unwanted pollutants like dyes and heavy metals as reported in Senthil Kumar *et al.* (2010), Senthil Kumar *et al.* (2011a), Senthil Kumar *et al.* (2011b), Senthil Kumar *et al.* (2011c) (Vieira *et al.* 2012).

Figure 6. Municipal waste. Truncated photo by Kelly Lacy

(<https://www.pexels.com/photo/photo-of-a-dump-truck-across-buildings-2382894/>).

Similarly as Reynel-Avila *et al.* (2016), Trevino-Cordero *et al.* (2013) and Vargas *et al.* (2011), have published, flamboyant and mango biomass have the capacity to remove heavy metals from polluted waters. The husk of mango seed in particular, can be used as an adsorbent for the removal of acid dyes of the monoazo and anthraquinone class (Davila-Jimenez *et al.* 2009) and may be possible to be employed for the adsorption and removal of dyes from textile effluents (Shoukat *et al.* 2016). Similarly, dyes can be removed from wastewaters using dried and powdered mango leaves. Such a powder can be easily formed in abundance. (Uddin *et al.* 2017). Moreover, as Memon *et al.* (2009) report mango kernels can adsorb toxic chemicals such as parathion and Kanjilala *et al.* (2014) have shown that mango seed and husks can also adsorb heavy metals, whereas Reynel-Avila *et al.* (2016) mention that the biomass of bush mango seeds with the combination of the biomass of flamboyant can be used for heavy metal removal from aqueous solutions. It is also worth mentioning that activated carbons made from mango husks have been used as CO₂ adsorbents. (Correia *et al.* 2017).

Castor seed hull can remove heavy metals from aqueous solutions (Mohammad *et al.* 2011) while walnut shell can be used as a precursor for the absorption of benzene and toluene from waste gases. (Karimnezhad *et al.* 2014). Peach palm can also remove heavy metals from wastewaters Duranoglu *et al.* (2010), Salvado *et al.* (2012), Massocatto *et al.* (2015).

Peach stones can remove emerging contaminants from aqueous solutions such as stimulants, anti-inflammatory and psychiatric drugs ibuprofen and tetracycline (Álvarez Torrellas *et al.* 2015), Álvarez Torrellas *et al.* (2016b), real pharmaceutical wastewaters, such as hospital effluents, Álvarez Torrellas *et al.* (2016a) and phenol, Hannafi *et al.* (2008). Finally, they can also be used for the removal of dyes. Attia *et al.* (2006), Álvarez Torrellas *et al.* (2016a).

Heavy metals dyes and pharmaceuticals can be also removed from wastewaters by means of chicken feathers, a high volume food- biomass. Reynel-Avila *et al.* (2015). Chicken feathers can also be appropriately treated so as to be used in the process of cleaning wastewaters. They can remove organic material and ammoniacal nitrogen, Moon *et al.* (2017), and phenol, Banat and Al-Asheh (2001). Activated feather carbon was efficient absorbent of amoxicillin in surrogate wastewater and other persistent antibiotic pollutants Li *et al.* (2017). They have been also used as very effective absorbents of different types of dyes from wastewaters, Mittal *et al.* (2012), Gupta *et al.* (2006), Cervantes-González *et al.* (2017).

Research has shown potential additional uses of other waste biomass. As such, waste meat bones have been also used for the production of bone char adsorbents. It has been shown that bone chars are good for the removal of pharmaceutical compounds, Reynel-Avila *et al.* (2009) or heavy metals, Rojas-Mayorga *et al.* (2017), or endotoxins Rezaee *et al.* (2009) from wastewaters, or formaldehyde from air, Rezaee *et al.* (2013).

Waste biomass can be also used for the production of pharmaceuticals as is shown for example by Tian *et al.* (2014) and Rodriguez *et al.* (2018).

2.3 Conclusions

The scientific community is very active in the research on the valorization of residual biomass in many different forms. There is extensive work conducted on the characterization of potential second generation biomass which can be used as a source for different biofuels production. The objective is to develop new methods and technologies to exploit their potential in the best possible way. In this work, we focused mainly on amply available, sufficiently well characterized residual biomass, which has the highest potential for immediate exploitation or for biomass, the feasibility of the exploitation of which imposes the need for substantial technological improvements. Anaerobic fermentation of wastes for biogas production can be used as a simple form of mixed waste valorization for a wide extend of waste. However, after biogas generation, a substantial residual waste mass remains. The potential of more efficient and multipurpose methods of treatment are presently sought. In addition to the issues of availability of biomass and the management of its

collection and transportation to the treatment facilities-sites, the variability of the biomass quantity and quality can pose significant technological challenges. Methods which can be used for the pretreatment of different kinds of biomass have to be developed. Pretreatment can aim to the production of selected key intermediates which can be further treated for the production of biofuels. Such a break-down of biomass treatment may be the solution to the variability of feedstock quality. Different waste biomass sources can be used for the production of the same intermediates and the temporal variability of the major sources can be topped up by using smaller and varying alternative sources of a different origin.

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