## Biomass and biofuels

MARCO FIALA(\*) and LUCA NONINI(\*\*)

Department of Agricultural and Environmental Sciences - Production, Landscape, Agroenergy University of Milan - Via G. Celoria, 2, 20133 Milan, Italy

Summary. — Biomass includes all materials that contain organic carbon bound in the chemical structure of molecules, resulting from the chlorophylline photosynthesis, carried out by autotrophies organisms. Lots of biomass from agricultural, agri-food and forestry sectors can be used for energy purposes, representing an essential renewable energy source that, if appropriately managed, can help to reduce the negative environmental impacts arising from the exploitation of fossil fuels. The possibility of using biomass for a specific production process mainly depends on its physical and chemical properties. This paper is organized in two sections: in the first one, the most important biomass used worldwide for energy generation (thermal energy and/or electric energy), as well as its properties, are described. In the second one, the main biomass-to-energy processes (thermochemical and biochemical conversions) are shortly explained. Finally, some emerging techniques (such as bio-methane and bio-hydrogen production) are discussed in more detail.

<sup>(\*)</sup> E-mail: marco.fiala@unimi.it

<sup>(\*\*)</sup> E-mail: luca.nonini@unimi.it

### 1. - Biomass: Source of energy

1.1. Definition of biomass. - The term biomass includes all the materials that contain carbon (C) in an organic form. Plants in general, as autotrophies organisms(1), through chlorophylline photosynthesis are able to transform C from the inorganic form (carbon dioxide, CO<sub>2</sub>) into an organic form, by chemical bonds with other elements, such as hydrogen and oxygen, using solar energy. The solar energy is, thus, converted into chemical energy able to assemble organic molecules. The structure of these molecules can be very simple (as in the case of glucose and other monosaccharides) or more complex (as in the case of hemicellulose, cellulose and lignin). The demolition of these molecules through biological or physical processes causes —closing the cycle— CO<sub>2</sub> regeneration, which comes back to the atmosphere. The chemical energy is thus released and can be converted into other energy types. As a result, as long as in the human time scale equilibrium is maintained between the use (through energy conversion processes) and the production (through photosynthesis), biomass is —as renewable— an inexhaustible energy source. Therefore, its use does not affect natural resources for future generations. Biomass used for energy purpose is considered to be "neutral" both in terms of the increase of atmospheric CO<sub>2</sub> concentration(2) and of global warming (caused by the greenhouse effect enhancement). In fact, the mass of CO<sub>2</sub> released during the energy conversion processes (e.g., combustion) is the same which was previously absorbed by plants during the chlorophylline photosynthesis.

In general, biomass can be classified, taking into account the *source sectors*, as follows [1,2]:

- forestry (wood and derived products);
- agricultural, resulting from both crops (by-products and energy crops) and livestock waste (manure and slurry);
- industrial (agri-food and industrial residues or waste, in particular);
- *urban* (Organic Fraction of Municipal Solid Waste (OFMSW) and residues derived from trees and green public areas management);
- different (e.g., seaweed).

Biomass-to-energy transformations (or conversions) can be carried out in two different ways [1,3]:

- directly, in the case of solid (lignocellulosic) biomass;
- indirectly, through transformation into a liquid or gaseous carriers (biofuels).

 $<sup>(^{1})</sup>$  Autotrophies organisms are able to feed using only simple inorganic substances, as it happens for plants, which need only  $CO_{2}$  from the air, water and mineral substances that absorbed from the soil.

<sup>(2)</sup> Fossil fuels utilization —organic compounds stored for millions of years in the underground— is the main cause of the exponential increase of CO<sub>2</sub> concentration in the atmosphere, recorded from the early decades of 1800 (about 280 parts per million (ppm)) to nowadays (408 ppm in the 2016). These enormous quantities of emissions would not have been registered in the absence of human activities (extraction and utilization —combustion— processes).

- 1.2. Chemical and physical properties. In the natural state, the Fresh (wet) Mass (FM) of each biomass ( $m_{\rm FM}$ , kg) consists of a Water Mass ( $m_{\rm H_2O}$ , kg) and a Dry Mass ( $m_{\rm DM}$ , kg). Expressing these masses as percentages, the Moisture Content (MC, see below) and the Dry Matter content( $^3$ ) (DM; %FM) can be respectively defined [4]. The possibility of using biomass in an energy conversion process rather than in another depends on its chemical and physical properties, the most important of which are i) Moisture Content and ii) carbon/nitrogen ratio (C/N).
- 1.2.1. Moisture Content. In a generic biomass, water is contained in two forms: i) bound, to the molecular structure and ii) free, within cells and plant tissues. The mass of contained water depends on: i) climatic conditions, ii) harvesting period and iii) conservation processes. The drying process (both natural and artificial), aims to reduce free water, while the amount of binding water remains unaltered. The free water content (variable from 4–5% to 90–92%) is the parameter that, as well as affecting chemical and physical properties, and thus the energy content, mostly influences the type of supply chain where biomass can be used. The Moisture Content can be referred to both the  $m_{\rm DM}$  or to the  $m_{\rm FM}$  ( $m_{\rm H_2O} + m_{\rm DM}$ ). In the first case we talk about Moisture Content calculated on dry basis (MC<sub>DM</sub>; %DM), while in the second case we talk about Moisture Content calculated on wet basis (MC; %FM). As a result, the water content can be calculated as follows (eq. (1)):

(1) 
$$MC_{DM} = \frac{m_{H_2O}}{m_{DM}}$$
 and  $MC = \frac{m_{H_2O}}{m_{FM}} = \frac{m_{H_2O}}{m_{H_2O} + m_{DM}}$ .

- 1.2.2. C/N ratio. C/N is the ratio between C and N content of the dry mass. This ratio is dimensionless and i) in biomass that derives from plants and crops in general (e.g., crop residues) it indicates the lignification degree, while ii) in biomass that derives from animals (manure, slurry), it depends on i) animal species, ii) diet, iii) farm characteristics and iv) type of waste management.
- 1.2.3. Density and bulk density. Density  $(\rho; \text{kg/m}^3)$  is defined as the mass contained in the unit of volume  $(\text{m}^3)$ . It is important because it influences both physical-mechanical properties (size or resistance to stress) and chemical characteristics. The  $\rho$  of biomass depends on MC: the greater the MC, the higher the  $\rho$ , due to the increase of both the FM and (slightly) the volume. In addition to  $\rho$ , it is important to consider the Bulk (apparent) Density  $(\gamma, \text{kg/m}^3)$ , which indicates the mass contained in the unit of volume also considering the empty spaces [4]. This parameter strongly influences the technical and economic aspects concerning biomass storage, handling and transport (table I).
- 1.2.4. Heating value. Generally speaking, the *Heating Value* (HV, MJ/kg) represents the *energy released from the full combustion* of biomass and, thus, it is the fundamental

<sup>(3)</sup> Or Total Solids (TS, %FM).

Table I. – Biomass: preparation, bulk density and main dimensions.

Biomass	Preparation	Bulk density $(\gamma)$ kg/m <sup>3</sup> FM	Dimensions $V = \text{volume};$ $\phi = \text{diameter}$
Carrala atrona	Raw material	30-40	_
Cereals straw herbaceous stem	Small bales (prismatic)	80–120 (stacked)	$V = 0.1 - 0.2 \mathrm{m}^3$
	Cylindrical bales	120–180 (stacked)	$V = 1.5 - 3.0 \mathrm{m}^3$
and leaves energy	Big bales (prismatic)	120–180 (stacked)	$V = 2.0 - 4.0 \mathrm{m}^3$
crops	Chopped	150–250 (piled)	10–250 mm
Mais stem and	Raw material	50–60 (piled)	_
leaves	Cylindrical bales	100–150 (stacked)	$V = 1.5 - 3.0 \mathrm{m}^3$
	Raw material	50-70	_
Pruning residues	Small cylindrical bales	150–210 (stacked)	$V = 0.6 - 0.8 \mathrm{m}^3$
Fruning residues	Chinned	200–300 (piled)	1–100 mm;
	Chipped		$V \le 2.5 \cdot 10^{-3}  \mathrm{dm}^3$
	T	600-700 (stacked)	300-1000 mm;
Wood	Logs	300–400 (piled)	$V = 1.5 - 15  dm^3$
wood	Chipped	200–300 (piled)	1-100 mm;
	Cmpped	200–300 (piled)	$V \le 2.5 \cdot 10^{-3}  \mathrm{dm}^3$
Sawdust	Milling process	120–180 (piled)	1-5 mm
Maia aila ma	Cut	450–750 (pressed)	10. 25
Mais silage	Cut	350–400 (piled)	$10-25\mathrm{mm}$
Pellet	Extrusion process	800–900 (piled)	$\phi < 25\mathrm{mm}$
Deimother	Total and the second	100 240 (-:1-4)	$\phi > 25 \mathrm{mm};$
Briquettes	Extrusion process	190–340 (piled)	$V = 1-1.5  dm^3$
Olima sil masi dana	Compression.	400–500 (piled)	1 7
Onve on residues	live oil residues centrifugation process		1–5 mm
Grape residues	Compression process	250–500 (piled)	1–5 mm
Rice/cereals husk	Separation process	130–140 (piled)	1–5 mm
Animal slurry	Collected/moved by pumps	1000 (piled)	-
Animal manure	Collected/moved		-

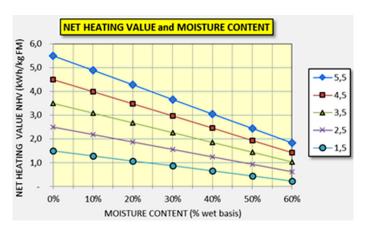


Fig. 1. - Variation of the lignocellulosic NHV vs. MC for different values of LHV (source: [4]).

energy parameter to characterize lignocellulosic biomass that can be used for *thermo-chemical conversions*. HV can be expressed as

- Gross Heating Value (GHV, MJ/kg DM), which represents the energy released from the complete combustion, at a constant pressure, of a unit of dry lignocellulosic biomass after cooling at 25 °C the combustion fumes and, therefore, taking into account the Thermal Energy (ET; MJ) released in the condensation of the water generated during the complete C oxidation(4). GHV can be calculated taking into account the amount of C, H, O, N, S, as well as ash, as follows [5] (eq. (2)):

(2) GHV = 
$$85.65 + 137.04 \cdot [C] + 217.55 \cdot [H] + 62.56 \cdot [N] + 107.73 \cdot [S] + 8.04 \cdot [O] - 12.94 \cdot [Ash]$$
 (MJ/kg DM)

- Lower Heating Value (LHV, MJ/kg DM) which is determined subtracting from GHV the heat of water condensation (in fact the vapor is usually released and lost via a chimney into the atmosphere);
- Net Heating Value (NHV, MJ/kg FM), which represents the ET really recoverable from the biomass, taking into account the heat for evaporating  $m_{\rm H_2O}$ . Practically, a fraction of the ET released during the full combustion process must be used to evaporate the biomass free water and, consequently, it is not available for final user (eq. (3)):

(3) 
$$\text{NHV} = \text{LHV} \cdot \left(1 - \frac{\text{MC}}{100}\right) - 2.261 \cdot \frac{\text{MC}}{100},$$

where 2.261 MJ/kg (equal to 540 kcal/kg) is the heat of water vaporization.

<sup>(4)</sup> The cumulative reaction of the complete combustion of an organic compound is  $C_xH_yO_z + O_2 \rightarrow CO_2 + H_2O + Energy$  (heat).

Thus, in the definition of the energy characteristics of a lignocellulosic fresh biomass, it is necessary to know the MC value, by which to calculate the NHV (fig. 1).

1'3. Plant derived biomass. – This biomass essentially consists of a mixture of three organic compounds with high molecular weight: i) cellulose (a linear polymer of anhydrous glucose), ii) hemicellulose (a relatively short and branched mixed polymer consisting of sugars with 5 and 6 C atoms) and iii) lignin (a complex of three-dimensional polymer mainly consisting of phenols, that ensure compactness and mechanical strength of the tissues).

In addition, there may be other compounds (such as resins, fats, oils, waxes, starches, sugars, proteins, tannic substances, pigments, alkaloids, etc.) and, in smaller quantity, inorganic elements (Na, K, Mg, Ca, Cd, Zn, As, Pb, S, Cl, N, P, Si, Al, etc.). Concerning the elemental composition, the main elements are: i) C, ii) H, iii) O, iv) N and, in smaller amount, v) alkaline and heavy metals. Compared to fossil fuels, the content of C, N and S of biomass is lower but the content of O, H and ash is higher.

1.3.1. Agricultural by-products. Agricultural by-products are available in the field: i) during the crop's biological cycle (e.g., pruning residues) and ii) at the harvesting operations of the main product (e.g., cereals straw, corn stumps, etc.). Although by-products have some critical aspects, such as i) strong seasonality, ii) harvesting period tightness, and iii) high dispersion on territory, the advantage is the great availability [6]. In temperate climates, by-products available at the end of the crop's biological cycle have a C/N > 50 (lignified) and MC < 30%; conversely, if their availability occurs at earlier stages of the biological cycle, C/N is much lower (< 30) and MC is higher (> 40-50%). The opportunity to recover an agricultural by-product for its valorization (raw material for industrial purposes, energy conversion, etc.) must always be carefully evaluated taking into account that nutrients and organic matter are removed from the soil and will not be available for the subsequent crops( $^5$ ). With the repetition of the same production cycle (monocropping), the by-products use should be generally avoided in all cases where their removal obliges the farmer to a subsequent soil resources reintegration (N-P-K fertilization and/or livestock waste —manure and/or slurry distribution).

1.3.1.1. Straw by-products. In this category all by-products derived from *herbaceous grain crops* are included: i) *cereal straw* (mainly from soft and hard wheat, barley), ii) *rice straw* and iii) *corn and sunflowers stalks*. This type of biomass is made up of *leaves* and *stems* that, when the main product is harvested, are left on the soil. The C/N ratio is fairly high and the MC is generally < 20%. Ash content is higher than

 $<sup>(^5)</sup>$  By-products derived from herbaceous crops that supply the products during the biological crop cycle (berries, roots, tubers), very rich in N-P-K, are usually left on the soil and buried with the subsequent tillage operations. On the other hand, by-products derived from herbaceous crops that supply the product (typically, seeds) at the end of the crop cycle, with high contents of hemicellulose/lignin and slowly decomposable from soil bacteria, are harvested and utilized (e.g., for energy purposes).

Table II. - Agricultural by-products (for straw): yield, composition, LHV and energy equivalent.

Straw biomass	Yield	Moisture Content (MC)	С	Н	0	N	S	Cl	Ash	Lower Heating Value (LHV)	Energy equivalent
	$t/ha\ DM$	%FM	$\%_{\mathrm{DM}}$	$\%_{\mathrm{DM}}$	$\%_{\mathrm{DM}}$	% <sub>DM</sub>	$\%_{\mathrm{DM}}$	$\%_{\mathrm{DM}}$	$\%_{\mathrm{DM}}$	MJ/kg DM	toe/ha
Wheat straw	2.5-7.0	12-15	43.2	5.0	39.4	0.6	0.11	0.28	11.4	16.3–16.7	0.98-2.76
Barley straw	2.0-4.5	12-15	39.9	5.3	43.8	1.3	_	_	9.8	16.0–16.4	0.78-1.75
Rice straw	3.5-6.0	20-30	41.8	4.6	36.6	0.7	0.08	0.34	15.9	15.1-15.5	1.3-2.2
Corn stalk	4.5 - 7.5	40-60	43.7	5.6	43.3	0.6	0.01	0.60	6.3	16.3-16.7	1.8-3.0
Corn cob	0.7-0.8	40-50	46.6	5.9	45.5	0.5	0.01	0.21	1.4	17.4-17.8	0.29-0.34
Sunflower stalk	3.0-5.0	15-20	45.0	5.1	38.0	1.1	0.11	0.16	10.5	16.1–16.5	1.2–1.9

 $\label{thm:composition} \begin{tabular}{l} Table III. - Agricultural by-products (for wood residues): yield, composition, LHV and energy equivalent. \end{tabular}$ 

Pruning residues	Yield	Moisture Content (MC)	С	Н	0	N	S	Cl	Ash	Lower Heating Value (LHV)	Energy equivalent
	t/ha DM	%FM	$\%_{\mathrm{DM}}$	MJ/kg DM	toe/ha						
Grapevine	1.5-2.0	45–55	46.8	5.8	43.5	0.8	0.03	0.09	2.9	17.6–18.0	0.64 - 0.85
Olive trees	1.0-1.5	35–45	50.0	6.0	41.0	0.5	0.04	0.01	2.5	18.4–18.8	0.44 - 0.67
Fruit trees	0.5-1.7	35–45	48.0	5.5	43.0	0.5	0.03	0.01	3.0	18.1–18.5	0.22 - 0.74

wood biomass; in some species (rice) the ash has a low *melting point* due to the high silica content. In the European Union (EU), the straw harvesting is generally carried out by round/square balers in: i) June-July for cereals, ii) late October for rice, and iii) September-October for maize (depending on the maturity FAO class(<sup>6</sup>)). Table II shows the main energy characteristics of this type of biomass.

 $<sup>(^6)</sup>$  The classification adopted by FAO (Food and Agriculture Organization of the United Nations) is based on the maturation days of the crop variety, assigning a number from 100 (the earliest) to 800 (the latest) and increasing the maturation days of about 5–10 in each class.

1.3.1.2. Wood by-products. This category includes pruning residues resulting from cutting operations of fruit tree crops [2]. The most important species are: i) grapevine, ii) olive trees with different breeding forms and iii) fruit trees. These residues are released on the soil during pruning operations. Their wood tissues have a medium-low C/N ratio and the MC is approximately 45–55%. Ash content, mainly due to the presence of bark, is not negligible. The recovery period is after pruning operations, that usually takes place during the vegetative period, when the main product has been already harvested<sup>(7)</sup>. Table III shows the main energy characteristics of wood by-products coming from pruning operations.

#### 1.3.2. Herbaceous energy-crops.

- 1.3.2.1. For grains. The use of cereal grains for energy production, although is not widespread in the EU, is based on the starch contained in the grain endosperm, as: i) fuel for heat generation (combustion process) and ii) raw material for bioethanol production (fermentation process). In Italy, corn ( $Zea\ mais$ ) is the most used crop for energy production [4] because, compared to winter cereals (wheat, barley), it has a higher LHV (15.1–16.2 MJ/kg DM) and a higher grain yield (7.5–10 t/ha DM). As a fuel, corn grain has "standard" characteristics (size,  $\gamma$ , MC, LHV) and it is easily available. This allows the easy organization of very short supply chains. Moreover, it enables the use of products previously contaminated by mycotoxins, whose use as food is prevented (or strongly restricted). The main limits, in addition to the ethical aspects associated with the use of food as an energy source, concern i) chlorine emissions and ii) ash production (1.2% DM) with a low melting point.
- 1.3.2.2. For lignocellulosic biomass. In southern Europe, growing attention is focused on some herbaceous crops with a long (poliannual) biological cycle and high biomass yields. These crops are: i) miscanthus (Miscanthus spp.), ii) giant cane (Arundo donax) and iii) sorghum (Sorghum vulgare). The yield of these crops (table IV) can respectively reach 29 t/ha·year DM, 27 t/ha·year DM and 14 t/ha·year DM. These biofuels generally have a high ash content with strong level of silica (low melting point) that reduces the efficiency of the conversion process and that can be a source of pollution.
- 1.3.2.3. For fermentable biomass. The use of biomass derived from crops dedicated to the Anaerobic Digestion (AD) process, such as organic matrices in addition (co-digestion) to livestock waste (slurry, manure), or even as the only component of the "ration" supplied to digesters, has progressively spread [7]. Also in this case, although the use of triticale, sorghum and ryegrass silage has recently been spreading, the reference species in the areas where the concentration of AD plants in co-digestion is greater (Po Valley area) is corn (harvested at waxy maturation). Table V shows the main characteristics of the most widespread crops cultivated in Italy for fermentable biomass production.

<sup>(7)</sup> Usually, the pruning residues remain between two rows of trees until the beginning of spring, partially drying.

 $\label{thm:composition} \begin{tabular}{l} Table IV.-Herbaceous\ energy\ crops\ (for\ lignocellulosic\ biomass):\ yield,\ composition,\ LHV\ and\ energy\ equivalent. \end{tabular}$ 

Lignocellulosic biomass		Moisture Content (MC)	С	Н	0	N	S	Cl	Ash	Lower Heating Value (LHV)	Energy equivalent
	t/ha DM	%FM	$\%_{\mathrm{DM}}$	MJ/kg DM	toe/ha						
Miscanthus spp.	15.5–29.0	15-20	41.3	7.4	48.3	0.1	0.10	0.00	2.8	17.4–17.8	6.5–12.2
Arundo donax	17.0-27.0	50-60	41.2	7.2	46.9	0.8	0.19	0.00	3.7	17.4–17.8	7.2–11.4
Sorghum vulgare	11.0-14.0	22-26	38.8	7.3	49.5	0.6	0.09	0.00	3.7	16.6-17.0	4.4–5.6

Table V. – Herbaceous energy crops (fermentable biomass): yield, composition, biogas yield,  $CH_4$  content and energy equivalent.

Fermentable biomass	Yield	Dry matter (TS)	Volatile Solids (VS)	N tot <sup>(#)</sup>	Biogas yield	CH <sub>4</sub> content	Energy equivalent
	t/ha DM	%FM	%TS	kg/t DM	$m_N^3/t$ VS	% vol. <sup>(*)</sup>	toe/ha
Maize silage (FAO 700)	13.0-23.0	30-35	85-90	1.1-2.0	500-600	52-57	2.6-4.6
Sorgum silage	13.0-16.0	28-35	89–93	1.4-1.9	550-650	50-55	2.8-3.5
Sugar beet	1.2-1.7	21-25	90-95	2.4-2.8	450-550	55-60	0.24-0.34

<sup>(#)</sup> Organic and inorganic.

1.3.2.4. For oil. The oil-energy supply chain is widespread all over the world and lots of autochthonous species are currently cultivated for this purpose: in tropical areas (Southeast Asia, India, China and Africa) the most important cultivated crops are: i) oil palm (Elaies guineensis), ii) jatropa (Jatropha curcas) and iii) pongamia (Pongamia pinnata) while in temperate areas (Central-South Europe, North America) the most important cultivated crops are: i) rapeseed (Brassica napus), ii) sunflower (Heliantus annuus), iii) castor (Ricinus communis) or iv) protein-oleaginous crops, such as soybean (Glicine max). Table VI shows the main energy characteristics of herbaceous oilseeds crops compared to those of other oilseeds species.

1'3.3. Tree species energy crops. Among the sources of cultivated wood biomass, *Short Rotation Coppice* (SRC) species have represented the ones that have attracted most interest in the last decade [8]. This form of wood arboriculture is interesting because

<sup>(\*)</sup> LHV of CH<sub>4</sub>:  $31.6 \,\mathrm{MJ/m_N^3}$ .

Oil crops	Seeds yield	Oil content	SVO lower Heating Value (LHV)	Energy equivalent
	t/ha FM	%FM	$\mathrm{MJ/kg}\ \mathrm{DM}$	toe/ha
Helianthus annuus (sunflower)	4.0-4.5	39-40	37.1–37.5	1.3-1.4
Brassica napus (rapeseed)	4.0-4.5	40-42	36.9–37.3	1.3–1.5
Glycine max (soybean)	4.0-5.0	17–19	36.6-37.0	0.57 – 0.71
Elaeis guineensis (palm oil)	10.0-11.0	34-38	36.4–36.8	2.8-3.1
Jatropha spp. (jatropa)	0.2-4.0	27-29	36.5–36.9	0.04-0.88
Seaweed	50.0-100.0	65–75	44.5–44.9	3.7-7.5

Table VI. - Herbaceous energy crops (oil): seed yield, oil content, LHV and energy equivalent.

of the possibility to simplify the cultivation technique (mechanization of the harvesting-transport operations). This has progressively led to the cultivation of some tree species in short cutting turn, similarly to herbaceous crops [6]. In Italy, especially in the Po Valley, the most successful cultivated species is *poplar* (*Populus spp.*(8)) [9]. The aspect that characterizes plant of poplar is the cutting turn, which defines both the number of trees per unit of areas (ha) and the type of mechanization for harvesting and transport. Currently, there are poplars with the following cutting cycles:

- two-year cycle (Short Rotation Forestry, SRF). The wood chips (30–40 t/ha·year FM; MC = 50–55%; LHV = 17.3–18.7 MJ/kg DM) have a wood/bark ratio higher than the annual cutting cycle crops;
- five-year cycle (Medium Rotation Forestry, MRF). The wood chips characteristics are similar to those of the two-year cutting cycle (25–40 t/ha·year FM; MC = 50–55%; LHV = 18.0–19.4 MJ/kg DM) but, because in this case the ratio between wood and bark is higher (because of the lower ash content), the biofuel has a higher quality ("white chip").

The soil is occupied for 10–15 years, after which the crop has to be explanted (elimination of the radical apparatus), restoring the conditions suitable for the cultivation of another crop [6].

1.3.4. Forestry wood and wood derived products. Wood-based biomass comes from: i) primary sources (forestry wood, directly linked to the photosynthetic activity of wood trees) and ii) secondary sources (wood derived products, related to industrial processes and maintenance activities, such as fruit arboriculture, public greenery, etc.) [10, 11]. Wood tissues almost entirely consist of: i) C (49–51%), ii) O (41–45%) and iii) H (5–

<sup>(8)</sup> Abbreviation of the plural of the term "species".

7%), with small quantities of iv) N (0.05–0.4%), v) S (0.01–0.05%) and vi) other mineral elements that form the ash (0.5–1.5%). Wood biomass can be used as: i) natural material and ii) treated material, after size and shape transformations. The types currently available on the market are: i)  $logs(^9)$  (pieces of wood, 0.3–1 m length), ii) wood  $chips(^{10})$ , iii)  $pellets(^{11})$  and iv)  $briquettes(^{12})$ .

1.3.4.1. Forestry wood. The main forest management tools that define the use of forest biomass for energy purposes( $^{13}$ ) are the Forest Management Plans (FMPs). FMPs establish the organization and the sequence of the operations for wood biomass production, yarding and transport outside the forest for different final uses (energy and/or building material). Many commercial wood assortments are available, bringing the production of waste (cuttings residues) which can reach 20–25% of the total tree mass [8]. The cutting residues are generally abandoned into the forest (or close to the working areas), causing some management problems (mainly fires and parasitic attacks). If economically sustainable( $^{14}$ ), they can be recovered and transformed into wood chips (MC = 50–55% and  $\gamma = 250$ –350 kg/m³ FM, depending on the species and the chipping techniques) [9]. Table VII shows the most important energy characteristics of forestry wood.

Normally, the firewood is reduced in pieces (diameter: 50–300 mm; length: 1 m approximately), to facilitate the operations of stacking, measurements and estimation, handling and loading/unloading from the trucks [10]. Moreover, wood in pieces is usually seasoned (about 1 year) to reduce the MC from 55–60% to 25%(<sup>15</sup>). Chipping, applied to branches and cutting residues, greatly reduces the volume (3–4 times) and, although this is an advantage for handling-transport-storage operations, the bulk density of wood chips is always lower (2–3 times, on average) than the bulk density of round wood (at the same MC). As a result, where the operating conditions are favorable and the transport distances are rather high, it is more convenient to carry out forestry yards able both to cut the small material and to arrange the medium-large diameter biomass in round wood logs (fig. 2). The chips size depends on the type of chipper. Generally, the length is

<sup>(9)</sup> UNI EN ISO 17225-5:2014-Part 5: Graded firewood.

<sup>(10)</sup> UNI EN ISO 17225-4:2014-Part 4: Graded wood chips.

<sup>(11)</sup> UNI EN ISO 17225-2:2014-Part 2: Graded wood pellets.

<sup>(12)</sup> UNI EN ISO 17225-3:2014-Part 3: Graded wood briquettes.

<sup>(13)</sup> The dominant forest government in hilly and medium mountainous areas is *coppice* for the production of firewood (trunks or logs).

<sup>(&</sup>lt;sup>14</sup>) Because for coppice the production process can be very costly (especially in the case of energy supply chain), it is important to chip all the available wood. For tall trees, which always give assortments with high commercial value, preliminary operations on young plants (whose purpose is to increase the stability of the forest to maximize the final yield) are carried out. These operations cause the production of large quantities of branches, other residues or small trees with a very low commercial value. Even in this case, the integral chipping is the only sustainable solution to obtain a lignocellulosic biofuel.

<sup>(15)</sup> In the case of longer periods of seasoning (2 years), in our climates, MC can be reduced down to 12–15% (atmospheric dry at hygroscopic equilibrium with the air).

Table VII. - Forest wood: yield, composition, LHV and energy equivalent.

Tree species cutting period (years)	Yield	Moisture Content (MC)	С	Н	О	N	S	Cl	Ash	Lower Heating Value (LHV)	Energy equivalent
	t/ha DM	%FM	$\%_{\mathrm{DM}}$	MJ/kg DM	toe/ha						
Abies alba (90–110)	190–270	40-50	49.0	6.0	44.3	0.5	0.01	0.01	0.3	18.5–18.9	85.0–120.9
Picea abies (110–140)	160-240	40-50	50.5	6.3	41.9	0.6	0.01	0.03	0.7	18.3–18.7	70.5–105.8
Pinus sylvestris (60–80)	120–145	40-50	49.6	6.5	42.0	0.8	0.01	0.01	1.1	21.7-22.1	62.6-75.7
Populs spp. (9–12)	130–170	45-55	48.5	5.9	43.7	0.5	0.01	0.01	1.4	18.0–18.4	56.5-73.9
Fagus spp. (80–100)	190–220	40–50	48.3	6.0	44.3	0.6	0.01	-	0.8	18.4–18.8	84.5–97.9
Quercus spp. (70–100)	180-220	45–55	49.5	5.4	43.1	0.4	0.01	0.04	1.6	18.1–18.5	78.8–96.3
Carpinus spp. (30–40)	55-105	45–55	47.1	6.1	44.1	0.9	0.01	0.04	1.8	17.3–17.7	23.0-43.9
Robinia pseudoacacia (30–75)	30–75	45–55	49.1	5.7	42.0	0.6	0.01	0.04	2.5	18.3–18.7	13.3–33.1
Eucalyptus spp. (60–70)	130–190	40–50	49.0	5.9	44.0	0.3	0.01	0.13	0.7	18.0–18.4	56.6–82.7



Fig. 2. – Stacked round wood logs (left) and wood chips (right) (source: pixabay.com).

between 15 and  $50 \,\mathrm{mm}$ , the width is about 50% of the length and the thickness is about 10-20% of the length [9].

1.3.4.2. Wood derived products. Pelletized lignocellulosic biofuels (pellets) derive from an animal feed industrial process of extrusion of fine-size materials, at high pressure (> 100 bar) through horizontal or annular grooves with special section holes. According to a current definition( $^{16}$ ), the pellet is a "compressed biofuel that generally has a cylindrical form, obtained compressing finely chopped biomass with or without the use of pressing additives". Because the composition of the raw materials can be very different( $^{17}$ ), the energy characteristics of the final extruded biofuels can also be variable. Pellet consists of small cylinders (diameter = 6–10 mm, length = 10–50 mm), with a high "energy density" ( $\rho_{\rm MC}$  = 1150–1400 kg/m³,  $\gamma$  = 650–700 kg/m³, MC = 6–12%). The ash content is very low (0.3–1.0%).

Another densified fuel consists in *briquettes*, also obtained —in different shapes (cylindrical, prismatic)— by the compression of a previously dried and powdered biomass (MC = 10-15%). Briquettes production takes place by mean of alternative (piston) presses and the most commonly used row materials are: i) *sawdust*, ii) *straw*, iii) *rice husk*, iv) *nuts shells*, v) *coffee shells*, vi) *bark-free chips*, with or without additives.

1.3.4.3. Wood residues. Wood residues (especially if they have an *industrial origin*) and, more generally, the so-called *end-life wood*, are very heterogeneous and include packaging and containers, building materials, pallets, beams and boards for demolition and refurbishment, sawdust waste, wood and furniture industry residues, etc. Due to the long life cycle, the end-life wood residues are perfectly seasoned (MC < 20%) and, consequently, their quality as a biofuel is excellent.

1'4. Livestock waste. – Livestock waste includes i) excreta (feces and urine) and ii) animal waste (mixture of excreta, litter, water, feed residues and other animal residues). The composition of livestock waste depends on: i) animal species, ii) breeding methods, iii) feed characteristics and iv) waste management system (table VIII). In general, livestock waste can be managed as: i) slurry (mainly made by excreta, food residues and water) with fluid or semi-fluid consistency (DM < 15%) and moved by pumps, ii) manure (mainly made by excreta, food residues, water and litter) with semi-solid or solid consistency (DM  $\geq 20\%$ ), moved by shovels. The energy potential of livestock waste depends on its composition, Volatile Solids content (VS; %DM) in particular. The waste can be used in biochemical processes to produce gaseous biofuels, such as biogas, biomethane (bio-CH<sub>4</sub>) and bio-hydrogen (bio-H<sub>2</sub>) with high calorific values. Slurry has the most suitable chemical composition for the AD (table IX), for which the key factors are: i) composition of the biomass, correlated to the degradation rate, ii) degradability, which has decreasing values for protein, fat, cellulose and lignin(18) respectively, iii) toxicity

<sup>(16)</sup> PROBIO Project, 2004.

<sup>(17)</sup> D.L. n.152 of April 3rd, 2006.

<sup>(18)</sup> Manure is degraded more slowly than slurry because of its higher cellulose content.

Table VIII. – Breeding species and excreta daily production.

Animal category	Weight	Excreta production
Allillai Category	kg	kg/day
Calf (0–3 months)	70	4-5
Calf (3–6 months)	140	8–9
Young beefs (6–12 months)	230	20-22
Young cow (12–24 months)	390	32–36
Beefs (12 months)	400	20-25
Milk cow (12–72 months)	650	50-55
Young swine	6-30	2-3
Growing pigs	30-80	$4.0^{(\#)}; 7.0^{(\S)}; 14.0^{(*)}$
Fat pigs	80–160	10-13
Sows	_	8–9
Hens (10–12 months cycle on land)	1.8-2.0	$0.15\mathrm{m}^3/\mathrm{year}\cdot\mathrm{t}$
Broilers (2 months cycle on land)	1.0-1.2	$2.0\mathrm{m}^3/\mathrm{year}\cdot\mathrm{t}$
Turkey (4–5 months cycle on land)	7.0-7.5	$0.9\mathrm{m}^3/\mathrm{year}\cdot\mathrm{t}$

<sup>(#)</sup> Dry feed 2.5:1.

Table IX. – Animal waste (slurry and manure): composition, biogas yield,  $CH_4$  content and energy equivalent.

	Dry matter	Volatile	N tot <sup>(#)</sup>	Biogas	$\mathrm{CH}_4$	Energy
Biomass	(TS)	Solids (VS)	IN tot,	yield	content	equivalent
	%FM	%TS	kg/t TS	$m_N^3/t$ VS	% vol.(*)	toe/t FM
	SLU	RRIES				
Milk cows	10-16	75–85	3.0-4.8	300-450	55-60	0.013-0.021
Beefs	7–10	75-85	3.8-5.3	300-450	55-60	0.009-0.013
Calves	0.6-2.9	60-75	7.4–17.7	300-450	55-60	0.001-0.003
Pigs	1.5-6.0	65-80	4.0-13.3	450-550	60-65	0.003-0.010
Hens	19–25	70-75	7.0-14.5	300-500	50-55	0.022-0.029
		MAN	URES			
Bovine	11-25	65-85	1.2-2.8	200-300	55-60	0.009-0.020
Pig	20-28	75-90	1.8-2.0	450-550	60-65	0.039-0.055
Ovine	22-40	70-75	1.9-3.5	240-500	60-65	0.028-0.051
Broiler	60-80	75–85	4.3-6.7	400-500	50-55	0.086-0.114
Chicken (dryed)	40-80	60-70	3.4-6.4	450-550	50-55	0.052-0.103

<sup>(#)</sup> Organic and inorganic.

<sup>(§)</sup> Wet feed 4.0:1.

<sup>(\*)</sup> Whey feed.

<sup>(\*)</sup> LHV of  $CH_4$ : 31.6  $MJ/m_N^3$ .

 $\label{eq:table_equivalent} \begin{tabular}{ll} Table $X.-Agro-industrial residues (lignocellulosic biomass): composition, $LHV$ and energy equivalent. \end{tabular}$ 

Biomass	Moisture Content (MC)	С	Н	0	N	S	Cl	Ash	Lower Heating Value (LHV)	Energy equivalent
	%FM	$\%_{\mathrm{DM}}$	MJ/kg DM	toe/t DM						
Rice husk	10-15	41.0	4.3	35.9	0.4	0.02	0.12	18.3	15.1–15.5	0.361-0.370
Almond shells	10-20	44.3	6.0	43.0	1.2	0.02	_	5.6	18.0-18.4	0.430-0.439
Walnut shells	10-20	50.0	5.7	43.4	0.2	0.01	0.03	0.7	18.8-19.2	0.449-0.459
Peach stones	15-20	53.0	5.9	39.1	0.3	0.05	_	1.6	19.4–19.8	0.463-0.473
Plum stones	15-20	49.7	5.9	43.6	0.3	-	_	0.5	21.9-22.3	0.523-0.533
Olive stones	15-20	48.8	6.2	43.5	0.4	0.02	_	1.1	20.1-20.5	0.480-0.490
Olive oil virgin residues <sup>(#)</sup>	20-30	_	_	_	_	_	_	-	15.3–15.7	0.365-0.375
Olive oil virgin residues <sup>(§)</sup>	58-72	_	_	_	_	_	_	_	15.3–15.7	0.365-0.375
Olive oil virgin residues <sup>(*)</sup>	48-52	_	_	_	_	_	_	_	15.3–15.7	0.365-0.375
Olive oil exhaust residues <sup>(o)</sup>	10-15	43.7	5.3	37.8	_	0.64	_	12.5	14.3–14.7	0.342-0.351
Grape residues (marc)	55-65	_	_	_	_	_	_	_	6.8-7.2	0.162-0.172

<sup>(#)</sup> Discontinuous oil extraction process.

of some elements if they are present in high quantities (especially Na, K, Ca, Mg) and iv) presence of heavy metals (Cu, Cr, Ni, Zn, Pb) which can cause damage to bacterial metabolism. *Pig slurries*, due to the different types of animal breeding and of excreta removal system, have a rather variable DM. The use of "fresh" slurry, avoiding any intermediate storage (tanks or lagoons) promotes the reduction of CH<sub>4</sub> emissions and odors [4].

1.5. Industrial waste. – Large quantities of residues (or waste) obtained from food processing can be conveniently transformed into energy. This residual biomass is extremely heterogeneous (table X) but, compared to agricultural by-products, is much less spread on territory.

<sup>(§)</sup> Continuous oil extraction process.

<sup>(\*) 3-</sup>phase oil extraction system.

<sup>(</sup>o) Oil extraction by solvent.

1.5.1. Olive oil extraction residues, rice husk and grape skin residues. Virgin olive oil extraction residue (pomace) is the biomass remaining after the extraction by mechanical systems, while the exhaust olive oil extraction residue derives from the previous one after extraction by solvents (mainly hexane). MC and composition of the virgin residues depend on the extraction process(19), which may (or not) include the addition of water to the olives. Before combustion, the residues from continuous systems must be dried; the drying process is expensive but leads to a significant increase in NHV. The process for production of the exhaust residues starts from the virgin residues drying phase (up to MC = 8-12%), followed from the extraction by hexane. The obtained biomass (equal to 50–55% of the virgin residue mass) is granular, with excellent energy characteristics (fuel for domestic or industrial combustion plants). Rice husk is the residue of rice processing and it includes the external grain coatings (glumes). It represents about 20% of the whole rice grain weight. Rice husk chemical composition and quantities depend on: i) rice variety, ii) maturation degree, iii) harvesting techniques, iv) drying process. Rice husk utilization as a biofuel has some problems because of: i) high hardness, ii) strong abrasiveness, iii) high silica content, iv) low  $\gamma (= 130-140 \,\mathrm{kg/m^3})$  and v) high ash content (15-20%). The most important residues from oenological industry are the grape skin residues. They are produced by crushing and pressing the grapes together with the solid parts of the grape bunch, in quantities ranging from 15 to 30% of the grape. Depending on the degree of pressing, the grape skin residues contain 2-5% of alcohol and 2-6% of tartaric acid salts. The high MC makes them suitable for biochemical conversions, but a preventive drying process promotes their use also as biofuel.

1.5.2. Wet processing waste and urban waste. Wet processing waste, conveniently used in AD plants, mainly refers to agri-food industry residues (skins and waste from the processing of fruit, whey, threshing operations, vegetation waters, etc.) [8]. Because of a VS content higher than animal waste (table XI), these organic materials increase the biogas yield. In Germany and Italy there are hundreds of AD plants fed with wet processing waste, mixed with other biomass and/or animal waste (co-digestion). In wet processing waste animal residues (blood, fat, whey, gut, stomach contents, etc.), mainly from meat industry, are also included. These residues have a high VS and fats content (which increase the methanigenic power). However, their utilization as biomassfor-energy processes must comply with strict hygienic standards, especially in relation to the high odorous power. Therefore, these residues must be carefully treated in AD plants, adequately conceived (pre-treatment section). Lastly, there are two other types of fermentable biomass, remarkable for quantity and, above all, because of their capillary collection network already present in the territory: i) OFMSW and ii) sewage sludge. The OFMSW (table XII) is mainly composed of food residues (kitchen waste) that have: i) high MC (70–85%) and ii) high  $\gamma$  (500–700 kg/m<sup>3</sup>). In Italy, despite the

 $<sup>(^{19})</sup>$  In Italy, 46% of the olive oil production is carried out by discontinuous methods (hydraulic press), 45% by continuous or 3-step methods (centrifugal separation), with water addition. The remaining 9% is carried out with mixed methods.

Table XI. – Agro-industrial residues (fermentable biomass): composition, biogas yield,  ${\rm CH_4}$  content and energy equivalent.

	Dry matter	Volatile	N tot <sup>(#)</sup>	Biogas	CH <sub>4</sub>	Energy
Fermentable biomass	(TS)	Solids (VS)	N tot."	yield	content	equivalent
	%FM	%TS	kg/t TS	$m_N^3/t$ VS	% vol.(*)	toe/t FM
Fruit juices residues	25-45	90-95	1.1-1.2	500-600	55-60	0.055 - 0.100
Fruits and vegetable fresh residues	5-20	80-90	3.0-5.0	350-500	50-60	0.008-0.030
Molasses	80-90	85–90	1.3-1.7	300-450	50-55	0.104-0.117
Potatoes residues	6-7	85–95	5.0-13.0	500-600	50-53	0.011-0.013
Tomatoes peels	27-35	96–97	3.1-3.2	300-400	30-55	0.029-0.038
Cereals distillation residues	6-8	83-88	6.0-10.0	400-500	50-55	0.009-0.012
Beer residues	20-25	70-80	4.0-5.0	300-400	50-55	0.021-0.026
Whey	4-7	80-92	0.7-1.0	330-400	50-55	0.005-0.009
Olive oil residues (liquid)	3.5–4	70-75	4.0-5.0	450-550	50-55	0.005-0.006
Grape residues (liquid)	10–14	85–95	nd	650-750	50-54	0.025-0.035

<sup>(#)</sup> Organic and inorganic.

Table XII. – Waste materials (wet biomass): composition, biogas yield,  $CH_4$  content and energy equivalent.

Biomass	Dry matter (TS) %FM	Volatile Solids (VS) %TS	N tot <sup>(#)</sup>	Biogas yield m <sub>N</sub> <sup>3</sup> /t VS	CH <sub>4</sub> content % vol. (*)	Energy equivalent toe/t FM
Food residues (catering industry)	9-37	80–95	0.6-5.0	650-800	50-60	0.024-0.098
Pigs stomach content (slaughterhouses)	12–15	75–86	2.5-2.7	650-800	60-65	0.033-0.041
Bovine rumen content (slaughterhouses)	18-20	90-94	2.0-3.0	650-800	60–65	0.057-0.063
Blood (slaughterhouses)	6-20	93–95	14.7–17.0	600-850	60-65	0.019-0.064
Incubating process waste	44-48	41–45	5.0-5.5	600-800	60-65	0.063-0.068
Broken eggs	21-25	95–97	7.8–8.5	600-850	60-65	0.069-0.082
Bread processing waste	88-92	90-94	nd	740-840	50-60	0.266-0.278
Bread (out-of-date)	78-82	96–98	nd	710-810	53-57	0.239-0.282
Biscuits (out-of-date)	90-94	98-99	nd	750-850	50-54	0.279-0.291
Flours (out-of-date)	86-90	96–98	nd	705-805	51-55	0.253-0.264
Cellulose pulp	12-14	89–91	5-13	450-550	50-55	0.021-0.025
OFMSW	40-75	50-70	0.5 - 2.7	300-450	50-60	0.037-0.070

<sup>(#)</sup> Organic and inorganic.

<sup>(\*)</sup> LHV of CH<sub>4</sub>:  $31.6 \,\mathrm{MJ/m_N^3}$ .

<sup>(\*)</sup> LHV of  $CH_4$ : 31.6  $MJ/m_N^3$ .

strong variability among different urban areas, OFMSW represents, on average, 25–35% of the total mass of municipal solid waste(<sup>20</sup>). The average composition, if the waste derives from dry-wet differentiated domestic collection, does not differ greatly from the collectable organic residues from selected users (such as fruit and vegetables wholesalers, fish markets, grocery stores, and refreshments). The presence of other foreign materials (plastic, glass) must be less than 5% of the total mass.

#### 2. – Biomass-to-energy processes

**2**<sup> $\cdot$ </sup>1. Generality. – In the thermochemical conversions, where chemical bonds are broken through heat, lignocellulosic biomass with the following properties can be used [1,3]:

- low MC (15–40%);
- high C/N (> 30).

In the *combustion* process, lignocellulosic biomass is transformed directly into energy, while in others (*gasification*, *pyrolysis*) biomass-to-energy conversions occur through the intermediate generation of liquid or gaseous compounds [11]. These "energy carriers" are generally used as fuels for *Internal Combustion* (*IC*) *engines* (mainly reciprocating but also rotary), generating Mechanical Energy (EM) and, then, Electric Energy (EE) [4].

On the contrary, for *biochemical conversions* (where chemical bonds breaking occurs through the action of bacteria) biomass with the following properties can be used [1,3,7]:

- high MC (70-90%);
- low C/N (< 30).

Even in this case, biomass-to-energy conversions (usually through fermentation) occur through the production of liquid or gaseous intermediates, subsequently used as fuels for IC engines.

Lastly, there are other processes (mechanical or chemical extraction) through which vegetable fats (oils), finally used as pure (pure vegetable oil) or after a chemical modification into methyl-esters, are removed from biomass (seeds, but also algae in the near future) and used as biofuels for vehicles. Figure 3 shows the general scheme of the biomass-to-energy conversion processes.

- **2**. Thermochemical processes. Depending on the amount of air used to support the C oxidation, these processes are classified as follows [6, 11, 12]:
  - combustion, performed with a mass of air greater than the stoichiometric mass required for complete oxidation;

 $<sup>(^{20})</sup>$  According to ISPRA (*Urban Waste Report 2009*), the Italian production of urban solid waste in 2008 was about 32.5 Mt (541 kg/inhabitant per year, with 541, 619 and 496 kg/inhabitant per year, respectively, in North, Center and South-Islands Italian Regions). The landfill is still the most widespread processing mode, but the mass of collected urban solid waste in differentiated way is increasing, representing about 30.6% of total urban solid waste.

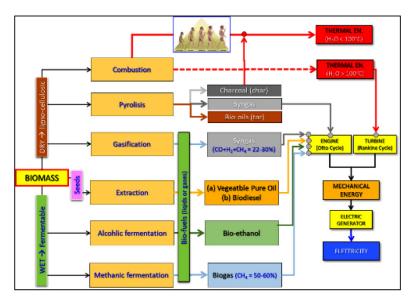


Fig. 3. – Biomass-to-energy conversion processes: general scheme (source: [4]).

- gasification performed with less air than the stoichiometric need;
- pyrolysis, performed without air.
- **2**<sup>•2</sup>.1. Combustion. Combustion is a long sequence of chemical reactions according to which an organic substance (C) combines with an *oxidizing agent* (O<sub>2</sub> of the air), carrying out an exothermic redox reaction and producing heat (ET), CO<sub>2</sub> and H<sub>2</sub>O. The process presupposes the simultaneous presence (fire triangle), in correct proportions, of fuel, oxidizing agent, as well as starting heat( $^{21}$ ). In the case of *lignocellulosic biomass* (that has a complex chemical structure if compared to some fossil gaseous hydrocarbons, such as CH<sub>4</sub>) the process consists of the following *three phases* that, in a combustion biomass bed, *take place at the same time*:
  - drying: the lignocellulosic mass receives heat from the surrounding environment and progressively increases its temperature, evaporating the contained free water (until 105 °C is reached). The dry biomass continues to heat, reaching very quickly the gasification-pyrolysis threshold (about 600 °C). Because the evaporation absorbs a fraction of the energy that is released by the process, to limit the process slowdown, biomass should not have MC > 60-65%;

<sup>(&</sup>lt;sup>21</sup>) In the absence of even one of these factors, the process does not take place and, if the fuel/oxidizing agent ratio is incorrect, incomplete combustion can occur, causing the formation of still oxidizing carbonaceous compounds.

- gasification-pyrolisis: the heat propagates from the external to the internal layers of the biofuel particle, causing —starting from a biomass temperature of 200 °C and in the absence of oxygen— the formation of (22): i) a volatile fraction (gases and tar) that rapidly leaves the ii) remaining solid fraction (char) that consists of fixed C and ash;
- oxidation: the gasification-pyrolisis products, coming in contact with the oxygen of the air, cause the combustion. A highly exothermic reaction occurs both above the char bed for volatile fraction —very intensively (flame formation) with emission of light radiation in the visible spectrum— and also inside the char bed for the fixed C —but much more slowly (ember without flame) and with light emission mainly in the infrared spectrum.

To fully oxidize the char, primary air is blown into the lignocellulosic biofuel bed, while secondary air is blown over the bed, to oxidize gaseous and tar compounds. If an incomplete combustion takes place, a reduction of the energy conversion efficiency can occur, with a significant increase of the emission of organic carbonaceous compounds to the chimney. The "quality" of the combustion is, therefore, strongly linked to three key-factors connected with the conversion device: i) gases residence time, ii) combustion room temperature and iii) turbulence. The excess air ratio ( $\lambda$ ) is the ratio between the real air mass used in the combustion process and the stoichiometric air mass. For wood logs, this technical parameter ranges from 1.25 to 1.40. Generally, O<sub>2</sub> into dry fumes should represent 5–8% (in volume), while —at these levels of O<sub>2</sub>— the CO<sub>2</sub> concentration should reach 13–16%. The combustion chamber temperature should be in the range of 850–1200 °C(<sup>23</sup>). Fumes temperatures should remain below 150–170 °C. Moreover, the greater the uniformity of the biomass and the DM, the better the combustion results [12]. Figure 4 shows a schematic representation of the combustion process.

The type of the devices used for biomass combustion processes (boilers or thermal generators) differ in terms of i) fuel and its characteristics (size, shape and granulometric distribution), ii) thermal power (domestic or industrial purposes) and final energy use (Thermal Energy, Electric Energy), iii) complexities and technological solutions adopted (manual or automatic feeding and ash removing systems). The main characteristics of the lignocellulosic combustion devices are shown in table XIII.

**2**<sup>•</sup>2.2. Gasification. Gasification means incomplete oxidation of a substance in a high-temperature environment (900–1000 °C) to produce a gas (*producer gas*). As oxidant agent: i) air, ii) steam or iii) pure oxygen can be used. In the most common air gasifiers, the producer gas has a LHV =  $3.9-4.3 \,\mathrm{MJ/m_N^3}$ , while, in the less widely used oxygen

 $<sup>\</sup>binom{22}{1}$  The first component that is degraded by heat is hemicellulose, followed by cellulose, and finally, by lignin.

 $<sup>(^{23})</sup>$  The technical parameter is linked to the NO<sub>x</sub> production.

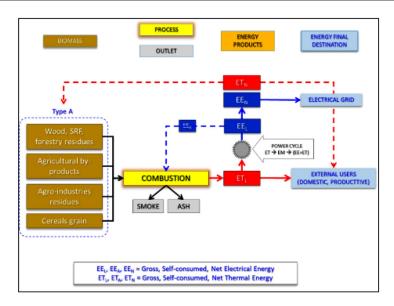


Fig. 4. – Combustion process scheme. The  $ET_L$  can be sold to neighboring external utilities through a distribution network (district heating). The EE generation (EE<sub>L</sub>) is carried out only in high power plants (dedicated or cogenerated power cycle units) with the sale of residual heat to external utilities. A small fraction of the gross production is used for self-consumption (EE<sub>A</sub>) while the rest (EE<sub>N</sub>) is sold to the grid at feed-in tariff (source: [4]).

gasifier ( $^{24}$ ), the gas has a LHV = 13.0– $14.0\,\mathrm{MJ/m_N^3}$ . The gas cleaning phase, that follows the gasification phase, is always particularly complex. For the gasification process, the biomass physical-chemical characteristics must be as constant as possible, especially in terms of MC and size (often related to an increase of management costs due to biomass preparation). The producer gas can be used to feed: i) gas-burners for heat production or, more conveniently and diffusely, ii) IC engines to generate EM and, thus, EE that is sold to the grid at feed-in tariff (biomass-to-electricity efficiency: 18–21%). This last solution can be also carried out by co-generated IC engines (CHP, Combined Heat and Power unit) for the simultaneous generation of electricity and heat, to use within the same process (e.g., for biomass drying) and/or for external final users (fig. 5).

As an alternative to energy generation, the gasification products can be used (only for medium-high power plants) as raw materials for *liquid biofuels synthesis*. For this purpose, the producer gas is transformed into a *syngas* and then into liquid biofuels (Biomass-To-Liquid, BTL)( $^{25}$ ). Depending on the applications, the requested character-

<sup>(&</sup>lt;sup>24</sup>) For gaseous fuels, the LHV refers to the volume unit under *normal* conditions (MJ/m<sub>N</sub><sup>3</sup>): anhydrous gas at  $T=0\,^{\circ}$ C and atmospheric pressure  $p=760\,\mathrm{mm_{Hg}}$  (1.013 bar). Commercially, however, reference is often made to 1 m<sup>3</sup> standard (m<sub>S</sub><sup>3</sup> at  $T=15\,^{\circ}$ C and  $p=760\,\mathrm{mm_{Hg}}$ ). (<sup>25</sup>) Fischer-Tropsch synthesis.

Table XIII. - Main characteristics of the devices for lignocellulosic biomass combustion.

Type of device	Biomass load	Power (kW)	Type of energy and destination	Biomass used	Energy efficiency (%)
Boiler with grate	Manual <sup>(#)</sup>	15-35	ET, Domestic	Wood logs	65-75
	Manual <sup>(*)</sup>	15–35	ET, Domestic	Wood logs	85-90
	Mechanical	15–35	ET, Domestic		
		> 100	ET+EE,	Pellet	80-85
			Products processing		
	Mechanical	15–35	ET, Domestic	Corn grain	70-75
	Mechanical	15–35		Straw residues	
			ET, Domestic	Agricultural	70-75
				by-products	
	Mechanical <sup>(o)</sup>	> 500	ET, District Heating	Wood chip	
			ET+EE,	Agricultural	70-75
			Products processing	by-products	
Blowup boiler	Mechanical	15-35	ET, Domestic	Food processing	
			D1, Domestic	residues	70–80
		> 100	ET+EE, Products processing	Processing waste	10 00

<sup>(#)</sup> Upwards flame combustion.

istics of the gas mixture are variable. Because of this, the reactors and the subsequent  $gas\ cleaning$  are based on different technological solutions. Considering the high amount of impurities transported by the gas flow (especially tars and particulate), all biomass gasification plants are equipped with a  $gas\ cleaning$  and a  $gas\ cooling$  section. For low power plants ( $<300\,\mathrm{kW}$ ),  $fixed\ bed\ gasifiers$  are used (fig. 6) as well as coarse lignocellulosic biomass, while for high power plants ( $>1\,\mathrm{MW}$ )  $fluidized\ bed\ gasifiers$  are used as well as fine or powdered lignocellulosic biomass.

 $2^{\circ}2.3$ . Pyrolysis. When biomass heating is performed in the *absence of O*<sub>2</sub>, only chemical bonds breaking is recorded and, consequently, the formation of simple organic molecules (that at room temperature can be solid, liquid or gaseous, in relation to

<sup>(\*)</sup> Reverse combustion.

<sup>(</sup>o) Inclined grate.

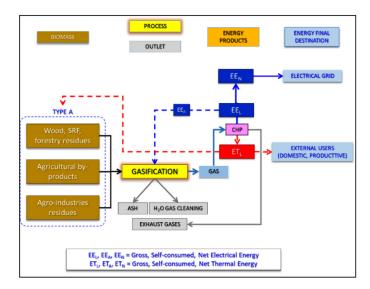


Fig. 5. – Gasification process scheme. The producer gas supplies IC engines, generating  $EE_L$ . A fraction of this  $EE_L$  is reused ( $EE_A$ ) while the remaining ( $EE_N$ ) is sold to the grid (feed-in tariff). Operating with CHP engines, the  $ET_L$  can be used for biomass drying or for neighboring utilities through a heating distribution grid (source: [4]).

their molecular weight) takes place. The ET required for this pyrolytic splitting is then provided —at temperatures between 400 and 800 °C: i) indirectly, through the *pyrolysis reactor wall* or ii) directly, by the recirculation of a heating agent in the bed (fig. 7). Pyrolysis products can be divided into the following:

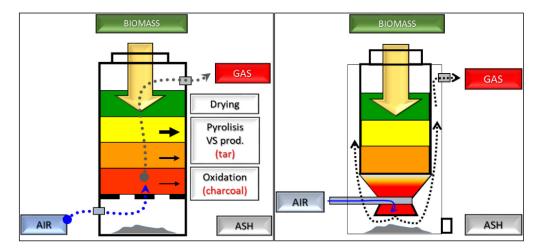


Fig. 6. – Fixed bed gasifiers: updraft type (left) and downdraft type (right) (source: [4]).

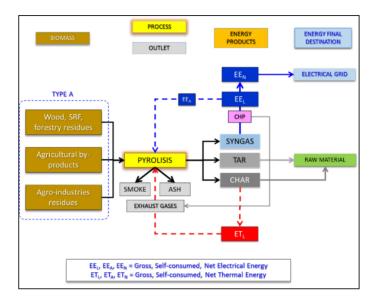


Fig. 7. – Pyrolysis process scheme. The products have different destinations: i) syngas, which is generally used to generate EE<sub>L</sub> powering an IC engine, ii) tar (bio-oil) and iii) char which may be used as raw materials in subsequent transformation activities. Char is frequently reused as a fuel to produce the process heat (source: [4]).

- non-condensable gases (syngas), mainly composed of CO, H<sub>2</sub>O, H<sub>2</sub>O, H<sub>4</sub>, CH<sub>4</sub> and other light hydrocarbons. The syngas can be burnt to provide heat to the pyrolysis reactor or —more conveniently— to feed a turbogas system or a reciprocating IC engine, generating EM and, thus, EE;
- condensable volatile compounds (tar) of complex and variable composition, that consist of a mixture of heavy hydrocarbons which —when condensed— forms a black liquid fuel (bio-oil);
- solid compounds (char), which consist of carbonaceous residues similar to charcoal and ash. Char can be used as a fuel (also in the same pyrolytic reactor) for active carbon production or as intermediate in the chemical industry.

The way through which the pyrolysis is carried out determines different yields and proportions in the products. Generally, as time decreases and the process temperature increases, the amount of tar and syngas increases at the expense of char:

- conventional pyrolysis: T < 600 °C, permanence time  $t_r = 300$ –1800 s and medium heat rate; the three fractions in the same proportion can be obtained;
- fast pyrolysis: 500 < T < 650 °C,  $t_{\rm r} = 0.5-5.0$  s and high heat rate; it promotes the production of the liquid fraction (tar) (70–80% of the biomass weight);

- flash pyrolysis: T > 700 °C,  $t_r < 1$ s and very high heat rate (1000 °C/s); as the previous one, it promotes the production of tar.

A well-known process of *slow pyrolysis*, carried out worldwide since ancient times (especially in the developing countries), is *carbonization* (charcoal production) that lasts for a few days and it is usually carried out outdoors with the production of stacked wood covered with soil. T is low (300–500 °C) and, thus, the final product is almost completely represented by char, because the other components are released in the atmosphere.

- 2.3. Biochemical processes and oil extraction. In the biochemical transformation processes (fermentations, under anaerobic conditions), the organic molecules of the biomass are used as a food substrate by different bacteria, resulting in liquids or gaseous biofuels production [8, 13]. These biofuels can supply heat generators to generate ET or, more widely, EM by IC engines [2]. Depending on the fermentation type (i.e., on bacteria and substrate), it is possible to obtain [7]:
  - biogas, a gaseous mixture (CH<sub>4</sub> based), obtained by methanic fermentation;
  - bioethanol, an alcohol (CH<sub>3</sub>CH<sub>2</sub>OH), obtained by alcoholic fermentation.

A third important supply chain for biofuels production is the extraction of oil contained in seeds of some oleaginous species and its use as biofuel for IC engines in the form of: i) pure vegetable oil (Straight Vegetable Oil, SVO) or, more widely, ii) after the transformation into methyl esters (biodiesel) [13]. Taking into account the energy destination, biogas is mainly used for EE generation by fixed point engines, while bioethanol and biodiesel are used for EM production by mobile point engines for vehicles traction. In these big markets, the distribution and the marketing of biodiesel and bioethanol is managed by the same operators that control the fossil fuels supply and distribution. Due to the fact that the raw materials used in the "first-generation biofuels production" are agricultural products (such as cereal grains, sugar cane, sugar beet, forages, etc.) which conflict with their use in the food/feed supply chains(<sup>26</sup>), serious problems in terms of resources management can occur.

2.3.1. Methanic fermentation. Methanic fermentation (or AD) is a complex biological process through which the organic substance is degraded in the absence of  $O_2$ , producing a gaseous mixture with energy characteristics that are similar to natural gas. This degradation process is carried out through different stages by a bacterial consortium. The biogas is (in volumetric terms) mainly composed of i)  $CO_2$  and ii)  $CH_4$ . Some gases that take part in the biogas mixture (nitrogen, oxygen) do not affect its energy characteristics; others, on the contrary, are very powerful (hydrogen), while others are

<sup>(&</sup>lt;sup>26</sup>) This ethical aspect, moreover, also concerns the biogas production, which has become —especially in Italy— more and more widespread thanks to the use of feed crops (corn and other cereals silages with very high biogas yields), instead of other by-products or livestock waste.

Gas		Content	
		(% vol. dry gas)	
Methane	CH <sub>4</sub>	55–65	
Carbon dioxide	$CO_2$	35–40	
Nitrogen	$N_2$	1–2	
Hydrogen	$H_2$	0-1	
Hydrogen sulphide	$_{ m H_2S}$	0.02-0.2	
Oxygen	$O_2$	traces	
Ammonia	NH <sub>4</sub> <sup>+</sup>	traces	
Mercaptans	-	traces	

Table XIV. – Average biogas composition.

undesirable (ammonia and hydrogen sulphide) because they are harmful to the process and to the environment as well (table XIV). The amount of CH<sub>4</sub> contained in the biogas mixture depends on the chemical characteristics of the substrate and on the conditions under which AD takes place; it generally ranges from 50 to 80% of the total volume of the dry biogas mixture. Consequently, the biogas LHV ranges from 14.4 to 25.2 MJ/m $_{\rm N}^{3}$ ( $^{27}$ ). Thanks to its high LHV, biogas —suitably treated— can easily feed CHP units to produce both heat (ET, partially reused for digester heating) and EE (sold to the grid at feed-in tariff). In addition to biogas, a co-product —the digestate— is obtained from AD; the composition and the characteristics of this co-product depend on the substrate type. In general, the digestate is rich in N (organic and mineral form) and it can be efficiently used as agronomic fertilizer (fig. 8).

The anaerobic bacteria that degrade the substrate usually have low growth and reaction rates; consequently, to optimize the process inside the AD digester, it is necessary to generate and maintain the optimum environmental conditions (T, pH, concentration of metabolites, etc.) for the bacterial metabolism. The whole degradation process is very complex and it is carried out by different groups of bacteria that implement a series of reactions, partly overlapped.

Simplifying the reactions sequence, the first two steps (that can be grouped together into a single *acidogenic phase*) act as a "preparation" for the final step (*methanigenic phase*), during which the biogas production takes place [2]:

- hydrolysis: hydrolytic bacteria cause the degradation of the complex organic compounds (proteins, fats, carbohydrates) present in the substrate, with the formation of simple and soluble compounds (amino acids, fatty acids and monosaccharides, respectively);
- acidification and acetogenesis: at the same time as hydrolysis, fermentative acidogenic bacteria oxidize the simple organic substrates to obtain pyruvate, which

 $<sup>(^{27})</sup>$  The LHV of CH<sub>4</sub> is  $31.6 \,\mathrm{MJ/m_N^3}$   $(7565 \,\mathrm{kcal/m_N^3})$ .

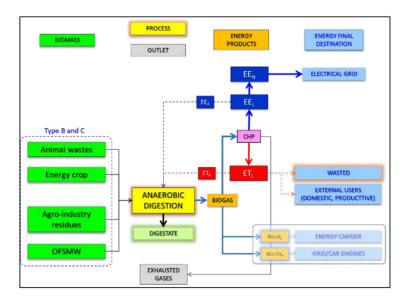


Fig. 8. – AD scheme. Biogas normally supplies a CHP unit with an electric generator, producing  $EE_L + ET_L$ . A small fraction of  $EE_L$  is reused ( $EE_A$  for self-consumption) while the remaining ( $EE_N$ ) is sold to the grid. Also a fraction of  $ET_L$  is reused for substrate heating ( $ET_A$ ) while the remaining fraction can be sold to external final users through a distribution network (but in many cases the residual heat is inefficiently dissipated). The digestate (co-product) is used for agronomic purposes. Bio-CH<sub>4</sub> can be produced purifying the biogas and concentrating the  $ET_A$  can be used as a fuel for vehicles or pumped into the natural gas distribution grid. Also the bio-H<sub>2</sub> production —prior to biogas production— is a plant variant (but it is still at experimental level) the purpose of which is to explore the potential of H<sub>2</sub> as energy carrier (source: [4]).

is subsequently transformed into ketones, alcohols and *Volatile Fatty Acids* (VFA; acids with a short chain, such as *propionic* and *butyric acids*); starting from VFA, acetogenic bacteria produce *acetic acid*, *formic acid*, CO<sub>2</sub> and H<sub>2</sub>. NH<sub>3</sub> is also produced by the fermentation of the amino acids;

methanogenesis: represents the conclusion of the anaerobic trophic chain, as CH<sub>4</sub> is the only non-reactive compound in the whole process.

The AD takes place in closed and isolated structures (usually cylindrical), called digesters (or digestion reactors). The biomass fed into digester (only one or —more frequently— a mix of different organic matrices) is heated and maintained inside the digester under:

- mesophilic conditions (35–45 °C);
- thermophilic conditions (50–55  $^{\circ}$ C).

The ET needed for biomass heating is recovered from the cogeneration unit (CHP; IC engine + electric generator) powered by the biogas. In general, increasing the process

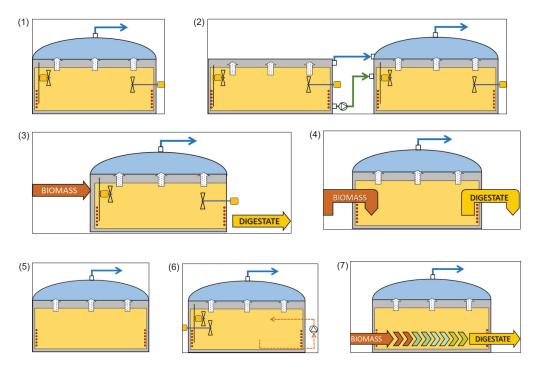


Fig. 9. – AD plant types (from left to right and from top to bottom): (1) single-stage plant, mechanical mixing; (2) two-stage plant, mechanical mixing; (3) continuous load system; (4) discontinuous load system (batch); (5) not mixed plant; (6) mixed plant (Completely Stirred Tank Reactor, CSTR); (7) plug-flow plant.

temperature, the mass of digested substrate increases and, consequently —at the same flow  $(m^3/day)$  of fresh substrate put into the digester— the *Hydraulic Retention Time* (HRT, days) decreases, reducing the digester volume (and investment costs of the AD plant). The *technical-operational criteria* for splitting out the AD plants are (fig. 9):

- TS content of the inlet substrate:
  - wet digestion:  $4\% < TS \le 10\%$ ; it is the most widespread AD solution in Italy, operating with animal slurry only or —very often— in co-digestion conditions (slurry mixed with other organic matrices such as cereals silages, food processing residues or other organic residues);
  - semi-dry digestion: 10% < TS < 20%;
  - dry digestion:  $20\% < TS \le 35\%$ ; it is generally applied for particular organic substances or for biogas plant fed with OFMSW.
- plant layout (biological phases):
  - single-stage AD plants, in which the acidogenic and methanigenic phases occur simultaneously in a single digester (very common and easy-management solution, low investment costs);

- two-stage AD plants, in which the acidogenic phase takes place in a 1st stage digester and methanigenic phase in a 2nd digester (more efficient and sophisticated solution, high investment costs).

#### - digester loading mode:

- discontinuous load (batch mode): only one substrate load is performed when the process starts, and the digestate is extracted from the digester once the HRT ends; with this (uncommon) solution, biogas flux over the time is not steady (there is a strong initial increase, a very short-term stability and a rapid decline) and some technical layout arrangements are necessary;
- continuous load: high-frequency (12–48 times per day) fresh substrate loads and simultaneous discharges of an equal volume of digestate are carried out; this solution is currently the best choice to guarantee: i) high-automation in process management and ii) constant biogas production over the time (m<sub>N</sub><sup>3</sup>/h).

#### - substrate mixing inside digester:

- not-mixed digester;
- digester equipped with mixing devices (currently, propellers devices submerged in the substrate represent the most widespread solution in wet digestion and in single-stage AD plants);
- digester equipped with piston systems: the lateral inlet of the substrate generates a push along the longitudinal axis of the digester (that usually has a parallelepiped shape), moving forward the substrate that is already in it and releasing the digestate on the opposite side.

Co-digestion consists in the digestion, at the same time, of i) livestock waste (pigs, cows and poultry waste, mainly), ii) energy crops (maize and other cereals silage, sorghum, loin, etc.) and iii) different organic residues or waste (fig. 10). The main advantage of the co-digestion, compared with the use of animal waste only, is the big increase in the organic matter input and, thus, in the significant growth in the biogas yield (energy production).

Moreover, the possibility of using different types of biomass in an AD plant can promote an *integrated management of the resources* (at both farm and landscape level), allowing —in the case of recovery and reuse of processing residues— the rational disposal/valorization of many materials. From this point of view, residues from *vegetable processing* (potatoes, onions, legumes and fruit, etc.), which are usually clean organic materials, are of great interest and represent excellent matrices for the AD plants. In Italy, co-digestion was mostly based on the use of *corn silage* (or silage of triticale, barley, wheat or sorghum), in AD plants with a "standard" electric power just below of 1 MW

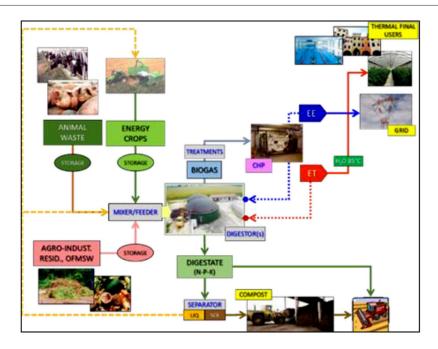


Fig. 10. – Co-digestion supply chain scheme. Biogas production aims to generate EE. Heat should also be used but final users must be very close to the AD plant (source: [4]).

(see footnote( $^{28}$ )) and with an energy share from energy crops often largely prevalent on animal waste rate. Under these conditions, attention has to be paid to the massive amounts of digestate available at the farm level which: i) has to be stocked and disposed of in accordance with the current regulation( $^{29}$ ), ii) generates a significant increase in the farm N concentration. This latter issue is a problem of not easy solution in those areas (vulnerable zones) where the above-mentioned regulation( $^{30}$ ) defines a limit about the N rate (kg/ha), coming from livestock waste, that can be spread over the time.

2.3.2. Bio-CH<sub>4</sub>. Bio-CH<sub>4</sub> originates from biogas subjected to an upgrading process (CO<sub>2</sub> removal, mainly) in order to generate a gas with a CH<sub>4</sub> concentration of 95–98%

<sup>(28)</sup> This electric power represented —up to 31.12.2012— the upper limit for the application (15 years) of the all-inclusive feed-in-tariff (TO) equal to 280 €/MWh. For AD plants put into operation after this date, the value of the TO has been reduced (TO = 210-220 €/MWh, for a 20-year period) and the upper electric power has been set to 300 kW (http://www.gse.it/it/Qualifiche%20e%20certificati/DM%2023%20giugno%202013/Pagine/default.aspx).

 $<sup>\</sup>binom{29}{}$  The need to find new digestate distribution areas in accordance to the N loading limits imposed by the regulation is indicated (*Il Sistema agro-forestale della Lombardia*, Report 2011) as one of the causes of the significant increase in the land rentals in agricultural areas of Lombardy where the number of AD in co-digestion is higher than in other Italian regions.

<sup>(30)</sup> MIPAF Ordinance of April 7th, 2006.

in volume, to be used as biofuel: i) for vehicles engines (cars, trucks and tractors, in particular) or ii) to supply the natural gas distribution grid. The cleaning and upgrading processes consist of the following steps: i) purification, ii) dehydration, iii) desulphurization(<sup>31</sup>), iv) undesirable components removal. The sequence of these phases depends on the adopted technology: i) physical (such as oscillating pressure adsorption, washing with pressure water, washing with organic solvents and separation with membranes) or ii) chemical (such as washing with mono-ethyl-amine, MEA).

The introduction of bio-CH<sub>4</sub> into the distribution network allows —in addition to a reduction in the AD plant investments costs (biogas storage systems and the cogeneration unit are unnecessary)— a more flexible and efficient biogas utilization [4]. Bio-CH<sub>4</sub> utilization is widespread in northern Europe (especially in Germany, Austria, Sweden and Denmark), while in Italy —despite the National Energy Plan objectives and a general law about it(32)— protocols, technical standards and, above all, the TO for the "nonelectric biogas" ( $\in$ /m<sub>N</sub>), have been approved only recently. The advantages of bio-CH<sub>4</sub> networking are not negligible. In particular, they are linked to the chance of using this biofuel in different (and even far) locations than the production sites, with the possibilities of: i) use it in more powerful cogeneration units located close to heat final users (global efficiency improving), ii) use it as a fuel for urban vehicles. The disadvantages are essentially related to the relatively high energy demand for bio-CH<sub>4</sub> pressurization; in particular, compression is advantageous only for medium-pressure pipes (1 ,while for high-pressure pipes  $(p > 12 \,\mathrm{bar})$  it is much more expensive. Finally, before entering the distribution network (and also before its use in service stations as a fuel), bio-CH<sub>4</sub> has to undergo a purification process, achieving the full compatibility with natural gas characteristics, established by the current legislation.

 $2^{\circ}3.3$ . Bio-H<sub>2</sub>. H<sub>2</sub> represents the simplest, lightest, and more abundant chemical element in the Universe, making up, in combination form, about the 75% of all matter. However, in free form, H<sub>2</sub> represents only 0.07% of the atmosphere and 0.14% of the Earth's surface.

Currently, the most attractive application for pure  $H_2$  is the use as energy carrier in fixed and mobile conversions. In the simplest case,  $H_2$  combustion generates an exothermic reaction producing, in addition to ET, only water vapor. The environmental repercussion is only the considerable amount of  $NO_x$  generated inside the combustion chamber of the Otto cycle engines, caused by the high operating temperatures (2000–3000 °C). This is why the most important vehicle manufacturers have started studies concerning the development of engines derived from the Diesel cycle. Recent studies have shown that the adoption of special engines (Homogeneous Compression Charge Ignition, HCCI;  $\eta = 45\%$ ), avoids the problem, maintaining considerably lower operating temperatures.

 $<sup>(^{31})</sup>$  Attention has to be paid to this phase, especially when the biogas is produced from AD of cows waste, because the production of a mixture rich in  $H_2S$  can occur.

 $<sup>(^{32})</sup>$  Legislative Decree No. 28 of March 3rd, 2011 defines, in general terms, the characteristics that bio-CH<sub>4</sub> must have to be introduced into the natural gas distribution network.

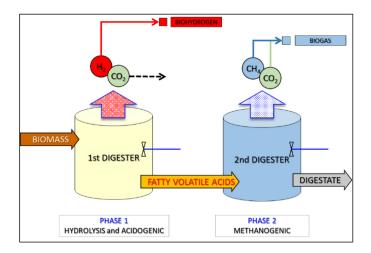


Fig. 11. – Bio-H<sub>2</sub> from biomass: two-stage AD plant with H<sub>2</sub> production (source: [4]).

 $H_2$  is also strictly linked to the Fuel Cell technology [13], which —unlike the common IC engines— allows the use of  $H_2$  to produce EE under isobaric and isotermic conditions without any combustion reaction. Since electrolytic  $H_2$  production is very expensive, many alternatives have been exploited and they are still in an experimental phase. At the same time, many other researches have been focused on improving technologies to store and transport this very peculiar gas. Concerning the new solutions to produce  $H_2$ , a special two-stage AD seems to be very promising. This technique is based on the physical separation of hydrolysis (acidogenic and acetogenic) phase from the methanigenic one [4]. Practically, there are two different reactors operating in series (fig. 11). By the modulation of the HRT, it is possible to optimize the metabolic processes of VFA and  $H_2$  production (bio- $H_2$ ) in the first reactor, thus stripping out the  $H_2$  and moving the VFA into the second reactor, where biogas rich in bio-CH<sub>4</sub> is produced.

The interest in this solution is also justified by the fact that, under the same conditions, the two-stage process is —compared to a traditional single-stage AD— able to produce more energy (higher conversion efficiency). During recent experimental tests(<sup>33</sup>), a two-stage laboratory scale plant, fed by a mixture of slurry and OFSMW (65% and 35% on the total mass, respectively) and operating with a HRT of 2 days in the first digester, showed that the specific bio-H<sub>2</sub> production (ratio between the volume of bio-H<sub>2</sub> produced and the volume of the reactor) was about 3.2–3.3 dm³/dm³ of reactor per day. In the extracted gas mixture from the first digester no CH<sub>4</sub> was present and the average content of H<sub>2</sub> was 42% vol. (H<sub>2</sub> yield: 125–130 dm³/kg VS). Under this optimal conditions, comparing the total efficiency between the single- and the two-stage solution (9.4 and 15.8 MJ/kg VS, respectively), the conversion efficiency of the second was higher.

<sup>(33)</sup> Produzione di bio-idrogeno ed energia rinnovabile da residui agro-zootecnici (AgrIdEn) Project, Regione Lombardia.

## APPENDIX A.

# List of symbols and acronyms

Name	Symbols and acronyms	Unit of measure
All-inclusive feed-in-tariff	ТО	€
Anaerobic Digestion	AD	_
Bio-hydrogen	Bio-H <sub>2</sub>	_
Biomass-To-Liquid	BTL	_
Bio-methane	Bio-CH <sub>4</sub>	_
Bulk (apparent) Density	γ	${ m kg/m^3}$
Carbon/Nitrogen ratio	C/N	_
Combined Heat and Power unit	СНР	_
Completely Stirred Tank Reactor	CSTR	_
Density	ρ	${\rm kg/m^3}$
Dry Mass	$m_{ m DM}$	kg
Dry Matter content or Total Solids	DM or TS	%FM
Electric Energy	EE	MJ
European Union	EU	_
Excess air ratio	λ	_
Food and Agriculture Organization of	FAO	_
the United Nations		
Forest Management Plan	FMP	_
Fresh (wet) mass	$m_{ m FM}$	kg
Gross Electric Energy	$\mathrm{EE_{L}}$	MJ
Gross Heating Value	GHV	MJ/kg DM
Gross Thermal Energy	$\mathrm{ET_{L}}$	MJ
Homogeneous Compression Charge Ignition	HCCI	_
Hydraulic Retention Time	HRT	days
Internal Combustion	IC	_
Lower Heating Value	LHV	MJ/kg DM
Mechanical Energy	EM	MJ

Medium Rotation Forestry	MRF	_
Moisture Content (dry basis)	$\mathrm{MC}_{\mathrm{DM}}$	%DM
Moisture Content (wet basis)	MC	%FM
Mono-Ethyl-Amine	MEA	_
Net Electric Energy	$\mathrm{EE_{N}}$	MJ
Net Heating Value	NHV	MJ/kg FM
Net Thermal Energy	$\mathrm{ET}_{\mathrm{N}}$	MJ
Organic Fraction of Municipal Solid Waste	OFMSW	_
Permanence time	$t_{ m r}$	S
Self-consumed Electric Energy	$\mathrm{EE_{A}}$	MJ
Self-consumed Thermal Energy	$\mathrm{ET}_{\mathrm{A}}$	MJ
Short Rotation Coppice	SRC	_
Short Rotation Forestry	SRF	_
Straight Vegetable Oil	SVO	_
Thermal Energy	ET	MJ
Volatile Fatty Acids	VFA	_
Volatile Solids	VS	%TS
Water Mass	$m_{ m H_2O}$	kg

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