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**EXPERIMENTAL ANALYSIS AND SIMULATION OF BIOMASS ENERGY CONVERSION
PROCESSES AND TECHNOLOGIES**

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Index

Abstract (Italiano)	1
Abstract (English)	3
Introduction	4
Chapter 1. Energy characterization of biomass	8
1.1. Biomass	8
1.2. Energy characterization.....	11
1.2.1. Proximate analysis.....	11
1.2.2. Ultimate analysis	13
1.2.3. Heating value.....	13
Chapter 2. Biomass conversion processes	15
2.1. Biomass conversion processes	15
2.2. Thermochemical processes	21
2.2.1. Pyrolysis	22
2.2.2. Gasification	24
2.2.2.1. Fixed bed gasifiers.....	25
2.2.2.2. Fluidised bed gasifiers.....	28
2.2.3. Combustion	30
2.3. Biochemical processes	31
2.3.1. Fermentation.....	31
2.3.2. Anaerobic digestion.....	32
2.3.2.5. BATCH processes	35
Chapter 3. Fluidised Bed Gasification Model and Simulations	37
3.1. Gasification process	37
3.2. Process parameters	40
3.3. Gas conditioning technologies	41

3.4. Modelling of the gasifier process	43
3.4.1. Gasification model	45
3.4.2. Experimental tests	48
3.4.3. Model validation.....	51
3.5. Simulations and Results	54
Chapter 4. Anaerobic Digestion	63
4.1. Process details	63
4.2. Process stages.....	64
4.2.1. Process kinetics	66
4.3. Conditions and variables influencing anaerobic digestion.....	70
4.3.1. Temperature.....	71
4.3.2. pH	71
4.3.3. C/N ratio	72
4.3.4. Retention time	72
4.3.5. Organic Loading Rate.....	73
4.3.6. Mixing	73
4.4. Bio-Methane Potential (BMP)	74
4.4.1. Manometric method	75
4.4.2. Volumetric method.....	76
4.5. Laboratory plant	77
4.6. Experimental tests	79
4.6.1. Co-digestion tests with Olive Mill Solid Waste.....	79
4.6.2. Co-digestion of Poultry Manure and Cheese Whey Wastewater ...	90
4.7. AD Model.....	97
4.7.1. AD Simulation Result	98
Chapter 5. Fusion Energy	101

5.1. Introduction	101
5.2. Fusion reactions	104
5.3. Magnetic and Inertial Confinement	108
5.4. ITER and DEMO	112
5.4.1. Thermal load issue.....	114
5.5. Divertor Tokamak Test	116
5.6. Analysis of DTT advanced magnetics configurations	117
Conclusions	121
Bibliography	125

Abstract (Italiano)

Il proposito della ricerca è stato quello di analizzare la fattibilità e la produttività di impianti di produzione di energia da fonti non tradizionali, come la biomassa, per dare un contributo alla crescente richiesta di energia elettrica mondiale senza far ricorso ai combustibili fossili. Viene presentata quindi una ricerca ad ampio spettro su due possibili processi di conversione della biomassa: termochimici e biochimici. Nel primo caso vengono riportate delle simulazioni effettuate con il software ChemCAD[®] di un impianto di gassificazione a letto fluido bollente con candele filtranti catalitiche, Water Gas Shift (WGS) e Pressure Swing Adsorption (PSA) realizzato nell'ambito del progetto europeo UNIfHY per la produzione di idrogeno puro. Nel secondo caso vengono presentate delle prove sperimentali di digestione anaerobica a scala di laboratorio, anche nell'ambito del Piano di Sviluppo Rurale (PSR) Misura 124, in cui sono stati utilizzati come biomassa in ingresso scarti provenienti da aziende agricole e allevamenti che rappresentano ad oggi degli inquinanti per i terreni ed i corsi d'acqua, o addirittura delle fonti di perdita monetaria per le aziende. Viene inoltre proposto un modello di digestione anaerobica sviluppato e implementato nel software AQUASIM 2.0 al fine di studiare tramite simulazioni i singoli stadi del processo e l'attività batterica, per poter così verificare a priori la fattibilità e la bontà del processo in funzione del substrato in ingresso. Lo scopo di questo lavoro quindi è quello da un lato di dare una valida alternativa alle aziende che possono trovare negli scarti delle proprie attività una fonte di reddito e, dall'altro, promuovere lo sviluppo e la realizzazione di nuovi impianti di produzione di energia a piccola scala, e contemporaneamente dare una risposta al cambiamento climatico.

Inoltre, nell'ambito di una collaborazione dell'Università della Tuscia e del Centro di Ricerca ENEA Frascati, viene riportato uno studio effettuato su un reattore a fusione termonucleare. Questa tecnologia potrebbe rappresentare una effettiva risposta alla crescente richiesta di energia mondiale tra le fonti di energia alternative che non utilizzano combustibili fossili. In questo lavoro vengono presentate delle simulazioni relative ad un nuovo reattore a fusione termonucleare, DTT, il cui progetto è stato presentato da ENEA nel Luglio 2015. Attraverso tali simulazioni sono state trovate

delle possibili risposte alla problematica dei carichi termici presenti su questo tipo di macchina.

Abstract (English)

The purpose of this research has been analysing the feasibility and productivity of energy production plants by non-traditional sources as biomass, to contribute to the growing demand of energy without using fossil fuels. A broad-spectrum research on two possible biomass conversion processes is presented: thermochemical and biochemical. In the first case, ChemCAD[®] software simulation of a bubbling fluidised bed gasifier plant with catalytic filter candles, Water Gas Shift (WGS) and Pressure Swing Adsorption (PSA) are reported; these were realized as part of the European project UNIfHY for pure hydrogen production.

In the second case experimental tests of anaerobic digestion at lab-scale are presented also as part of Rural Development Plan (RDP) project Measure 124. In these tests wastes, from agricultural companies and farms, which are pollutants for soils and watercourses or actually a monetary loss for the companies have been used. Furthermore it is proposed an anaerobic digestion model developed and implemented in the software AQUASIM 2.0 to study via simulations the single stages of the process, the bacterial activity, and to verify *a priori* the feasibility and the functionality of the process as a function of the input substrate. The purpose of this research is, on one hand providing a valuable alternative to companies, finding in their activity wastes a source of income and, on the other hand promoting the development and the realization of new small-scale energy production plants, thus at the same time to provide a response at the climate change.

Furthermore a study on a thermonuclear fusion reactor, as part of the cooperation between the University of Tuscia and the ENEA Frascati Research Centre, is reported. This technology could represent a valid response at the growing worldwide energy demand among the alternative energy sources that do not use fossil fuels. In this work, simulations of a new thermonuclear fusion reactor, DTT, whose design has been presented by ENEA in July 2015, are introduced. With these simulations a possible solution to the thermal load issue on this kind of machine has been found.

Introduction

The energy world consumption has exponentially increased with the industrial, technological and economic development, in different trends in each Country. Nowadays the supply of electricity comes essentially from large power plants, mainly fueled with fossil fuels and nuclear energy. Although these power plants had provided a worldwide efficient service for decades, the demand for energy is growing rapidly due to the rapid social developments in many parts of the world, also because modern economy depends increasingly on the availability of electrical energy. At the same time, modern societies understood that, to fight climate change, it is necessary to reduce the emissions. Moreover an optimum use of traditional energy sources, is required to support the development of energy production from non-traditional sources, such as biomass and thermonuclear fusion.

These issues were the basis of the activities carried out during the three years of the PhD in “*Agricultural and forestall system engineering*” in Tuscia University, in collaboration with CIRDER (“*Centro Interdipartimentale di Ricerca e Diffusione delle Energie Rinnovabili*”) and ENEA Frascati Research Centre.

In the first chapter of this thesis a general introduction on biomass and its physico-chemical characteristics has been done. Furthermore details of the procedure of

the laboratory test for its energy characterization according to the European rule have been emphasised.

In the second chapter different biomass conversion processes have been introduced with particular regard to gasification, for the thermochemical processes, and to anaerobic digestion for the biochemical processes.

In chapter three biomass gasification process has been investigated, in particular for small size power plants using waste biomass. Waste biomass gasification is an economic process to produce pure hydrogen. In particular, small scale applications are very interesting because they follow the low energy density and perishability of this fuel exploiting the biomass directly *in loco* avoiding therefore disposal costs. At first it has been developed and validated experimentally a model, capable of predicting the performance of a steam blown fluidized bed biomass gasifier during steady state operation. Then simulations activities have been carried out within the European 7FP UNIfHY project. The plant analysed in this research is mainly composed of bubbling fluidized bed gasifier with catalytic filter candles, Water Gas Shift (WGS) and Pressure Swing Absorption (PSA). Focusing on the hydrogen production, a sensitivity study was carried out with ChemCAD[®] software by varying the steam to biomass ratio and the gasifier operating temperature.

In chapter four anaerobic digestion of waste biomass in co-digestion process has been studied. After biomass energy characterization, experimental tests to evaluate biogas yield from waste biomass have been done with the BATCH mini-digester in a co-digestion process in mesophilic conditions. For the first tests olive mill solid waste (OMSW) has been used in a co-digestion process with cattle manure (CM) and cattle slurry (CS). The other set of tests investigate the biogas production from mixture of Poultry Manure (PM) and Cheese Whey Wastewater (CWW). These tests are part of Rural Development Plan (RDP) project (Reg. 1698/2005 of Lazio 2007/2013), Measure 124: "Cooperation for development of new products, processes and technologies in agriculture, food and forestry: energetic use of agro-industry wastes". Furthermore an anaerobic digestion model has been developed and then implemented in the software AQUASIM 2.0. Anaerobic digestion simulations permit to verify the single process stages and study the bacterial activity, which is difficult to do in experimental tests. In

this way it is possible to evaluate the feasibility and the goodness of the anaerobic digestion process as a function of the input substrate.

In Chapter 5 the issue of thermal load in thermonuclear reactor has been investigated, as part of the cooperation between the University of Tuscia and the ENEA Frascati Research Centre. In this work analysis about the electromagnetic aspects that could have an influence on the tokamak divertor were made. In particular simulations on physic divertor of DTT (Divertor Tokamak Test) have been carried out, a project developed by ENEA on July 2015, with the MAXFEA code. The aim of these simulations has been to find an optimal divertor magnetic configuration and to test the performance of plasma when it is used a liquid metal divertor.

Together with the work described above the following articles have been published:

- Steam gasification of pine wood in a fluidized bed reactor: model development and validation at different operative conditions. 21st European Biomass Conference, 2013.
- Parametric experimental tests of steam gasification of pine wood in a fluidized bed reactor. Journal of Agricultural Engineering, 2013.
- State of art of small scale biomass gasification power systems: a review of the different typologies. Energy Procedia, 2014.
- Biomass to fuel cells state of art: A review of the most innovative technology solutions. International Journal of Hydrogen Energy, 2014.
- State of art of small scale solar powered ORC systems: A review of the different typologies and technology perspectives. Energy Procedia, 2014.
- Biomass waste shells analysis and advanced gasification tests. Green Building, Materials and Civil Engineering, 2014.
- Steam gasification of wood biomass in a fluidized biocatalytic system bed gasifier: A model development and validation using experiment and Boubaker Polynomials Expansion Scheme BPES. Int. Journal of Renewable Energy Development (IJRED), 2015.
- Simulations of a Plant with a Fluidized Bed Gasifier WGS and PSA. HIKARI Ltd, 2015.

- DEA (Data Envelopment Analysis)-assisted supporting measures for ground coupled heat pumps implementing in Italy: A case study. *Energy*, 2015.
- Anaerobic co-digestion of olive-mill solid waste with cattle manure and cattle slurry: analysis of bio-methane potential. *Energy Procedia*, 2015.
- Biogas Production from Poultry Manure and Cheese Whey Wastewater under Mesophilic Conditions in Batch Reactor. *Energy Procedia*, 2015.
- DTT Divertor Tokamak test facility Project Proposal. ENEA, 2015.
- Influence of the main gasifier parameters on a real system for hydrogen production from biomass. *International Journal of Hydrogen Energy* (under review).
- DTT and advanced magnetic configurations. (To be presented at 22nd PSI Conference, May 2016)

Chapter 1. Energy characterization of biomass

1.1. Biomass

A first biomass definition is present in Art. 2 of Legislative Decree 387/2003 that reproduces the Directive 2001/77/EC and establishes that “biomass means 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”. This definition has been expanded by Legislative Decree 28/2011 implementation of the Directive 2009/28/EC on the promotion of the use of energy from renewable sources and amending and subsequently repealing Directives 2001/77/EC and 2003/30/EC, in which in point e) of Article 2) defines biomass as “...the biodegradable fraction of products, waste and residues from biological origin from agriculture (including vegetal and animal substances), forestry and related industries including fisheries and aquaculture, as well as the biodegradable fraction of industrial and municipal waste”. By these definitions is clear that biomass is a resource available everywhere, clean and renewable. It may be converted in solids, liquids or gaseous fuels, or directly used as fuel. Biomass is composed of water (moisture), dry raw substances and ash. Physico-chemical properties can be established by the composition of the dry substances, highlighting the most suitable energetic conversion. Carbon content higher than nitrogen one indicates the presence of

organic compounds as lignin, characterized by a complex chemical structure and slow biologic biodegradability. The opposite is for the biomass with low C/N ratio, because it requires substances with high water content and minerals that are an optimum substrate for micro-organisms. In Table 1.1 main biomass usable in Italy to produce energy, the production characteristics, C/N ratio and moisture are shown.

Table 1.1. Average productions and C/N ratio of some Italian culture.

Biomass	Product	Average moisture [% H₂O]	Average production (as presented) [t/ha]	Average production of dry matter [t/ha]	C/N ratio
Common wheat	grain	12÷16	3,0÷4,0	2,5÷3,5	15÷24
	straw	12÷15	2,1÷2,8	1,8÷2,4	118÷129
Durum wheat	grain	10÷14	1,5÷2,5	1,3÷2,1	17-26
	straw	10÷13	1,2÷2,0	1,1÷1,7	110-130
Rice	grain	18-30	4,5-5,5	3,6-3,8	32-38
	straw	20-30	4,0-5,0	3,2-3,5	60-65
Corn	grain	20-30	6,0-7,0	4,8-4,9	23-29
	cob	40-50	1,8-2,1	0,9-1,3	70-80
Sugar beet	roots	73-78	40,0-50,0	10,0-13,0	45-65
	leaves	75-80	16,0-20,0	3,2-4,0	13-17
Potato	tubers	72-80	10,0-25,0	2,5-6,0	29-36
	stems	55-65	5,0-10,0	2,2-3,5	18-22
Sunflower	achenes	14-20	1,5-2,5	1,3-2,2	45-58

In Table 1.2 chemical composition and Low Heating Value (LHV) of some harvest wood products, culture by-products and wastes are reported. The chemical composition (C, H, O, N, S, Cl) is an important aspect that must be considered [1,2]. For lingo-cellulosic biomass the chemical composition (expressed on a dry and ash free basis) is generally more constant than that of other solid fuels (Municipal Solid Waste, coal). Furthermore, more than 80% of the biomass is volatile and the remaining 20% is charcoal. Coal is typically only 20% volatile, while the remaining 80% is unreactive coke. Generally biomass has very low Sulphur and Chlorine content compared to coal and MSW.

Table 1.2. Physico-chemical properties of some biomass.

Material	Moisture	C	H	O	N	S	Cl	Ashes	LHV
	[%]	[%]	[%]	[%]	[%]	[%]	[%]	[%]	[MJ/kg]
Straw wheat	10-20	43,2	5,00	39,4	0,61	0,11	0,28	11,40	16,49
Straw barley	10-20	39,92	5,27	43,81	1,25	0,10	0,03	9,75	16,24
Straw rice	20-30	41,78	4,63	36,57	0,70	0,08	0,34	15,90	15,34
Cobs Corn	40-50	46,68	5,87	45,46	0,47	0,01	0,21	1,40	17,58
Residual vine pruning	45-55	46,59	5,85	43,90	0,83	0,04	0,08	2,71	17,84
Wood white fir	40-50	49,00	5,98	44,75	0,05	0,01	0,01	0,2	18,74
Wood poplar	40-50	48,45	5,85	43,69	0,47	0,01	0,1	1,43	18,19
Wood oak	40-50	49,98	5,38	43,13	0,35	0,01	0,04	1,61	18,33
Rice husk	10-15	40,96	4,3	35,86	0,40	0,12	0,03	18,35	15,27
Nut shells	10-20	49,98	5,71	43,35	0,21	0,05	0,04	0,71	19,02
Pomace exhausted	10-15	43,73	5,29	37,82	1,5	0,64	0,02	12,52	15,50
Paper	15-20	43,40	5,80	44,30	0,3	0,2	0,4	6,0	18,00

Nowadays, there is a change in the biomass energy uses from traditional and non-commercial, as simple open combustion to produce heat, to a modern one, as advanced processes to produce electricity and bio-fuels integrated in food and biomaterials industries [3]. The technical and economic potentials of biomass are higher than the current world energy consumption [3,4], thus, the challenge is in its viable and sustainable use and not in its availability. Indeed, to really exploit the energy potential of biomass, reliable, high efficiency and low environmental impact, small scale power plants have to be developed, consistent with the low energy density and perishability of this fuel [5–8].

Indeed, one of the major limitations associated with the use of the large bioenergy potential (e.g. the Italian territory amounted to about 30 million metric tons/year [5,9]) is the biomass dispersion. Biomass is the fourth world-wide energy resource (following oil, coal and natural gas) but the energy use of the organic substances is limited by their low energy density, complexity of the supply chain (often in competition with the main uses of organic matter, as food and materials) and high local emissions of pollutants [10].

1.2. Energy characterization

For the biomass energy characterization the following analysis must be done:

- proximate analysis (moisture, ash and volatile matter content);
- ultimate analysis (content of C, H, N, O);
- heating value.

All the procedures refer to the international technical rules. In particular the standard techniques of the European Committee of Standardization (CEN) have been followed.

- EN 14774-1:2009. Solid biofuels-Determination of moisture content-Oven dry method- Part 1: total moisture-Reference method [11];
- EN 14774-2:2009. Solid biofuels-Determination of moisture content-Oven dry method- Part 2: total moisture-Simplified method [12];
- EN 14774-3:2009. Solid biofuels-Determination of moisture content-Oven dry method- Part 3: moisture in general analysis sample [13];
- EN 14775:2009. Solid biofuel-Determination of Ash content [14];
- EN 15148. Solid biofuels–Determination of the content of volatile matter [15];
- EN 15104:2011. Solid biofuels-Determination of total content of carbon, hydrogen and nitrogen. Instrumental methods [16];
- EN 14918:2009. Solid biofuels-Determination of calorific value [17].

Biomass analysis have been done in the CIRDER laboratory (Orte). Below the details and used equipment are reported.

1.2.1. Proximate analysis

Proximate analysis permits to evaluate moisture content on wet and dry basis, the ash content, and the volatile matter.

1.2.1.1. Total moisture content

Moisture content or water content is the quantity of water in the biomass. To evaluate the percentage of moisture, a representative sample (300 g) is placed in a container of aluminium, and it is dried in an oven at $105 \pm 2^\circ\text{C}$ until constant in mass. Constancy in mass is

defined as a change not exceeding 0,2% of the total loss in mass during a further period of heating over a period of 60 minutes.

The total moisture content M_{ar} in the biofuel, as received, is calculated with the equation presents in the regulation [12].

1.2.1.2. Moisture content of the general analysis sample

A fundamental test consists in the determination of the moisture content, M_{ad} , of the analysis sample [13]. The result of this test is used to evaluate the effective sample moisture. The obtained value is important to correct the heating value, volatile matter content, ash and the ultimate analysis.

The sample is previously finely grind and sieved (1 mm). Each analysis sample ($1\pm0,1$ g) must be dried at $105\pm2^\circ\text{C}$ until constant in mass. It is placed in a crucible with lid and for each sample two tests are necessary. Constancy in mass is defined as a change not exceeding 1 mg in mass during a further period of heating at $105\pm2^\circ\text{C}$ over a period of 60 minutes. In this way the moisture content of the general analysis sample may be calculated by the formula present in the technical rule.

1.2.1.3. Ash content

Ash content on dry basis represents the mass of residue remaining after the sample is heated under specific conditions, and it is expressed as percentage of mass on dry basis.

The sample is finely grind in a cutting mill and sieved (1 mm). Crucibles must be previously heated in a furnace at $550\pm10^\circ\text{C}$ for 60 minutes. Then $1\pm0,1$ g of sample is heated in the furnace raising the temperature from 250°C to $550\pm10^\circ\text{C}$ in accordance with the procedure EN 14775:2009. For each sample two test must be done.

1.2.1.4. Volatile matter content

Volatile matter is determined as the loss in mass, less that due to moisture, when biomass is heated under standardized conditions. The sample ($1\pm0,1$ g), finely grind and sieved (1 mm) is heated in a furnace at $900\pm10^\circ\text{C}$ for 7 minutes.

Volatile matters (Vd) on dry basis, expressed as percentage by mass, are calculated by the formula present in the technical rules [15].

1.2.2. Ultimate analysis

Ultimate analysis consists in the determination of the total carbon, hydrogen and nitrogen content in the biomass. The environmental importance of the nitrogen content is linked to emissions of NO_x . Hydrogen is important for calculation of the net calorific value. Carbon content is required for the determination of CO_2 emissions.

A sample of 0,150 g, previously finely gring and sieved (1 mm), is used for the test. The oxygen content is measured by empirical relationship (1.1):

$$O = 100 - (C + N + H + S) \quad (1.1)$$

The content of C, H and N are calculated by equations present in the standard EN 15104:2011.

1.2.3. Heating value

The heating value (or calorific value) of a substance, is the amount of heat released during the combustion of a specified amount of it. There are two different heating values: Higher Heating Value (HHV) and Lower Heating Value (LHV). HHV is determined by bringing all the products of combustion back to the original pre-combustion temperature, and in particular condensing any produced vapour. Such measurements often use a standard temperature of 15 °C. LHV is determined by subtracting the heat of vaporization of the water vapour from the HHV. In this study HHV has been determined with an isoperibol calorimeter (Parr 6200) according to EN 14918:2009 (Figure 1.1). In the instrument the shell is at constant temperature (30°C). The bomb, pressurized with excess pure oxygen (40 atm) and containing a weighed mass of a sample ($1 \pm 0,1$ g), is submerged under a known volume of water (2 l) before the charge is electrically ignited. The bomb, with a known mass of sample and oxygen, form a closed system - no gases escape during the reaction. The weighed reactant in the steel container is then ignited. Energy is released by the combustion and heat flow from this crosses the stainless steel wall, thus raising the temperature of the steel bomb, its contents, and the surrounding water jacket. The temperature change in the water is then

accurately measured with a thermometer. This reading, along with a bomb factor, is used to calculate the energy given out by the sample burn. A small correction is made to account for the electrical energy input, the burning fuse, and acid production (by titration of the residual liquid). After the rise of temperature is measured, the excess pressure in the bomb is released. The test gives the HHV referred to the sample with relative humidity as that measured for the general analysis sample. Three tests for each sample must be done and the final result is the average of the three obtained values.



Figure 1.1. Calorimeter Parr 6200.

Chapter 2. Biomass conversion processes

2.1. Biomass conversion processes

The organic material can be used “directly” by living organisms as their own source of energy and materials (food) or it can be used “indirectly” like a source of external energy (biomass) and materials: (clothing, furniture, buildings chemicals, etc.). Following oil, coal and natural gas, biomass is the fourth most used primary energy resource worldwide. Nevertheless, in industrialized countries it accounts only for about 4% of the share, often being the last remarkable energy resource, after nuclear and hydro, whereas it represents around 35% in the developing countries [4]. This happens because biomass is the most common form of renewable energy and the largest reservoir of solar energy. However, the energy use of the organic substances is limited by their low energy density and complexity of the supply chain, often in competition with the main uses of organic matter as food and materials, and by their high local emissions of pollutants [5]. Thus, as already mentioned, the challenge is in its viable and sustainable use not in the availability. The first element to consider in assessing viable biomass uses is the energy and economic feedstock production costs. The first one is evaluated by Energy Return On Energy Invested, EROEI, that is the

ratio of the amount of usable energy delivered from an energy resource to the amount of energy used to obtain that energy resource, while the second one is evaluated by the production cost divided by the useful Heating Value (HV), in €/GJ. The feedstock price is the largest component of the operating costs in a biomass plant and varies from negative price of some waste biomass to high price of some dedicated crops. Fixing an energy yield value of 100 GJ/ha (e.g. yield of 10 t/ha and a calorific value of 10 GJ/t), for a value of 10 GJ/ha for cultivation and harvesting, the energy production cost is 0,1, while a mean economic cost is about €4/GJ. These average optimistic values include, among other items, transport energy and its economic costs of 0,5 MJ/km and 0,02 €/km per ton [3]. Lower yield and lower HV biomass does not have proportionally lower costs; therefore, the energy and economic returns could become negative. For this reason, it is preferable to use low cost residual biomass. The main residual biomass are waste, shells, pruning, straw and agro-industrial residues. Among waste we can mention the Organic Fraction of Municipal Solid Waste (OFMSW) and the manure. Among shells the main used are the shells of pine, hazel, walnuts and almonds. The main pruning are the pruning of beech, oak, spruce, poplar, willow, eucalyptus, grape and olives. The main straw used are the straw of wheat, corn, rye, barley, rice. Among the agro-industrial residues, we can mention food, textile and wood industrial residues like cane trash, exhausted olives, pomace, etc. The second main element to take into consideration is the conversion process that mainly depends on biomass quality and final product desired, as heat, electricity and specific fuel. The efficiency and cost-effectiveness of these processes have a very large range. As in the first element, the energy and economic returns can be easily negative. Indeed, many processes have high-energy requirements and especially the most advanced technologies can have unaffordable investment costs. Strongly related to cost issues are the availability and the full-scale demonstration of advanced conversion technologies, combining high energy conversion efficiency and environmentally sound performance with low investment costs. Last but not least, environmental impacts have to be taken into account. The use of biomass, especially on the large-scale, involves a wide range of environmental implications: soil fertility; leaching of nutrients and biodiversity; deforestation and erosion; landscape, water use; fire and diseases; air, water and ground pollution; etc. In fact, if the “ideal” energy use of biomass produces just the CO₂ that the biomass has fixed, there are pollutant emissions over the whole production-use chain. Differently from other renewable energy sources, biomass, being classifiable as a fuel, and not an energy resource directly convertible like solar, wind, hydro, and geothermal energy, is subjected to all traditional steps

needed to make it available on the energy market (production, transport, conversion, distribution, end use). Nevertheless, residual biomass, if used *in situ*, is subjected only at the last three steps and an accurate analysis and design can change the potential negative impacts into positive ones. Indeed, the use of biomass can also remove soil contaminants and reduce pollution, if the biomass power plants meet strict environmental standards. Finally, social implications have to be carefully taken into account. Bio-energy systems require complex organization, many actors, substantial land areas and have, generally, negative social acceptance. However, biomass is always available and biomass plants can have positive economic, social and environmental impacts, particularly related to the equitable distribution of biomass and the close connection that it establishes between a community and its territory. Summarizing, biomass is a complex energy source that can be processed in many ways leading to a variety of products and by-products, as showed in Figure 2.1.

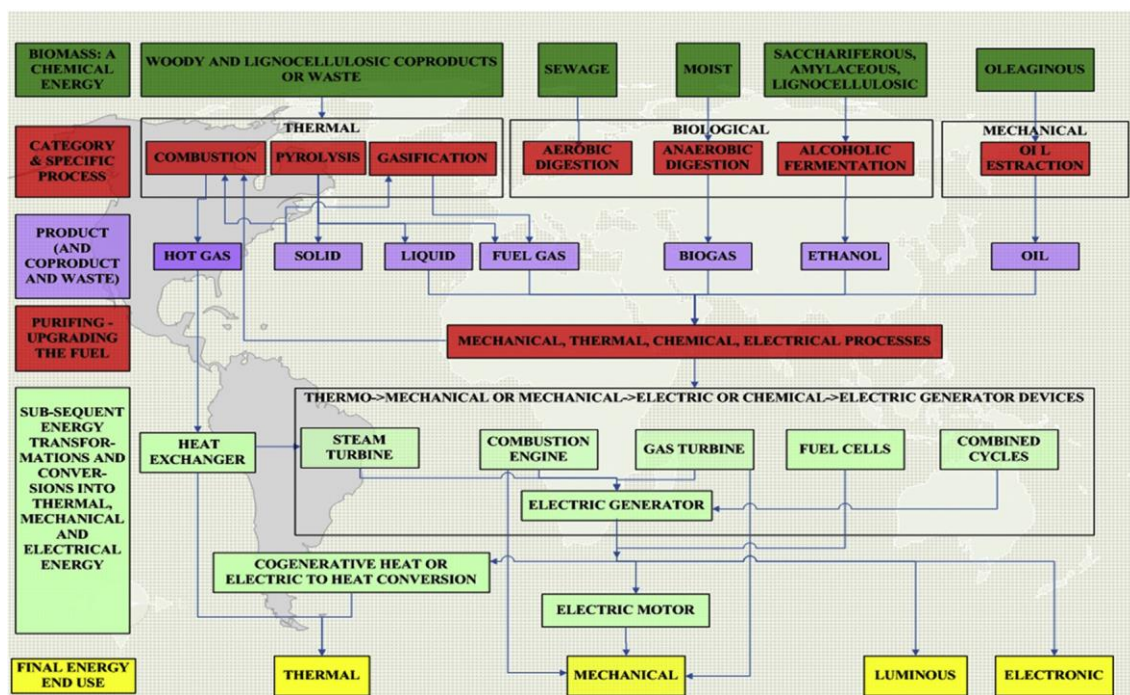


Figure 2.1. Biomass energy conversion processes.

The primary energy processes of biomass can be divided into three main categories, according to the main energy/ substance used in the process:

1. **THERMAL:** conversion using thermal energy (combustion; pyrolysis; gasification);

2. **BIOLOGICAL**: conversion using microbial or enzymatic activity (aerobic and anaerobic digestion, fermentation);
3. **MECHANICAL**: conversion using mechanical energy (oil extraction).

The process choice is mainly determined according to biomass properties and final products required. Biomass properties as moisture, carbon/nitrogen ratio and oil content affect the choice of process category. Thermochemical processes are based on the heat that permits the chemical reactions which transform matter in energy. All the cellulosic and harvested wood products and wastes with a C/N>30 and a moisture <30% are useful. The most suitable biomass for the thermochemical conversions are wood and its derivatives, ligno-cellulosic cultural by-products and some processing wastes. Biochemical processes permit to obtain energy for chemical reaction due to the contribution of enzymes, fungi and micro-organisms, which are formed into the biomass under particular conditions. They are used for biomass with a carbon to nitrogen ratio (C/N) <30 and a moisture >30%. For biochemical conversion aquatic cultures, some cultural by-products, livestock wastes, some processing waste and the biomass of landfills are suitable. In Table 2.1 main biomass with energy conversion processes have been reported.

Table 2.1. Main biomass and conversion processes

Biomass	C/N ratio	Moisture [%H ₂ O]	Conversion process
Plants and ligno-cellulosic wastes	C/N>30	H ₂ O≤30%	Combustion
			Carbonization
			Gasification
			Pyrolysis
Plants, cellulosic and starch wastes	20≤C/N≤30	H ₂ O>30%	Alcoholic fermentation
Plants and sugar wastes	20≤C/N≤30	15≤H ₂ O≤90%	Alcoholic fermentation
Plants and fermentable wastes	20≤C/N≤30	H ₂ O>30%	Anaerobic digestion
Plants and oleaginous wastes	-	H ₂ O>30%	Oil extraction

Animal wastes	$20 \leq C/N \leq 30$	$70 \leq H_2O \leq 90\%$	Anaerobic digestion
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The other properties influence the particular process technologies and the yield and reliability of the entire chain. The final energy vectors required, and in some cases the economic conditions and the environmental standards, influence the process choice. In fact, every process uses all the available chemical energy, but such energy is delivered in a particular way and at different level of efficiency. Aerobic digestion can supply only heat at low temperature thus the process is more useful to treat sewage rather than to produce energy. The direct combustion of solid biomass can supply only heat, which is converted into electricity at low efficiency. I.e. a solid fuel is burned with low efficiency, and, only at large scale, it produces steam suitable for a Steam Turbine (ST). Moreover, the combustion of solid biomass releases many contaminants, especially when air is the limiting reactant. E.g. in tobacco combustion, one of the most studied, until now several thousand products have been identified, many with toxic and carcinogenic action [18]. The other processes transform the chemical energy of biomass into chemical energy of solid (low temperature pyrolysis-carbonisation), liquid (fast pyrolysis, fermentation, oil extraction) and gaseous (gasification, anaerobic digestion) fuels. The fuels so obtained have to be purified and/or upgraded, through subsequent mechanical/physical/chemical or electrical or biological processes. Obviously, a High Calorific Value (HCV) fuel can be easily transported and is amenable to a more efficient use. In fact, producing HCV fuel and/or electricity allows the final energy use to be shifted in space (with fuel also in time) providing a more flexible answer to different energy demands. In fact, with liquid or gas fuels the electricity can be obtained via Combustion Engines (CE), Gas Turbines (GT), Fuel Cells (FC) or Combined Cycles (CC) having better efficiency respect to ST, especially in small scale plants. In brief, the conversion processes that provide an HCV liquid or gas follow the historical fuel trend to more powerful, efficient and clean fuel. The energy end uses are mainly: thermal, mechanical, luminous and electronic. Therefore, the fuels are mainly used to produce heat via combustion, mechanical energy via CE or GT (transport sector), and electricity directly via FC or indirectly via CE, GT, ST, CC and coupled electric generator.

Regarding biogas and syngas, as usual, different anaerobic digestion and gasification processes and different operating conditions give different composition and yield. The operating conditions are mainly temperature and residence time and, for biogas, type of

bacteria and acidity value, for syngas, type of oxidant and catalyst/sorbent used. Normally yield is in the range of 0,2-0,7 and 0,5-3 Nm³ of biogas and syngas, respectively, per kg of dry ash free biomass [18]. The impurity concentration (particulate, organic and inorganic trace elements) depends also on the specific type of biomass. Anyway, it is possible to estimate average biogas and syngas composition. Table 2.2 and Table 2.3, show the biogas and syngas dry average compositions.

Table 2.2. Biogas average composition [19–24]

Average biogas composition								
CH ₄ (Vol%)	CO ₂ (Vol%)	O ₂ -N ₂ (Vol%)	H ₂ S (ppmv)	Halogenated hydrocarbons (Vol%)	VOC (mg/Nm ³)	Siloxanes (mg/Nm ³)	NH ₃ (ppmv)	LHV (MJ/Nm ³)
50-80	30-50	0-10	0-4000	1-5	5-300	0-50	100-2000	18-28

Table 2.2 shows that biogas is mainly composed of methane (CH₄) and an inert (CO₂), thus different concentration of CH₄ gives the different Low Heating Value (LHV). Nitrogen and Oxygen are present only due to air infiltration owing to anomalous conditions. Therefore, the biogas feeding of the conversion devices fed by methane requires plant modifications to avoid a reduction of power and to guarantee the allowable plant level of the impurities. The impurities are mainly due to presence of sulphur compounds (mainly H₂S), halogens compounds (mainly chlorine compounds), Volatile Organic Compounds (VOC) and siloxanes (O-Si-O compounds).

Table 2.3 shows that syngas is mainly composed of H₂, CO, CO₂, CH₄ and N₂ and that the different concentration of CO, CH₄ and H₂ gives the different LHV. Nitrogen is present only if air is used like gasifying agent, or it is due to air infiltration owing to anomalous conditions. The impurities are mainly due to presence of organic compounds (mainly benzene and Topping Atmosphere Residues (TAR) like toluene, naphthalene, etc.), particulate, sulphur compounds (mainly H₂S), halogens compounds (mainly HCl) and alkali compounds (like sodium and potassium compounds). Therefore, the syngas feeding of the conversion devices fed by methane is more difficult not only owing to the lower calorific value and the higher production temperature (700-900 °C of syngas versus 10-55 °C of biogas) but also owing to the presence of different gases from methane and different impurities (mainly TAR).

Table 2.3. Syngas average composition [8,20,25–27]

Average syngas composition	
H ₂ (Vol%)	10-50
CO (Vol%)	10-45
CO ₂ (Vol%)	10-30
CH ₄ (Vol%)	1-20
N ₂ (Vol%)	0-50
TAR (g/Nm ³)	0,01-100
Particulate (g/Nm ³)	0-100
H ₂ S (ppmv)	20-200
HCl (ppmv)	<500
Alkali (ppmv)	~1
NH ₃ (ppmv)	100-1000
LHV (MJ/Nm ³)	3-20

In the next paragraphs thermochemical and biochemical processes are discussed in detail.

2.2. Thermochemical processes

Thermochemical processes are chemical to thermic energy conversions and vice versa, because they consist in endothermic and exothermic reactions: decompositions chemical reactions. These processes permit to obtain more useful and more exploitable fuels (Figure 2.2). All the thermochemical processes consist in a pre-treatment and then in a conditioning stage. The fuels are used to produce heat by combustion, mechanical energy by Combustion Engine (CE) or Gas Turbine (GT), electric energy by Fuel Cells (FC) or indirectly through mechanical energy (CE, ST, GT, CC) and an electric generator. Each process produces energy vectors (heat, electricity, and fuels with different characteristics) and also sub-products and wastes. Biomass best suited for the thermochemical processes are:

- wood and its derivatives;
- lingo-cellulosic sub-cultural products;
- by-products (shells, stones, etc.);
- “dry” urban solids wastes.

In the next paragraph different thermochemical processes are described.

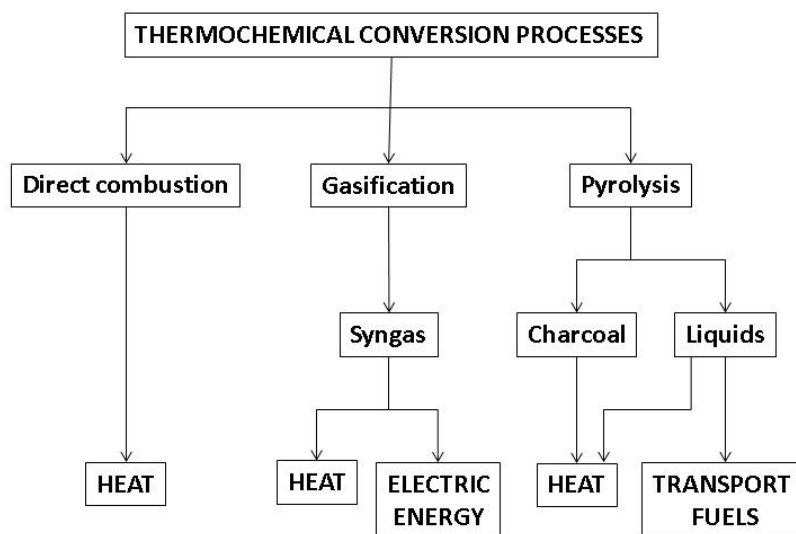


Figure 2.2. Thermochemical conversion processes

2.2.1. Pyrolysis

Pyrolysis is a thermochemical decomposition process of solid matter, obtained providing heat at low temperature (150-700°C). Between 100°C and 700°C exothermic and endothermic reactions take place, and the macro-molecules are broken in chains with low molecular weight as a function of the pyrolysis methods (Figure 2.3). All the thermochemical processes begin with pyrolysis which is the first stage of combustion and gasification.

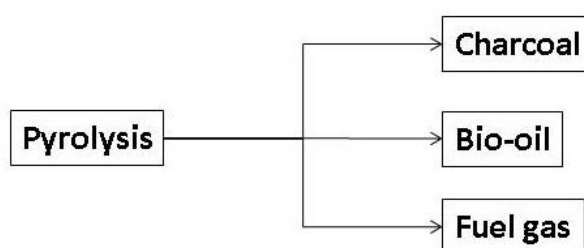


Figure 2.3. Scheme of pyrolysis

In biomass decomposition complex hydrocarbons molecules are broken down in less complex molecules. The process may take place both in total absence of oxygen and in presence of little amount of oxygen. In a first stage biomass is converted in solid particulate

(CHAR), gas and TAR, which can be broken down in non-condensable gas (as CO, CO₂, H₂, CH₄), liquid and char (Figure 2.4).

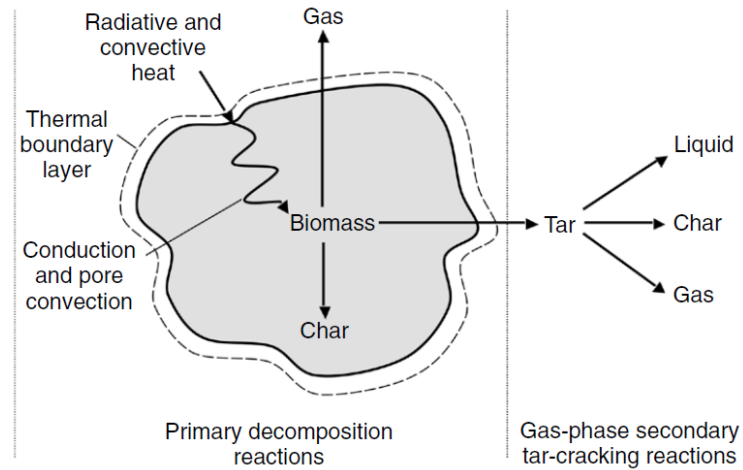
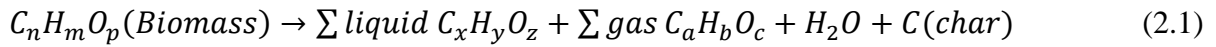


Figure 2.4. Two stages of pyrolysis: primary stage and secondary cracking

Reaction that represents process is (2.1):



Therefore the products are solids, liquids and gaseous. Solids are in particular char and ash, liquids are heavy hydrocarbons (TAR) and water, and the gases are CO₂, CO, H₂O, C₂H₂, C₂H₄ and volatile hydrocarbons. The composition and fraction of these products depend on different conditions as:

- biomass composition;
- particle size;
- heating rate;
- operating temperature;
- residence time.

Pyrolysis processes are characterized by the temperature rate (slow or fast pyrolysis, as a function of the residence time) and the presence of a medium (hydro-pyrolysis, methane-pyrolysis, etc.), that influence the obtainable products.

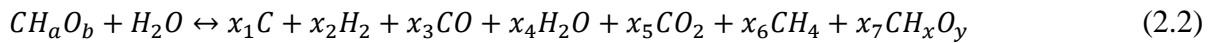
There are four different reaction stages:

1. Drying (100°C);

2. Initial stage (100°C-300°C): CO and CO₂ are released;
3. Intermediate stage (200°C-600°C): primary pyrolysis;
4. Final stage (300°C-700°C): secondary cracking.

2.2.2. Gasification

Gasification is a thermo-chemical process that converts biomass through partial oxidation into a gaseous mixture of syngas consisting of hydrogen (H₂), carbon monoxide (CO), methane (CH₄) and carbon dioxide (CO₂) [28]. The oxidant agent can be air, pure O₂, steam, CO₂ or their mixtures. The reaction that describes the process is (2.2):



Reactions products are:

- syngas;
- tar;
- char;
- ash.

The choice of the oxidant depends on the gas quality desired, plant complexity and the power demand. Gasification process can be applied at biomass that have:

- ash content < 5%;
- moisture < 30%;
- absence of melting material at the operating temperature.

The process consists mainly in three stages:

- drying (about 100°C): vaporization of moisture;
- pyrolysis (200-700°C): thermal decomposition of solid in gas, tar and char;
- oxidation-reduction processes (700-1000°C): pyrolysis products react with gasification agent generating the final products.

During the process different reactions take place:

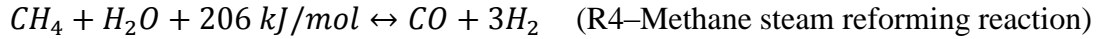
- pyrolysis of fuel;
- heterogeneous reactions:





in which the reaction rates are: $R1 \gg R2 \gg R3$

- homogeneous reactions:



in which the reaction rates are: $R5 \gg R4 \sim R6$

Therefore the process is globally endothermic and requires heat to occur.

There are different gasification technologies that can be distinguished as a function of the reactor (fixed or fluidised bed), biomass path, heating (direct or indirect) and operating pressure (atmospheric or pressurised). Within the fixed bed gasifiers it is possible to distinguish updraft (UD) configuration (countercurrent) when biomass move from the top and the gasifying agent from the bottom; downdraft (DD) configuration (concurrent), when the biomass and the gasifying agent move together from the top to the bottom of the reactor; crosscurrent when the biomass moves down and the agent is fed at right angles. Below the main characteristics of fixed bed (from which are derived the moving bed) and fluidised bed gasifier are reported [29].

2.2.2.1. Fixed bed gasifiers

Updraft gasifier

In the UD the downward-moving biomass is dried and pyrolysed, giving char which continues to move down to be gasified, and pyrolysis vapors which are carried upward by the upflowing hot produced gas (Figure 2.5). The TARs in the vapor either condense on the cool descending fuel or are carried out of the reactor with the produced gas, contributing to its low ash but high TAR content (up to 100 g/Nm^3). For the extremely high TAR content in the gas, this configuration is more suitable for direct firing, like the small cooking stoves.

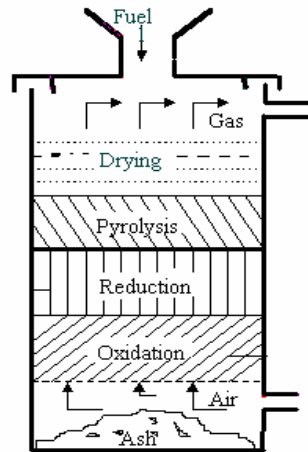


Figure 2.5. Updraft gasifier configuration

Downdraft gasifier

In the DD the biomass together with the oxidant is forced to pass through a constriction (throat) where most of the gasification reactions occur (Figure 2.6). The reaction products are intimately mixed in the turbulent high-temperature region around the throat (1100-1200°C), which aids TAR cracking. This configuration results in a relatively clean gas from TAR ($<10 \text{ g/Nm}^3$) even if particulates can be high. The high residence time of biomass leads to a high char conversion ($\approx 95\%$). Because the gases leave the gasifier unit at temperatures about 900–1000°C, the overall energy efficiency of a downdraft gasifier is low, due to the high heat content carried over by the hot gas. Downdraft is generally utilized for small-scale electricity generation with an internal combustion engine. Downdraft gasifiers are not suitable for scale-up to larger sizes ($>1 \text{ MW}$) because they do not allow for uniform distribution of flow and temperature in the constricted area (throat).

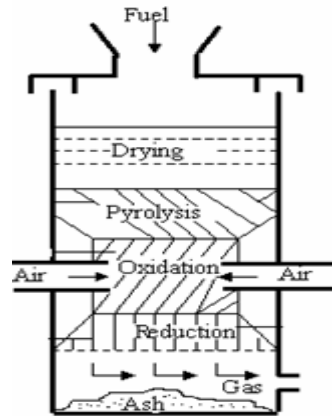


Figure 2.6. Downdraft gasifier configuration

Crossdraft gasifier

A crossdraft gasifier is a co-current moving-bed reactor, in which the fuel is fed from the top and air is injected through a nozzle from the side (Figure 2.7). One of its important features is a relatively small reaction zone with low thermal capacity, which gives a faster response time than that of any other fixed-moving-bed type. Because its TAR production is low ($0,01\text{--}0,1\text{ g/Nm}^3$), a crossdraft gasifier requires a relatively simple gas-cleaning system.

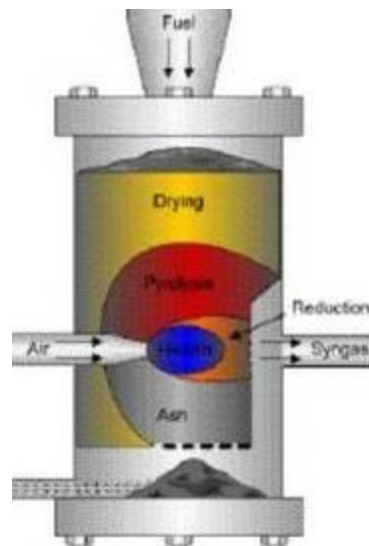


Figure 2.7. Crossdraft gasifier configuration

2.2.2.2. Fluidised bed gasifiers

In fluidised bed gasifiers (FB) the solid fuel, mixed with hot bed material (inert sand, catalyst), are kept in a semi-suspended condition (fluidised state) by means of the gasifying medium through them at the appropriate velocities called minimum fluidization velocity [30]. Unlike the fixed bed gasifier, because the intense gas-solid mixing, the different zones of drying, pyrolysis, oxidation and reduction, cannot be distinguished. Thanks to the excellent gas-solid mixing and to the large thermal inertia of the bed, the temperature and the solid/gas concentration are uniform in the entire bed. For these reasons the biomass conversion in the FB is close to 100% and the throughputs (biomass flow rate per installed reactor area) are double to ten times higher than in the fixed beds ($500\text{--}1000 \text{ kg}_{\text{biomass}}/\text{h m}^2$). For the same reasons, differently to fixed bed gasifiers, which need a fairly specific feedstock, FB are in general more tolerant and suitable for large installations. E.g. FB operate with uniform and relatively low temperatures ($700\text{--}900^\circ\text{C}$): most high-ash content fuels, depending on ash chemistry, can be gasified without problems of ash sintering and agglomeration. Finally FB do not require high temperature moving mechanical components (e.g. moving grids like in the moving bed) because the mixing effect is guaranteed in excellent way by the fluidization state. Because of these advantages, most of the current development activities are focused on large-scale FB. However FB still have the following disadvantages. The operation, even if more flexible than fixed bed, is more complicated. The concentration of particulates in the gas is generally higher (from 10 to 100 g/Nm^3). The fast movement of the bed material generates high abrasive action. Finally TAR production for fluidised bed gasifier lies between that for updraft ($\sim 50 \text{ g/Nm}^3$) and downdraft gasifiers ($\sim 1 \text{ g/Nm}^3$), with an average value of around 10 g/Nm^3 . The concentration can be reduced to few g/Nm^3 adding natural catalyst like olivine as gasifier bed [31].

Bubbling Fluidised Bed gasifier

Bubbling fluidised bed gasifier (BFB) works in minimum fluidisation point (Figure 2.8). The reactor is characterised by the presence of two phases: a fluid and gaseous phase at the bottom composed by heavy particles (fuel, char, ash, etc.) and only a gaseous phase (syngas) at the top (freeboard). In the BFB reactor, the velocity of the ascending gas flow is in the range of $1\text{--}3 \text{ m/s}$ and the expansion of the solid bed is only in the bottom. Thanks to the low gas velocity, there are not dragging phenomena outside the reactor. High quantity of inert

material (sand) is used to stabilize bed and temperature. Into the bed gas bubbles take place, which release giving the idea of the bed boiling. The presence of the bubbles permits a perfect mixing of the solids compounds.

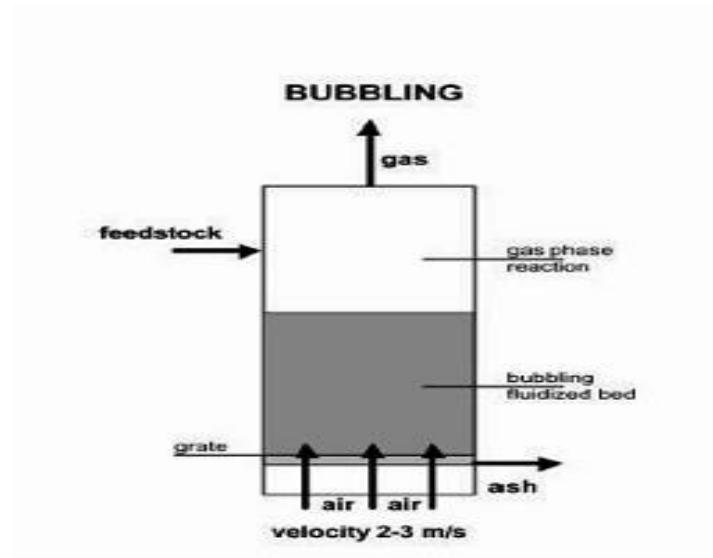


Figure 2.8. Bubbling fluidised bed gasifier

Circulating Fluidised Bed gasifier

CFB works after the minimum fluidisation point and particles circulate in the gas flow (Figure 2.9). A cyclone is used to separate these particles, which then return into the bed. The characteristic velocity of CFB is greater than 4 m/s, and for this bed expansion concerns all the gasifier height and there is not a freeboard zone.

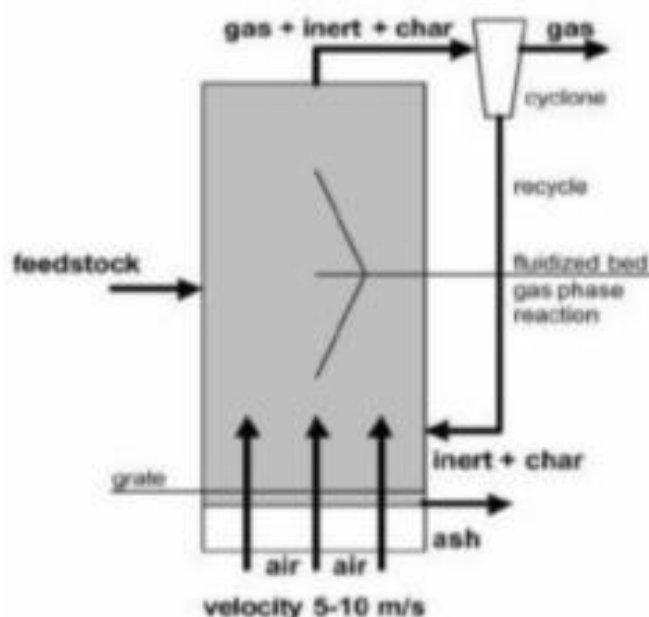


Figure 2.9. Circulating fluidised bed gasifier

Dragged Fluidised Bed Gasifier

In dragged fluidised bed gasifier the solid fuel is characterised by a particle size of 50-100 μm , improving intimate contact and so chemical conversion. These reactors work at high temperature (1200-1600°C) to achieve high reaction rates, overcoming ash melting point.

2.2.3. Combustion

Combustion is a high temperature exothermic redox chemical reaction between a fuel and an oxidant, usually oxygen contents in air, that produces a gas mixture.

Solid fuels first undergo endothermic pyrolysis to produce gaseous fuels whose combustion then supplies the heat required to produce more of them. Combustion is often hot enough that a flame is produced. Complete combustion is stoichiometric with respect to the fuel, where there is no remaining fuel, and ideally, no remaining oxidant. Thermodynamically, the chemical equilibrium of combustion in air is overwhelmingly on the side of the products. However, complete combustion is difficult to achieve, since the chemical equilibrium is not necessarily reached, or may contain unburnt products such as carbon monoxide, hydrogen and even carbon (ash). Thus, the produced gas is usually toxic and contains unburned or partially oxidized products. Any combustion at high temperatures in atmospheric air, which is 78% nitrogen, will also create small amounts of several nitrogen

oxides, commonly referred to as NO_x, since the combustion of nitrogen is thermodynamically favoured at high temperatures. Since combustion is rarely clean, flue gas cleaning or catalytic converters may be required by law.

2.3. Biochemical processes

Biochemical conversion processes mainly include aerobic digestion (fermentation) and anaerobic digestion (Figure 2.10).

They permit to obtain energy by chemical reactions with the contribution of enzymes, fungi and micro-organisms that are generated into the biomass in specific conditions. Aquatic cultures, manure, processes wastes, OFMSW, agriculture and animals sub-products can be converted by these processes.

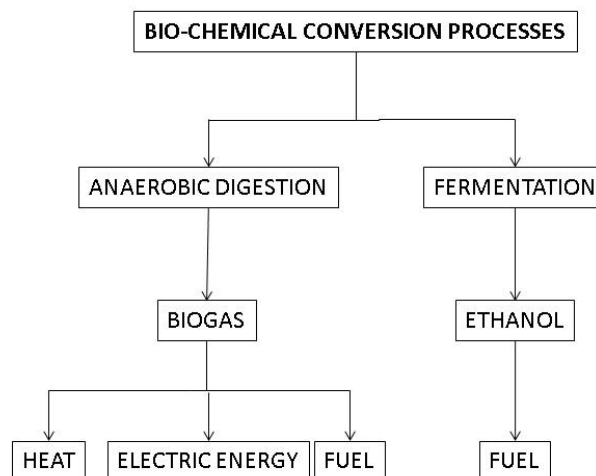


Figure 2.10. Biochemical conversion processes

2.3.1. Fermentation

Fermentation process permits to obtain ethanol from sugars in cultures and lingo-cellulosic biomass [32]. This process is suitable for all the products and sub-products with high content of glucose, as sugar, cellulose, hemicellulose, lignin and starch. Fermentation is an aerobic process that is characterized by three main steps:

- hydrolysis;
- fermentation of glucose;

- distillation of products to obtain ethanol.

Raw materials for the bioethanol production are:

- ad hoc cultivations (corn, sorghum, barley, chard and sugar cane);
- wastes of agroforestry cultivations;
- agricultural wastes;
- municipal solid wastes.

The products of the alcoholic fermentation are ethanol and carbon dioxide. The process is made by unicellular fungi (yeast). These microorganisms play an aerobic digestion in the substrate, using oxygen in the air and transforming sugars in water and carbon dioxide. Then, for lack of oxygen, yeast do fermentation oxidizing sugars in ethylic alcohol and carbon dioxide. The process takes place at ambient temperature (about 18-20°C) during 72-96 hours. Substrate becomes acid with a pH value of about 4 and the alcohol content is at most 12-18% vol. The reaction takes place in a mixed reactor that can work in continuous or in batch.

2.3.2. Anaerobic digestion

Anaerobic digestion is a degradation biologic process of organic matter in anaerobic condition (absence of oxygen) that has as product the biogas. The biogas is a gas mixture mainly composed of methane and carbon dioxide (see Table 2.2). The concentration of these substances in biogas depends by the kind of biomass and the digestion conditions [33]. In the process different bacterial species participate, and each in a specific stage (see Chapter 4). The bacteria can not be selected or modified, but the operating conditions like temperature, flows, mixing and pH can be controlled to promote the growth of the specific bacteria.

The areas of application of this process are three:

1. The treatment of waste water, in particular those with high organic load;
2. The treatment of livestock liquid wastes and biomass, produced for energy purpose or by-products;
3. The recovery of biogas produced by landfill wastes.

Biogas may be utilized in different ways [34]:

- direct combustion to produce heat;
- combustion in CHP (Combined Heat and Power) unit;

- injection in methane distribution system.

In general the most is the organic content in the substrate, the most is the biogas production. However is very important to control matter quality and in particular to consider:

- composition;
- the presence of essential elements (carbon, nitrogen, phosphorus, sulphur, etc.);
- the presence of toxics elements (sodium, potassium, calcium, magnesium, etc.).

Before being digested, the feedstock has to undergo pre-treatment depending on its characteristics. The purpose of such treatment is to mix different feedstock, to add water or to remove undesirable materials such as large items and inert materials to allow a better digestate quality, a more efficient digestion and it will avoid failure in the process. Digestate can be used as a fertilizer or further processed into compost to increase its quality [35]. The digestion process takes place in a digester, which can be classified in relation to [36]:

- Temperature
 - psychrophilic
 - mesophylic
 - thermophylic
- Solids content:
 - wet (up to 10%)
 - semi-dry (up to 20%)
 - dry (exceeding 20% and up to 40%)
- Number of stages in the reactor:
 - single stages
 - separated stages
- Operating conditions:
 - CSTR (Continuous Stirred Tank Reactor) or PFR (Plug-flow reactor)
 - BATCH reactor.

Below some of these process typologies are discussed.

2.3.2.1. Wet digestion

In wet digestion specific care must be taken for pre-treatments because during the digestion the heavier fraction and contaminants sink and a floating scum layer forms resulting in the formation of three layers in the reactor. The heavier fraction settles at the bottom and may damage the propellers, instead a floating layer accumulates at the top and disrupts mixing. For this, feedstock has to be clean prior to enter in the reactor. Thus the pre-treatments involve the removal of big particles and heavy contaminants. These pre-treatments cause a loss of 15-20% of volatile solids, with corresponding decrease in gas yield. Since total solids content have to be up to 10%, biomass need to be mixed with water [36].

2.3.2.2. Semi-dry digestion

In semi-dry system the solid content is in an intermediate range compared to wet and dry processes (15-20%). Generally a CSTR mixed reactor is used in this digestion, both in mesophilic and termophilic conditions [37]. Also in this case there is formation of three different layers in the reactor, even if the phenomenon is less important. Pre-treatment is important in this system and cause a loss of biodegradable organic matter.

2.3.2.3. Dry digestion

In dry systems the fermenting mass in the digester has a solid content in a range of 20-40%. The pre-treatment step is much simpler than the wet system. Due to the viscosity, plug-flow reactors (PFR) are used. The advantages are that it is technically simple and no mechanical devices need to be installed inside the reactor. Because no mixing occurs in the digester, wastes must be mixed with digestate to provide adequate inoculation. With plug-flow digesters no short-circuiting can happen as there are no moving parts. Feedstock is added at one end, thus pushing the digestate. Reactor is smaller because no water is added, so that the heat required to maintain the temperature in the digester at constant level is less important [35].

2.3.2.4. Multi-stages processes

The development of multi-stages anaerobic digestion aimed at improving the process by having separate reactors for the different stages, providing flexibility to optimize each of these reactions. Typically, two reactors are used, the first for hydrolysis/acetogenesis and the second for methanogenesis. In the first reactor, the reaction is limited by the rate of hydrolysis of cellulose; the second by the rate of microbial growth. The two-reactor process permits a certain degree of control of the rate of hydrolysis and methanogenesis. The main advantage of the two-stage system is the greater biological stability. In multi-stages digestion, a distinction must be done between the reactors with and without a biomass retention scheme in the second stage. The aim of biomass retention is to achieve high cell densities of methane-forming. There are two ways to achieve biomass retention. The first one is to rise the solid content in the reactor by coupling the hydraulic and solid retention time. The second one is attached growth, known as fixed film reaction. The microbes are attached to an inert medium such as rock or plastic in the reactor [35].

2.3.2.5. BATCH processes

In BATCH processes digester is filled once with organic matter having high total solid content (30-40% TS). The process works for subsequent stages. There is at first a hydrolytic and acidogenic stage, and then volatile fatty acids are processed in methane.

There are three plant designs:

- single stage;
- sequential stages;
- hybrid BATCH-UASB (Up-flow Anaerobic Sludge Blanket reactor).

In the single-stage plant the leachate is re-circulated at the top of the reactor, which is equivalent to a partial mixing.

The sequential stages system includes two or more reactors. The leachate from the first reactor, containing fresh waste, is re-circulated to the second reactor, containing stabilised waste and vice versa.

In the third type process the leachate produced in the digestion reactor goes to the Up-flow Anaerobic Sludge Blanket (UASB).

Batch processes are technically simple, less expensive than other processes and more robust. They work with an organic loading rate of 3-5 kgVS/m³d in mesophilic and thermophilic conditions, with biogas production of about 70 m³/t of waste [36].

Chapter 3. Fluidised Bed Gasification Model and Simulations

3.1. Gasification process

As said in Chapter 2 biomass gasification is a thermo-chemical conversion process, which utilizes oxidizing agents, to produce a fuel gas rich in hydrogen, carbon monoxide, methane; carbon dioxide, steam and nitrogen, in addition organic (TAR) and inorganic (H_2S , HCl , NH_3 , alkali metals) impurities and particulate are also obtained [38].

Analysing the small scale gasification power plants, initial attention has been given, to the different biomass feedstock suitable for gasification, focusing particularly on residues with low cost and low environmental impact. Using organic wastes as feedstock in high efficient micro-cogeneration plants would solve all the old-actual drawbacks associated to biomass utilization as energy source. For the selection of the feedstock to be used in gasification processes, the first criterion to be considered is the biomass availability on a significant scale (t/year). In every energy conversion process,

because of energy needs in terms of efficiency and power density, fuels with a high LHV are favourites. This means that biomass with lower humidity is preferable. Seasoning can reduce the moisture content or the excess of heat produced by the power plant could be exploited to dry the biomass in order to use also biomass with 50% of moisture. The density affects significantly any freight and storage.

Another important feature that must be considered is the size and shape of the biomass feeding the gasifier. Biomass must be processed to a uniform size or shape to feed into the gasifier at a consistent rate and to ensure homogeneous and efficient gasification. This can lead to significant costs for the shredding: chip size (1-2 cm) is at the moment the right compromise. The chemical composition (C, H, O, N, S, Cl) is another important aspect that must be considered [1,2].

Finally, ash and TAR contents are one of the main obstacles to economical and viable applications of biomass gasification technologies. Fuel with a high ash content require greater attention because ash brings sintering, agglomeration, deposition, erosion and corrosion problems. Furthermore they are elutriated by the produced gas, thus more the ash content is and much more problematic will be the gas cleaning system. TAR condenses at high temperature, causing clogging and damage to the downstream equipment. To sum up, the most suitable biomass for gasification must have availability on significant scale (t/year) and a good physical (low water content and high bulk density) and chemical characteristics (high Caloric Value, high volatile substances, low ash, high Carbon to Nitrogen ratio, low Chlorine and Sulphur content).

As said above (see also Chapter 2) gasification is a process that converts biomass through partial oxidation in syngas. The oxidant is the main parameter affecting the syngas composition, as shown in Table 3.1. Air is the most used gasifying agent, due to the great availability and zero cost, but the large amount of nitrogen not only requires higher power on blowers and bigger equipment, but especially lowers the heating value of the syngas produced. Pure O₂, avoiding the nitrogen content, increases the syngas heating value but also the operating costs due to the O₂ production. Steam, due to the great availability and about zero cost of water, increases the heating value and H₂ content of syngas, and can be produced using the excess of heat of the power plant [39]. Steam or CO₂ requires heat supply for the endothermic gasification reactions. This can be done indirectly, circulating a hot material or using heat

exchangers, or directly, feeding the gasifier via also air [40] or O₂ [41] to partially burn the biomass. The hot material in fixed bed has to go mechanically from the combustion to the gasification reactor; meanwhile in fluidised bed, the material can circulate via the different pressure/bed height. In any case, the exhaust fumes do not come in contact with the produced gases, which so have high heating value.

Table 3.1. Syngas composition with different oxidant [42,43]

Oxidant	Composition (vol%)					LHV(MJ/Nm ³)
	H ₂	CO	CO ₂	CH ₄	N ₂	
Air	9÷10	12÷15	14÷17	2÷4	56÷59	3÷6
Oxygen	30÷34	30÷37	25÷29	4÷6	-	10÷15
Steam/CO ₂	24÷50	30÷45	10÷19	5÷12	-	12÷20

Conventional small-to-medium scale gasification technologies utilize fixed bed reactors and air as gasification medium. This results in low conversion efficiency and in a syngas with a poor hydrogen fraction, because nitrogen contained in the gasification medium dilutes the syngas and its purification requires higher energy consumption. A possible solution to reduce the amount of N₂ in the produced gas is biomass gasification with oxygen and steam [41]. Nevertheless, cost of oxygen – today especially used in coal gasification [44] – is still too high for a feasible application in small scale plants [31,45–47]. A steam blown indirect heated biomass gasifier, as the one studied in this work, avoids problems caused by air producing a gas with high calorific value (12-14 MJ/Nm³) and high content of hydrogen [31,48], although the plant complexity increases owing to the additional combustor and the additional heat recirculation system between combustor and gasifier.

Gasification is followed by gas cleaning processes as filtration, scrubbing, reforming, cracking, etc. [48–50] (see Paragraph 3.3). Filtration and scrubbing at low temperature are at the moment the most used technologies. They make available a gas at temperature close to ambient. As a consequence the further hydrogen purification steps have low thermal efficiency because additional energy sources or extremely complex heat recovery would be necessary to re-heat syngas for the subsequent gas upgrading by high temperature processes as reforming and cracking [51,52]. Hot gas cleaning and conditioning methods, as the one here analysed, offer several advantages, such as thermal integration with gasification reactor, high TAR conversion and hydrogen rich

syngas production. The use of calcined dolomite, limestone and magnetite has been found able to increase the gas hydrogen content [53] even if they are not sufficient to produce a tar-free syngas. Catalytic filters have been proposed as an alternative to be coupled to biomass gasification processes [54,55] and can be integrated directly in the freeboard of the fluidized bed reactor, as in UNIQUE concept [56]. Such configuration produces a syngas free of TARs and sulphur compounds and allows a remarkable plant simplification and reduction of costs [56–58].

3.2. Process parameters

As mentioned before the main parameters are the fuel and oxidant quantity and physical and chemical composition; the process temperature; the residence time. The biomass composition influences the syngas composition and therefore LHV and chemical efficiency, defined by the following formula (3.1):

$$m_{chem} = \frac{m_c * LHV_c}{m_b * LHV_b} \quad (3.1)$$

Where m_c is the produced fuel, LHV_c is the fuel LHV, m_b is the input biomass and LHV_b is the biomass LHV. The second important parameter is the oxidant/biomass ratio, defined by the following formula (3.2):

$$\frac{O}{B} = \frac{\frac{kg}{h} \text{ of oxidant and water in biomass}}{\frac{kg}{h} \text{ of dry biomass}} \quad (3.2)$$

The equivalent ratio (ER) is the ratio between the amount of oxidizing agent used and the stoichiometric amount (the theoretical amount of any oxidizing agent required to burn the fuel completely). Thus generally the ER is used (always less than 1 in a gasification process) instead of the oxidant/biomass ratio but, using steam as oxidant, is common used the steam to biomass ratio. The LHV of the produced gas depends on the presence of H_2 , CH_4 and CO . The concentrations of these species in the output gas varies, varying temperature and ER, e.g. increasing temperature and S/B (in case the oxidant is steam) CH_4 decreases, instead H_2 and CO increase. In a thermochemical process a low temperature induces slow conversion processes, low conversions, and a greater production of CH_4 and CO_2 to the detriment of H_2 and CO . To achieve a high carbon conversion of the biomass and low tar content, a high operating temperature (above $800^\circ C$) in the gasifier is preferred. Yu et al. [59]

demonstrated that an increasing temperature promotes the formation of gaseous products at the expense of total tar. More than 40% reduction in tar yield was reported when the temperature was risen from 700°C to 900°C. Narvaez et al. [60] demonstrated that changing the bed temperature of the bubbling fluidized bed from 700°C to 850°C there was a drastic decrease (about 74% less) in tar content. According to Kinoshita et al. [61] tar yield and tar concentration decreases as the ER increases because of more availability of oxygen to react in the pyrolysis zone. This effect of ER is more significant at higher temperature. If the ER value is high, low concentrations of H₂, CO and higher CO₂ content in the produced gas are obtained. The residence time, given by the length of the reactor and the gas velocity ratio, influences gas composition and carbon conversion. In general increasing the residence time (less than 20 s), carbon conversion, gas yield, and H₂ and CO concentrations increase, while CH₄ and CO₂ content decrease. The residence time has little influence on the tar yield, but it significantly influences the tar composition [61].

3.3. Gas conditioning technologies

A clean-up – gas conditioning system is always necessary before using the produced gas into a power system. These systems normally have encumbrance and cost even greater the gasifier unit, thus they can be regarded as the unavoidable secondary unit in a gasification power plant. The gas conditioning technologies can be primarily divided following the physical apparatus where they are applied: downstream (secondary methods) or inside (primary methods) the gasifier. The secondary methods can be subdivided into two main categories based on the working temperature: cold and hot methods. The cold methods are mainly divided in “dry” methods (bag and sand filter) and “wet” methods (scrubber). The first one works at temperature of about 150-250°C. They have an efficiency of about 99% to separate the particulate, and about 20-80% (depends on temperature, active filter surface) for TAR separation. In the scrubber the gas cools down to 25-55°C, encountering cold water jet. In this way the scrubber removes particulate, TAR and nitrogen compounds. The disadvantage of this technology is the gas cooling and a water treatment downstream system. The water treatment can be avoided using vegetable oil or biodiesel or other TAR solvents instead of water, in order to not only increase the TAR removal but especially feed the gasifier

with these fuels avoiding the treatment and guarantee the heat supply for the gasification reactions. The first stage of the hot methods consists of a cyclone, which removes all the char and part of the particulate, using centrifugal and gravity force, then there are systems to remove TAR and the remaining particulate. The cyclone is present in all the fluidised bed reactors, and it works in a wide temperature spectrum. In general the cyclone can remove over the 90% of particles with diameter upper than 5 μm , it is partially efficient with the particle size between 1 and 5 μm , and it is ineffective for particles with diameter lower than 1 μm . The TAR cracking is used to remove TARs and to break down the alkali. The system consists in the introduction of a catalytic material into a secondary reactor. TARs and alkali condense on the catalyst surface which recirculating in the combustion zone burn the TARs. The high temperature filters separate, through adsorption, sulphur and chlorine compounds and filter fine particles, and they can be ceramic or metallic. The primary methods include gasifier modifications, optimization of operating parameters and the use of bed additive/catalyst/sorbent (e.g. dolomite, etc.) [62–65]. Regarding the catalyst more used in TAR reduction, there are Ni-based catalysts, calcined dolomites, magnetite, and olivine [62]. The catalysts reduce TAR production and influence the gas composition. The use of catalytic materials during biomass gasification promotes the char gasification, changes the product gas composition and reduces the TAR yield. Dolomite is the most popular and mostly studied in-bed additive [66]. Corella et al. [60] reported that the use of calcined dolomite inside the gasifier could decrease the TAR amount from 6,5 (without dolomite) to 1,3 %wt. An alternative can be olivine that is advantageous in terms of its attrition resistance over that of dolomite. Rapagnà et al. [31] investigated the catalytic activity of olivine and observed a TAR reduction (more than 90%). Other catalysts very used are the Ni-based catalysts. The major problem with Ni-based catalysts is fast deactivation due to carbon deposition on catalyst, but these problems can be avoided increasing the temperature. Thus introducing a catalyst in the bed material during gasification there are a change in product gas distribution, a decrease in TAR amount, an increase in hydrogen and CO_2 production, and a decrease of CO.

3.4. Modelling of the gasifier process

Among renewable energy sources hydrogen, as a clean energy vector, is one of the most promising options, because it can be used in various applications as fuel cells, internal combustion engines, transportation and for commercial and residential uses [67–70]. It is produced especially from fossil fuels [71], in particular by natural gas steam reforming, but a more economic process is waste biomass gasification [5,7,8]. In particular, small scale applications are very interesting because follow the low energy density and perishability of this fuel exploiting the biomass directly *in loco* avoiding disposal costs, but efficient and reliable systems have still to be developed.

The plant analysed in this research is mainly composed of bubbling fluidised bed gasifier with catalytic filter candles, Water Gas Shift (WGS) and Pressure Swing Adsorption (PSA). WGS and PSA, to further increase the hydrogen content and to separate H_2 from residual gases respectively, have been added in order to produce hydrogen fuel cells grade.

Today the industrial implementation of WGS takes place usually in a series of adiabatic converters where the effluent is converted in two steps with the second one at a significant lower temperature in order to shift the equilibrium towards the hydrogen product. Conventional WGS reactors are used for large scale application and operate at high pressure and thus they are not suitable to be coupled with atmospheric pressure gasification (suitable for small scale applications). During the UNIfHY project [72] a WGS reactor operating at atmospheric pressure with catalysts impregnated and supported on ceramic foams, to increase the efficiency of the gas-solid (catalytic surface area) contact, has been realized. The hydrogen rich gas at the outlet of WGS reactor (WGSR) is cooled down and then compressed to feed a PSA unit, which operates at relatively low pressure, to separate H_2 from residual gases producing hydrogen PEFC (Proton Exchange membrane Fuel Cell or PEMFC) grade.

The studied gasifier is based on UNIQUE concept [56], consisting in a compact gasifier integrating into single reactor vessel both the fluidised bed steam gasification of biomass and the hot gas cleaning system, by means of a bundle of ceramic filter candles operating at high temperature in the gasifier freeboard. Such a configuration produces a syngas free of TAR and sulphur compounds and allows a remarkable plant simplification and reduction of costs [56,58,73]. In these years a model capable of

predicting the performance of a steam blown fluidised bed biomass gasifier during steady state operation has been developed and validated experimentally. This model has been utilized for the simulations of a pilot scale steam fluidised bed gasifier (1 MW_{th}) fed with different biomass feedstock. The input variables of the computer program included steam flow rate and steam to biomass ratio. Among biomass, pine wood has been chosen as feedstock in the model development and validation. The model includes the hydrodynamics, transport and thermodynamic properties of fluidized bed composed of olivine sand. The hydrodynamic model is based on the two phase theory of fluidisation where the fluidised bed consists of two regions, bubble and emulsion, interacting with each other through one interchange mass transfer coefficient of gas, k_{be} . The properties of the fluidised bed like bubble gas ascend velocity and bubble diameter along the reactor axis were calculated using the typical correlations of the two phase theory of fluidisation. The chemical model is based on the kinetic equations for the heterogeneous and homogenous reactions solved together with mass and heat balances. The gasifier model for the simulation receives as input the results of the pyrolysis tests products because the biomass pyrolysis is the first step of the thermochemical process taking place in a fluidised bed gasifier, and it influences strongly the final produced gas composition as well as tar (heavy organics) production.

The analysis is based on a gasifier model that was previously developed [74]. Initially [74] only Naphthalene was chosen as TAR representative, while subsequently [39] TARs were divided in 4 main classes: Benzene, Toluene (1-ring), Phenol, Naphthalene (2-rings), Anthracene (3-rings), Pyrene (4-rings) aiming at improving the accuracy of the model. In the model in order to get realistic values for the pyrolysis products, experimental tests on a bench scale fluidised bed reactor were carried out in the temperatures range adopted for the simulation (750-850°C). The results of the tests include produced gas and TAR composition as well gas, TAR and char yield. Kinetics mechanisms adopted for the reactions are based on kinetic data published in literature. The derived ODE (Ordinary Differential Equation) for the gasifier model at steady state were implemented and solved with MATLAB.

Simulations of a bench scale reactor (8 cm internal diameter) were carried out varying steam/biomass ratio and operative temperature from 0,5 to 1 and from 750 to 850°C respectively.

Below the model, the plant for the tests and the results are described.

3.4.1. Gasification model

De-volatilization is a very complicated process and the distribution of products is particularly sensitive to the heat rate and the residence time in the reactor. The products of pyrolysis are composed of gaseous compounds (CO_2 , CO , H_2O , H_2 , and CH_4), light and heavy hydrocarbons (TAR) and char. In fluidised bed gasifiers, the pyrolysis reactions can be considered as instantaneous [75]. Then de-volatilization time was considered negligible. In order to get realistic values for the pyrolysis products and to validate the model of the biomass steam gasification, experimental tests on a bench scale fluidized bed reactor were carried out.

The model includes the hydrodynamics, transport and thermodynamic properties of fluidized bed composed of olivine sand.

The proposed gasification model was based on the following reactions:



The chemical model is based on the kinetic equations for reactions (R1-R9) solved together.

Kunii and Levenspiel [30] proposed an improved fluidised bed reactor model for various fluidisation conditions. The modelled fluidised bed is sketched (Figure 3.1). The

hydrodynamic model is based on the two phase theory of fluidisation where the fluidised bed consists of two regions, bubble and emulsion, interacting with each other through one interchange mass transfer coefficient of gas, k_{be} .

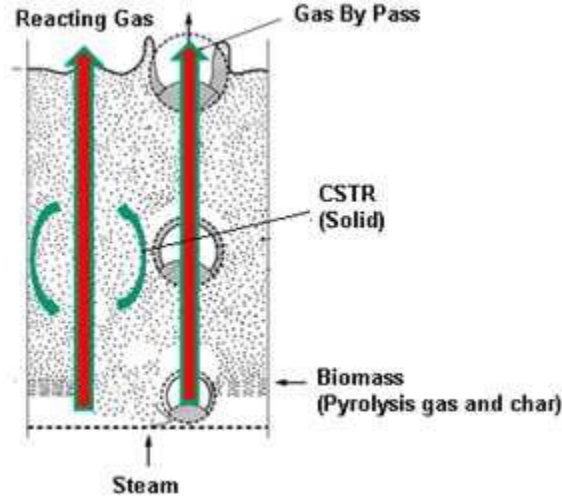


Figure 3.1. Kunii and Levenspiel fluidised bed reactor model

The model is PFR for gas in emulsion and in bubble phase and CSTR for solids in the emulsion phase. The hydrodynamic model was integrated with the chemical model. Several assumptions are employed. The wake and cloud regions are included in the emulsion phase, so only one dense phase is considered to be present in the gasifier and bubbles are assumed completely free of solid particles. In the emulsion phase, gas flows at the minimum fluidization velocity, u_{mf} (3.3).

$$u_{mf} = \left[(27.2^2 + 0.0408 \cdot Ar)^{0.5} - 27.2 \right] \cdot \frac{\mu}{d_p \rho_{gas}} \quad (3.3)$$

In the bubble phase, bubbles rise at the velocity u_b .

$$u_b(z) = 0.71 \sqrt{g d_b} + \left(\frac{Q(z)}{A} - u_{mf} \right) \quad (3.4)$$

The bubble diameter (d_b) at each bed height is calculated by Darton model [76].

$$d_b(z) = 0.54 \frac{(Q(z)/A - u_{mf})^{0.4}}{g^{0.2}} \left[z + 4 \sqrt{\frac{A}{N_{or}}} \right]^{0.8} \quad (3.5)$$

The volume fraction of bubbles in the bed is δ and that of the emulsion is $(1 - \delta)$.

$$\delta(z) = \frac{Q(z) / A - u_{mf}}{u_b(z)} \quad (3.6)$$

For gas exchange between bubbles and emulsion, the following transfer coefficient is considered [30]:

$$k_{be}(z) = \frac{u_{mf}}{4} + \sqrt{\frac{4\varepsilon_{mf} D_r u_b(z)}{\pi d_b(z)}} \quad (3.7)$$

where D_r is the average molar diffusion of all gaseous species with reference to steam.

Below, the continuity equations are reported for each species (except steam) in both gaseous phases, at steady state conditions, which combine the chemical and hydrodynamic model:

$$\frac{\partial}{\partial z} [(Q(z) - u_{mf} A) C_{bi}] = k_{be} A (C_{bi} - C_{ei}) \frac{6}{d_b} \delta + \varepsilon_{mf} A \delta \sum_{j,b} v_{ij} R_{bj}^g \quad (3.8)$$

$$\begin{aligned} \frac{\partial}{\partial z} [(u_{mf} \cdot A) \cdot C_{ei}] &= k_{be} A \cdot (C_{ei} - C_{bi}) \frac{6}{d_b} (1 - \delta) + A(1 - \delta) * \\ * &\left[(1 - \varepsilon_{mf}) \cdot \alpha_c \frac{\rho_c}{PM_c} \cdot \sum_{j,s} v_{ij} \cdot R_{ej}^c + \varepsilon_{mf} \cdot \sum_{j,e} v_{ij} \cdot R_{ej}^g + (1 - \varepsilon_{mf}) \cdot \alpha_{oliv} \cdot v_{ij} \cdot R_{ej}^{oliv} \right] \end{aligned} \quad (3.9)$$

Because of high temperature and low pressure in the gasifier, it was assumed that gaseous species obey the ideal gas law. Steam concentration was thus calculated as:

$$C_{H_2O} = \frac{P}{RT} - \sum_i C_i \quad (3.10)$$

As far as the solid phase is concerned, it is assumed that the net rate of char production by pyrolysis is equal to the sum of that withdrawn from the gasification zone and that consumed by gasification reactions, so to make the accumulation term in (3.11) always zero:

$$\frac{dm_c}{dt} = m_c^{in} - \dot{m}_c^{out} + \int_{V_{bed}} (1 - \delta)(1 - \varepsilon_{mf}) \alpha_c \rho_c \sum_j v_{ij} R_{ej}^c = 0 \quad (3.11)$$

where α_c (volumetric fraction of char in the bed composed of char and olivine) is defined as:

$$\alpha_c = \frac{m_c^{bed}}{\rho_c} \cdot \left(\frac{m_c^{bed}}{\rho_c} + \frac{m_{oliv}^{bed}}{\rho_{oliv}} \right)^{-1} \quad (3.12)$$

The solids circulation rate between gasification and combustion reactors should provide the heat flow necessary to support the gasification reactions that are globally endothermic:

$$\dot{m}_{oliv} c_{p,oliv} (T_{comb} - T_{gass}) = \Delta H_{tot,gass} \quad (3.13)$$

Where $\Delta H_{tot,gass}$ is the total enthalpy variation per unit time due to gasification, calculated from the knowledge of the outlet and the inlet species.

Solving the system equations equation (3.8), (3.9), (3.10), (3.12) and (3.13) (with the LHS term in (3.11) equal to 0) in the five variables, \dot{m}_{oliv} , α_c , C_{bi} , C_{ei} , m_c , by a trial and error procedure, it is possible to get the steady state solution corresponding to the gasifier operation.

The combustor was simulated by means of a stoichiometric reactor, considering the combustion reactions of char and additional fuel gas (the purge gas from PSA). They allow to heat up \dot{m}_{oliv} from T_{gass} to T_{comb} .

More details about the models can be found in the work of Bridgwater [38], Di Carlo et al. [40,74] and Orecchini et al. [77].

3.4.2. Experimental tests

High-temperature biomass pyrolysis is the first step of the thermochemical process taking place in a fluidised bed gasifier; it influences strongly the final produced gas composition as well as TAR (heavy organics) production. In the model, biomass devolatilization time was considered negligible, and in order to get realistic values for the pyrolysis products, experimental tests on a bench scale fluidised bed reactor were carried out at temperature near that adopted for the simulations (750-800°C). The results of the tests include produced gas and TAR composition as well gas, TAR and char yield. The results of the pyrolysis tests were integrated in the model as input for the

simulations. In order to consider TAR evolution in the gaseous stream during the gasification process different representative compounds were chosen: Benzene, Toluene (1-ring), Phenol, Naphthalene (2-rings). In Figure 3.2 is showed the physical test rig used.

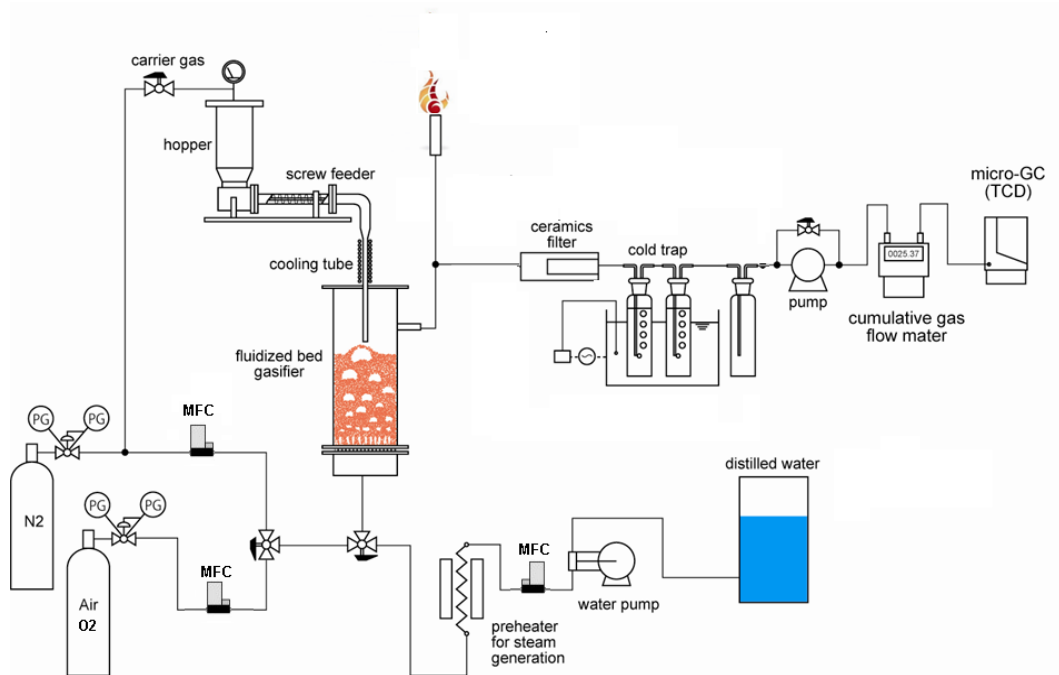


Figure 3.2. Experimental rig for pyrolysis and gasification tests

As shown in Figure 3.3, the physical test rig consists of the following elements.

- A pipeline for nitrogen, water, steam generation, air/oxygen and biomass feeding.
- A fluidised bed reactor (80 mm internal diameter) enclosed in a cylindrical electric furnace to maintain it at the desired temperature level. The bed consists of 350 μm olivine particles.
- A feeding system at the top of the reactor that enables the wood particles to be instantaneously dropped into the hot bed.
- A heated ceramic filter installed at the exit of the reactors for particulates removal.

- A cooling bath at ambient temperature and at $-20\text{ }^{\circ}\text{C}$ in order to sample TARs in 2-propanol filled impingement bottle. The tar is then analysed by Agilent GC-MS 5975C.

- A gas cumulative flow meter.

- A gas chromatography analysers Varian micro-GC to analyse the gas composition.

- A Mass Flow Controller (MFC) for each gas and water stream, in order to adjust the flow-rate at the desired value.

As mentioned above pine wood was chosen as biomass feedstock in the process. A preliminary biomass analysis is reported in Table 3.2, together with average particle size and density.

Table 3.2. Biomass Analysis

Type	Black Pine wood
Status	Raw
Moisture (wt %)	11
Ash (wt %)	0,5
Carbon (wt %)	49,1
Hydrogen (wt %)	6,36
Oxygen (wt %)	44,3
Particle size (mm)	1-2
Particle Density (kg/m ³)	510

Nitrogen was used as fluidizing media during pyrolysis tests. The composition of the produced gas was continuously monitored in terms of H_2 , CO, CO_2 and CH_4 . The mass flow of biomass was set equal to 170 g/h. Tests were carried out at 750°C . The time-averaged results are reported in Table 3.3.

Table 3.3. Average composition obtained from pyrolysis tests

Gas yield ($\text{Nm}^3/\text{kg}_{\text{bio}}(\text{as received})$)	0,81
Composition (% vol)	
H_2	32
CO	34
CH_4	19
CO_2	14

After pyrolysis, the residual air was used as fluidizing media, to burn residual char, allowing evaluating the CO and CO₂ produced in this process. Measuring the gas flow, it was then possible to estimate that the carbon (char) produced during pyrolysis tests was equal to 0,18 (g_{char}/g_{bio(ar)}).

Table 3.4 shows the produced TARs and their mass fractions, divided by 4 subgroups (Benzene, 1-ring, 2-rings, Oxygenated).

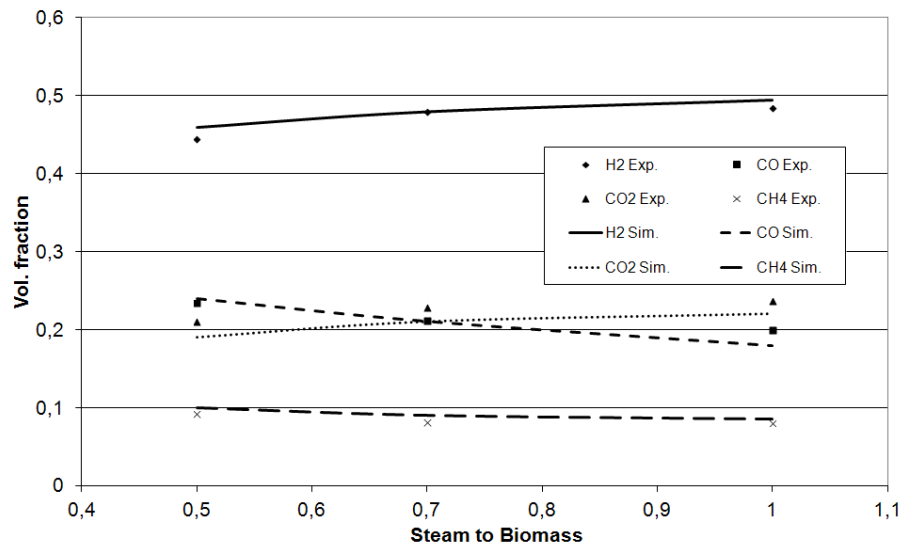
Table 3.4. Analysis of tar obtained from pyrolysis tests

Tar yields	108 g/Nm ³
tar /bio(dry ash free)	0,09 (g/g)
Composition (weight fraction)	
Benzene	0,44
Toluene+Styrene+Xylene (1-ring)	0,20
Naphthalene+Indene (2-rings)	0,21
Phenol (oxygenated)	0,07

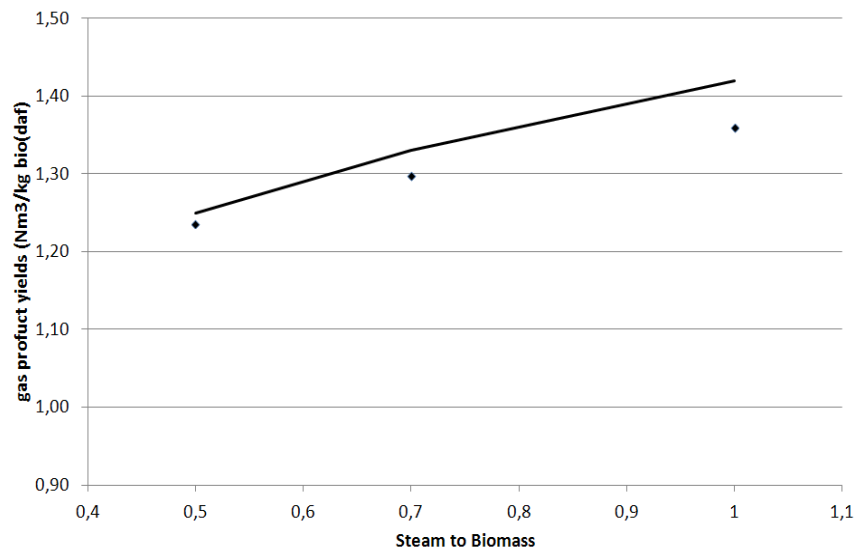
3.4.3. Model validation

The derived ODE equations for the gasifier model at steady state were implemented and solved with MATLAB. Simulations of a bench scale reactor (see Figure 3.2) were carried out varying steam to biomass ratio and operative temperature from 0,5 to 1 and from 750 to 850°C respectively. In order to validate the model, experimental tests were carried out at identical operative conditions, with the same test rig showed in Figure 3.2 but using steam as fluidisation gas.

Figure 3.3 shows, the gas composition (a) and the produced gas yields (b) at different S/B with a gasification temperature of 850°C obtained by the model and compared with experimental results.



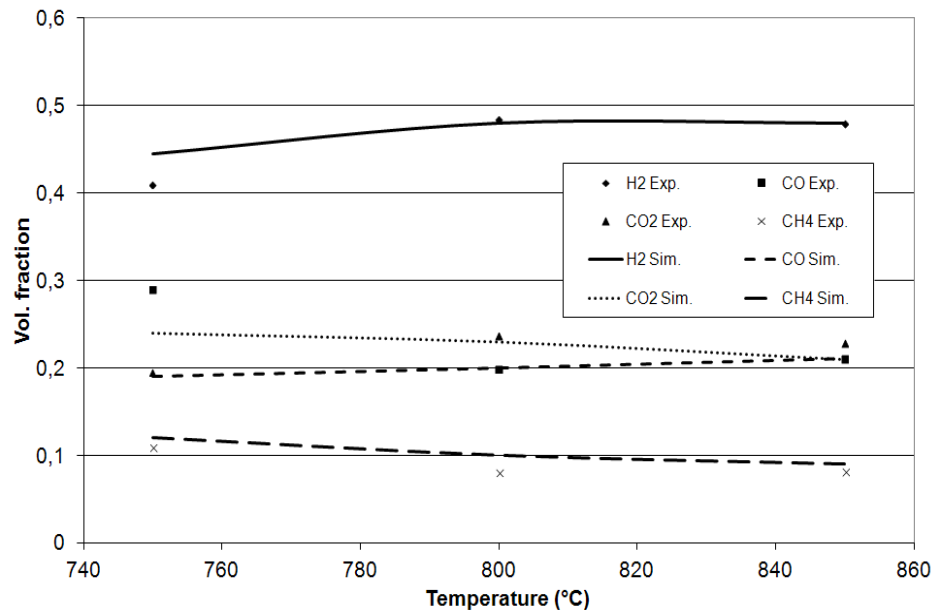
a)



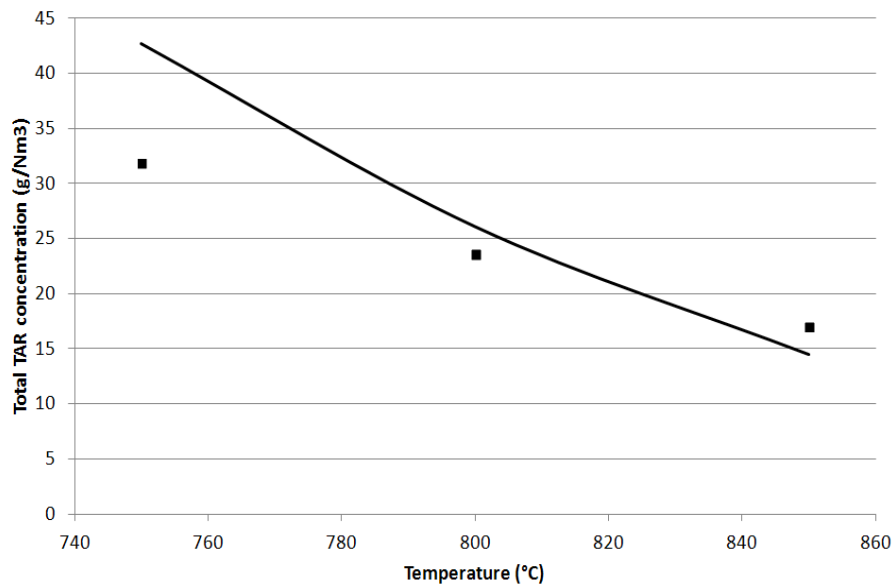
b)

Figure 3.3. a) gas composition and b) produced gas yields at different S/B with gasification $T = 850^\circ\text{C}$ obtained by the simulation (line), and compared with experimental results (dots)

Figure 3.4 instead shows the gas composition and the total TAR concentration in the gas varying temperature between 750 and 850°C maintaining the steam to biomass equal to $0,7$.



a)



b)

Figure 3.4. a) gas composition and b) total TAR concentration in the gas at different T with S/B=0,7 obtained by the simulation (line), and compared with experimental results (dots)

The comparison between the results of the model and those of experiments shows that model is fairly capable of predicting gas composition and production rate: in particular, the numerical and experimental results show a slight discrepancy lower than 2% for the gas composition and lower than 4% for produced gas yields.

Also about gas composition and total TAR concentration, the simulation results for composition are in good agreement with experimental results, the discrepancies is always lower than 2% for CO_2 , CH_4 . H_2 and CO show a bigger discrepancy at 750°C , but the error is always lower than 5%. Figure 3.4 (b) shows the comparison of the total TAR concentration obtained by simulation and by experiments. Also in this case the bigger error is at 750°C with a relative error of 11 %.

3.5. Simulations and Results

The simplified ChemCAD[®] flowchart used for the simulations is shown in Figure 3.5.

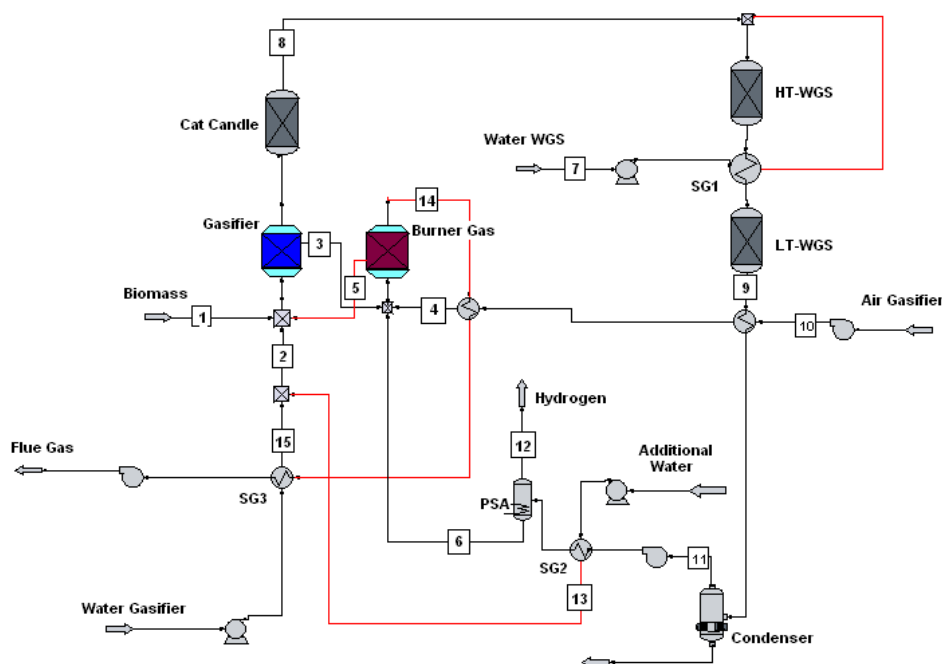


Figure 3.5. Flowchart (with thermal balance flows in red)

Biomass (stream 1) is fed into the gasification zone (Gasifier) and gasified with steam (stream 2). The bed material, together with some charcoal (stream 3), circulates to the combustion zone (Burner). The particulate solid in this zone is fluidised with hot air (stream 4) and the charcoal is burned, heating the bed material to a temperature higher than the inlet value. The hot bed material from the combustor is circulated back

to the gasifier (stream 5) supplying the thermal power needed for the gasification reactions. Off gas from PSA (stream 6) is also burned in the combustion zone to supply extra heat to the gasification process. Catalytic filter candles (Cat Candle) convert TARs to additional syngas and remove particulate directly in the freeboard of the gasifier. Injection of extra water/steam (stream 7) cools down the clean syngas (stream 8) and provides the necessary water content for HT-WGS (High Temperature WGS) and LT-WGS (Low Temperature WGS) reactors to increase the H_2 concentration in the gas. The steam required for this process is generated by a Steam Generator (SG1). The gas from LT-WGS (stream 9) is mainly composed of H_2 , CO_2 , residual steam and traces of CH_4 and CO. The gas (stream 9), first preheats the air (stream 10) supplied to the dual fluidised bed gasifier, and then passes through a condenser where residual steam is removed. The dry gas (stream 11) is compressed and cooled to ambient temperature to feed the PSA unit where pure H_2 is obtained (stream 12). The heat released by cooling stream 11 is used to generate extra-steam (SG2) for the gasification process (stream 13). The off gas (stream 6) is utilized in the gas burner as previously described. Finally, the heat content of the flue gas (stream 14) from the gas burner is used to enhance air pre-heating (stream 4) and to produce superheated steam (stream 15) for the gasifier in a steam generator (SG3).

The model described above has been used to simulate the steam-gasifier. The remaining components of the plant are simulated using conventional ChemCAD[®] blocks, in particular the catalytic reforming and the WGS reactors downstream of the gasifier were simulated using the Gibbs reactor computational routine, the burner was simulated via the stoichiometric reactor routine and PSA unit was simulated using the component separator routine with a specified separation efficiency for hydrogen, which was fixed according to experimental results [78].

In the simulations, biomass input flow and its moisture content have been fixed at 200 kg/h (1 MW_{th}) and 20%, respectively. Focusing on the hydrogen production, a sensitivity study was carried out by varying the following parameters:

- steam to biomass ratio (0,5; 1; 1,5; 2), to analyse possible improvements of the whole plant chemical efficiency when more steam is delivered to the gasifier.

Steam improves catalytic steam reforming and WGS reactions, however its production is consuming energy;

- gasifier operating temperature (750°C, 800°C, 850°C), in order to verify the influence of gasification temperature and its minimum level to reach the required chemical efficiency.

During the simulation the following main assumptions were done:

1. The temperature difference between the gasifier and the combustor chambers is set at 50°C [79], limiting in this way the temperature in the combustor to avoid thermal stresses, on one hand, and too high recirculation rates of the bed material, on the other hand.
2. The concentration of oxygen in the exhaust gas from combustor is imposed to be always higher than 6% (vol.) in order to guarantee low noxious emissions (CO, NO_x, etc.) from the combustion reactions.
3. The inlet temperature at the High Temperature WGS (HT-WGS) and Low Temperature WGS (LT-WGS) are set to 400°C and 200°C, respectively. In simulations, two WGS reactors are always considered, with the second at a significant lower temperature, in order to shift the equilibrium towards the favoured hydrogen product. With a single low temperature reactor, the reaction rate would be too low.
4. As reported in the paper by Rapagnà et al. [80], extremely high conversion of methane and TARs are expected with the process configuration chosen here; for this reason, the catalytic filter candles were considered able to enhance the reactions up to their thermodynamic equilibrium.
5. Residence time in the WGS reactors was assumed enough to justify a thermodynamic equilibrium approach [81].

The PSA unit was simulated by means of a component separator with a separation efficiency of 70%, fixed according to the results of the experimental activities carried out in the UNiFHY project [78] using a synthetic syngas to test the PSA unit. The permission to use and mention these data was kindly granted by HyGear research team (HYGEAR B.V. “Engineering for sustainable growth”).

These hypotheses influence considerably the results of the energy and mass balances. Assumptions 1 and 2 contribute to define the flow rate of bed material (including char) that should be circulated between the two reactor chambers of the gasifier and the air flow rate for the combustion process needed to assure steady state operation. As a consequence, they influence also the flow rate of the off gas stream recirculated from the PSA. The chemical energy content of the off gas should be used completely within the process to increase the overall efficiency, as shown below in details. Hypothesis 3 directly influences the amount of water/steam needed to cool down the syngas stream fed to WGS reactors and, what is more important, to enhance WGS reaction toward hydrogen production.

In what follows, the hydrogen energy ratio (HER) (3.14), referred to the single parts of the plant, has been calculated with reference to the Low Heating Value (LHV), and it corresponds to the hydrogen conversion chemical efficiency when the whole plant is considered:

$$\eta = \left(\frac{\dot{Q}_{H_2} * LHV_{H_2} * PM}{\dot{m}_{bio,daf} * LHV_{bio,daf}} \right) \quad (3.14)$$

Where \dot{Q}_{H_2} is the volumetric hydrogen flow produced by the plant, $\dot{m}_{bio,daf}$ is the mass flow rate of biomass dry and ash free feeding the plant and HV is the Heating Value (High or Low) of hydrogen and dry ash free biomass, respectively.

As mentioned above, biomass feedstock and its moisture content are fixed, so steam flow rate has been changed according to the value considered for the steam to biomass ratio (S/B). Under these conditions, the simulations show how the results depend on this ratio and on the gasification temperature. Figure 3.6 shows that the hydrogen energy ratio (HER) of the gasifier at each gasification temperature level first increases and then decreases when S/B is increased. This trend is clearly shown on the Figure at 750 and 800°C and it is probably present also at 850°C although the maximum would appear in this case for higher steam to biomass ratio. At 750°C and 800°C the maximum HER of the gasifier corresponds to S/B=1,5 (37,5% and 41%, respectively). As it is known from the literature [75,82,83], the hydrogen yield increases with the gasification temperature and with the steam to biomass ratio. The gas yield calculated at T=800°C and S/B=1,5 is 1,3 Nm³/kg.

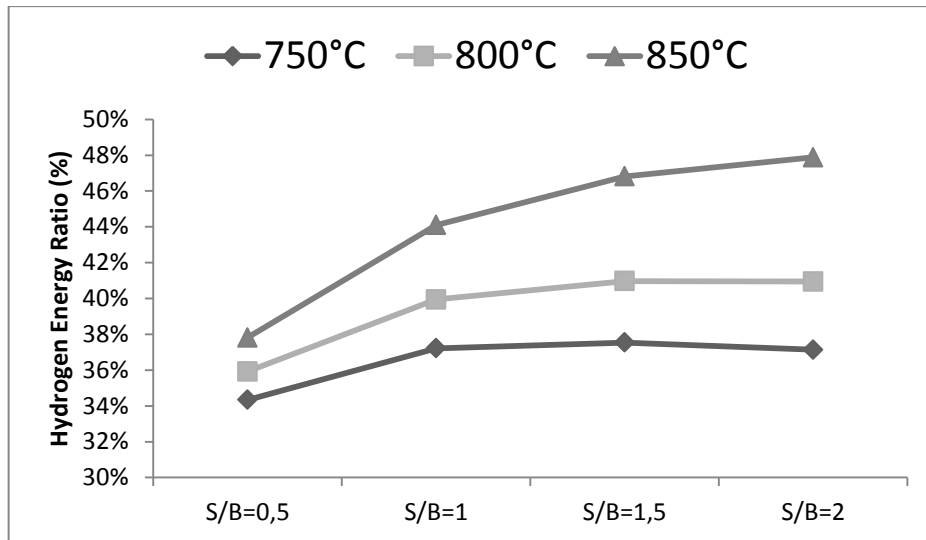


Figure 3.6. Hydrogen energy ratio at the outlet of the gasifier.

The catalytic filter candles (Figure 3.7) improve the HER. This is because methane steam reforming, tar steam reforming and water gas shift reactions occur inside the candles [80]. The steam reforming reactions are enhanced at high temperature, whereas the water gas shift thermodynamic equilibrium is more favourable at low temperature.

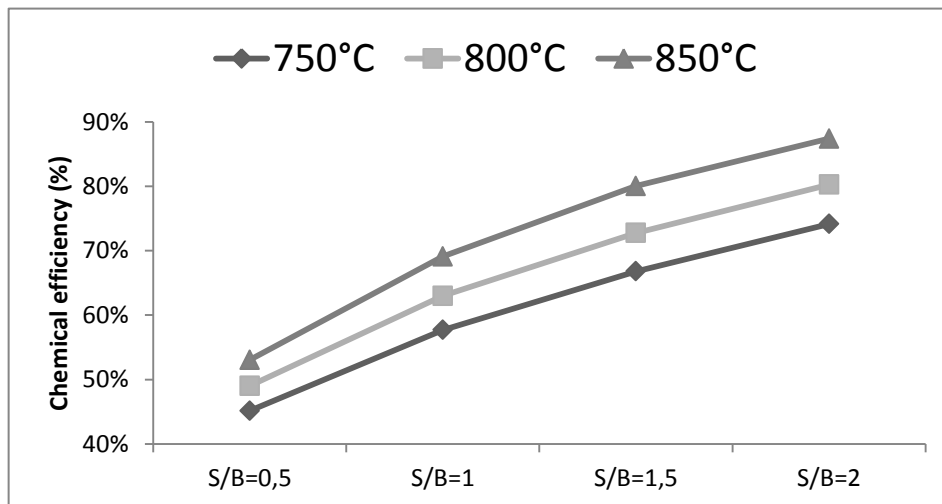


Figure 3.7. Hydrogen energy ratio at the outlet of the catalytic filter candle

Therefore, as shown in Table 3.5, gas quality and gas yield ($1,9 \text{ Nm}^3/\text{kg}$) increase. Increasing the steam to biomass ratio reduces the methane concentration and

also the temperature at the candle outlet, because endothermic reforming reactions occur inside the candles. However, the carbon monoxide concentration increases less than proportionally to the methane reacted: this behaviour is expected, because inside the candles the water gas shift reaction also occurs, which is enhanced at low temperature, whereas methane is preferentially reformed when the operating temperature is increased. Tar concentrations are predicted to be negligible in the candles output.

Table 3.5. Concentrations of CH₄, CO, CO₂ and Temperature at the outlet of the gasifier and of the catalytic filter candle, respectively, and at various temperature levels

T=750°C		S/B			
(mol/h)	0,5	1	1,5	2	
CH ₄ out gasifier	139	136	136	136	
CH ₄ out candle	123	100	79	58	
CO out gasifier	201	128	92	71	
CO out candle	227	148	110	91	
CO ₂ out gasifier	204	263	287	297	
CO ₂ out candle	246	355	419	462	
T out candle	612	584	567	559	

T=800°C		S/B			
(mol/h)	0,5	1	1,5	2	
CH ₄ out gasifier	138	134	134	135	
CH ₄ out candle	97	71	49	31	
CO out gasifier	242	166	124	99	
CO out candle	263	185	145	123	
CO ₂ out gasifier	191	260	292	308	
CO ₂ out candle	232	349	420	468	
T out candle	630	606	594	590	

T=850°C		S/B			
(mol/h)	0,5	1	1,5	2	
CH ₄ out gasifier	138	134	133	134	
CH ₄ out candle	81	50	28	13	
CO out gasifier	298	230	184	153	
CO out candle	324	252	210	184	
CO ₂ out gasifier	179	261	307	334	
CO ₂ out candle	220	346	427	480	
T out candle	650	634	629	634	

At the inlet of the HT-WGS reactor, water has been added in different concentrations, as functions of temperature and steam to biomass gasification ratio. In this way, the hydrogen conversion efficiency was further improved by increasing the HER from 87%, at the catalytic filter candle outlet, to 99%, at the WGS reactors outlet, as obtained by simulations at 850°C and S/B=2. The dry produced gas from the WGS reactors (at 800°C and S/B=0,5) is characterized by a calculated composition of 62% H₂, 6% CH₄, 0,4% CO and 31% CO₂ (by volume), in line with results reported in the literature [84] with a corresponding gas yield of 1,8 Nm³/kg daf biomass. The aim of these simulations is to check the possibility to reach a hydrogen conversion chemical efficiency of about 66% without input of auxiliary fuel, by exploiting off gas and waste heat recovery loops. The hydrogen chemical efficiency, calculated by (3.14), of the whole plant is shown below (Figure 3.8) as a function of the steam to biomass ratio and varying the operating temperature [84]. The PSA unit is assumed to operate at a pressure of 7 bar.

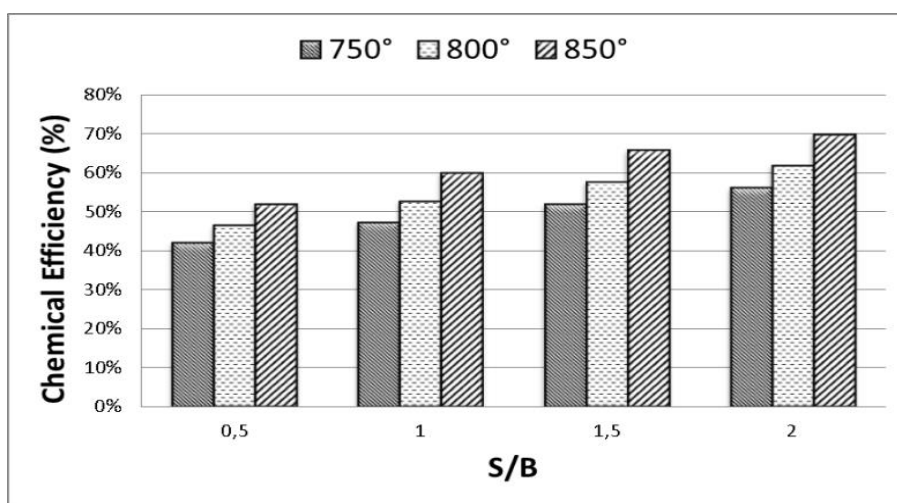


Figure 3.8. Chemical efficiency as a function of S/B

The hydrogen chemical efficiency always increases with the gasification temperature: at 850°C the gasification reaction rates are greater than at lower temperature. Moreover, thanks to the higher S/B, more steam can react in the different reaction processes, and this produces more hydrogen. The maximum chemical efficiency is reached at S/B=2 and temperature level of 850°C, with a value of about 70%, somewhat above the EU target of 66%. Koroneos et al. [84] have obtained an

hydrogen chemical efficiency of 47% with a PSA separation recovery of 77%, in line with about 46% obtained in the simulation at $T=800^{\circ}\text{C}$, $S/B=0,5$.

The above result is obtainable without using auxiliary fuel in addition to biomass feedstock, by feeding the whole off gas from PSA unit to the combustion chamber of the gasifier. Figure 3.9 illustrates these estimates, showing the calculated percentage of off gas recirculation to the combustor required to operate the process at steady state under different gasification conditions (temperature and steam to biomass ratio).

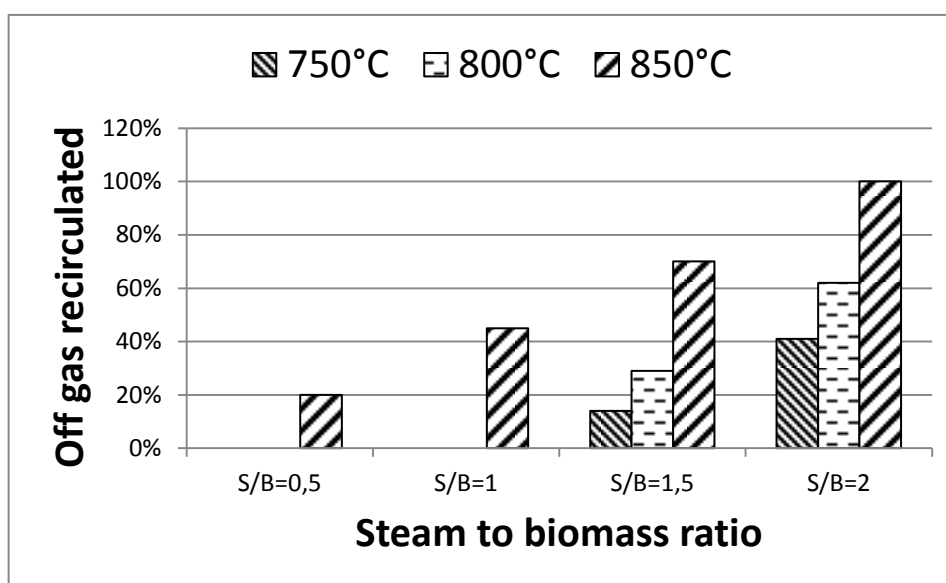


Figure 3.9. Off gas recirculated in the combustor as a function of S/B

The percentage of recirculated off gas always increases when increasing S/B and temperature. This occurs because increasing S/B and temperature, the combustor needs a higher flow rate of fuel to sustain the corresponding gasification conditions.

As it is shown in the Figure, in most operating conditions the off gas is recirculated to the combustor only in part, because its complete utilization would imply a power input surplus in both the gasifier and the combustor: its energy content is therefore available to be also exploited outside the conversion process. It should be considered here that the difference in temperature between the gasifier and the combustor has been set at 50°C , which implies a circulation of about 50 kg bed material per kg of dry biomass feedstock [79]. The off gas is totally recirculated only in the case of $S/B=2$ and $T=850^{\circ}\text{C}$.

As a result of these numerical simulations, the operating conditions needed to satisfy the hydrogen conversion efficiency target are identified: steam to biomass ratio of 2 and gasification temperature of 850°C. They allow reaching a plant chemical efficiency of about 70% under auto-thermal behaviour of the power plant.

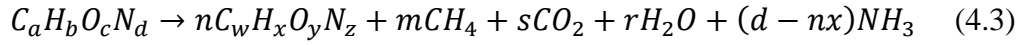
Chapter 4. Anaerobic Digestion

4.1. Process details

The biologic degradation of the organic matter in anaerobic condition produces different substances, especially two gases: methane and carbon dioxide. This process engages different microbial groups that interacts each other: hydrolitycs, acetogenic, homoacetogenic, and methanogens bacteria, which produce CO_2 and in particular methane, representing about 2/3 of the all biogas produced. The methanogens bacteria interest only the final position of the anaerobic process. Methane, that is not many soluble into the water, is in the gas phase, instead carbon dioxide is in gaseous and liquid phase. An example of an organic substrate anaerobic degradation is represented by the anaerobic digestion of the glucose. In a first phase it is converted in acetic acid and then in methane and CO_2 :



Considering composite compound, among the products of the anaerobic digestion there is also ammonia, which is originated from the protein demolition. For example in the case of a material with formula $C_aH_bO_cN_d$ the stoichiometric relation is:



With:

$$s = a - nw - m$$

$$r = c - ny - 2s$$

The composite material is decomposed with formation of methane, carbon dioxide, water and ammonia.

The operative temperature range of the anaerobic digestion is $-5 \div +70^\circ\text{C}$. However there are different species of microorganism that can be classified as a function of the optimal temperature range for their growth: psychrophilic ($T < 20^\circ\text{C}$), mesophilic ($T = 20^\circ\text{C} \div 40^\circ\text{C}$) and thermophilic bacteria ($T > 45^\circ\text{C}$).

4.2. Process stages

There are at least three bacterial species that take part into the Anaerobic Digestion (AD) process. In a first phase there is the hydrolysis of the complex substratum and the acidogenesis with the formation of volatile fatty acids, alcohols and ketones. After there is acetogenesis with the formation of acetic acid, carbon dioxide and hydrogen, and at the end methanogenesis with the formation of methane from acetic acid or by the reduction of carbon dioxide using hydrogen as co-substrate.

The flow chart of the process is shown in Figure 4.1.

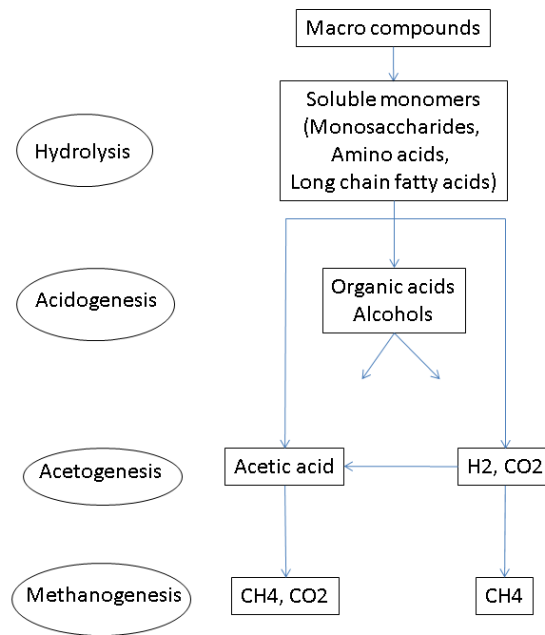


Figure 4.1. Anaerobic digestion flow chart.

Hydrolysis and acidogenesis

The first step is the degradation of the complex organic compounds, as proteins, carbohydrates and lipids, and the formation of simplex compounds as amino acids (AA), monosaccharides (MS) and long chain fatty acids (LCFA). At the same time there is acidogenesis with the production of propionic, butyric and valeric acids (short chain fatty acids (SCFA), or volatile fatty acids (VFA)).

Acetogenesis

In this phase acetogenic bacteria produce in particular acetic acid, CO₂ and hydrogen. Angelidaki et al. [85] show two different mechanisms as a function of the LCFA or VFA degradation. In general LCFA have more than 5 carbon atoms. During the production of the acetic acid, the presence of hydrogen has an inhibition function. But if hydrogen is at low concentrations, thanks to the activity of the methanogens H₂ oxidants, the degradation of fatty acids to H₂ by acetogenic bacteria is more probable, even if the H₂ formation is energetically disadvantaged.

Methanogenesis

The production of methane represents the conclusion of the anaerobic process. Methane, in fact, is the unique non-reactive compound in the whole process and, in this way, it could be considered the final product. The methane production occurs in two different ways: one is the methanogenesis by hydrogenotrophic bacteria, which oxidise hydrogen; the other way is the formation of methane and CO₂ from acetic acid. The most methane production occurs in the last way.

4.2.1. Process kinetics

A more detailed description of different process phases has been reported below, according to the International Water Association (IWA) model of the AD (ADM1) [86]. Below the main values of the kinetic and stoichiometric parameters referred to the mesophilic temperature, which are frequently used in anaerobic digestion process, have been shown.

Hydrolysis

The most organic wastes are composed by particulate material which needs a first disintegration step in macro-molecules, as carbohydrates, proteins and lipids, followed by hydrolytic step that is the limiting step of the whole process. Hydrolysis products are monosaccharides, amino acids and long chain fatty acids (LCFA). The process is generally described by the first order kinetic [87]:

$$r=K \cdot X_s \quad (4.4)$$

where:

r = the substrate hydrolysis rate (g/m³d);

K = the maximum hydrolysis rate (1/d);

X_s = the substrate concentrations (g/m³).

In Table 4.1 suggested values by Vismara et al. [36] have been reported.

Table 4.1. Suggested values for K hydrolysis in mesophilic conditions, for a heterogeneous substrate [36].

	IWA (1/d)
Carbohydrates	0,25
Proteins	0,2
Lipids	0,1

The constant K depends on temperature according to the Arrhenius law:

$$K_T = K * e^{\frac{E_a}{R}(\frac{1}{T_1} - \frac{1}{T_2})} \quad (4.5)$$

Where:

K_T = the kinetic constant at operative temperature;

E_a = the activation free energy (J/mol);

R = the ideal gas constant (8,324 J/molK);

T_1 and T_2 = the initial and operative temperatures respectively.

The K value is also influenced by pH. For the substrate the optimum pH value is around the neutrality.

Acidogenesis

The products of this step are volatile fatty acids (VFA), acetic acid, H_2 and CO_2 . The VFA are butyric, propionic and valeric acids. In particular the products of carbohydrates and proteins degradation are fatty acids and acetate, and from the degradation of LCFA only acetate is produced. The acidogens bacteria growth is described by Monod equation:

$$\left(\frac{dX}{dt}\right) = \mu_{max} \frac{S}{K_S + S} I_1 X - k_d X \quad (4.6)$$

and the substrate degradation is described by:

$$r = k_{max} \frac{S}{K_S + S} X I_1 \quad (4.7)$$

where:

μ_{max} = the maximum biomass growth rate (1/d);

S = the monosaccharides and amino acids concentration (g/m³);

X = biomass concentration (g/m³);

K_S = the semi-saturation constant (kg/m³);

k_{max} = the maximum substrate degradation rate (1/d, calculated as μ_{max}/Y , where Y is the specific growth of the bacteria);

k_d = bacteria death rate;

I_I = element that takes into account the inhibition [86].

Table 4.2. Kinetic constant for acidogenesis in mesophilic conditions, for heterogeneous substrate [36].

	Monosaccharides	Amino acids
μ_{max} (1/d)	3	4
k_{max} (1/d)	30	50
K_S (kg/m ³)	0,5	0,3
Y	0,10	0,08
K_d (1/d)	0,02	0,02

Acetogenesis

Acetogenesis is the process by which LCFA and VFA are degraded producing acetate, CO₂ and H₂. There are two different acetogenic bacteria, the first one utilizes VFA, the second one the LCFA, and the Monod kinetic (4.6) describes their growth. The fatty acids conversion in acetate represents an important step of the AD process, and the presence of high fatty acids concentration indicates an unbalanced process. About butyric and valeric acid degradation, IWA task group indicates a competitive effect among them:

$$r_{bu} = k_{max} \frac{S_{bu}}{K_S S_{bu}} X \frac{1}{1 + \frac{S_{va}}{S_{bu}}} I_2 \quad (4.8)$$

where:

r_{bu} = butyric degradation;

S_{bu} and S_{va} = butyric and valeric acid concentration respectively (g/m³).

The kinetic for the valeric acid is the same with inverted subscripts. In Table 4.3 kinetic constants are shown.

Table 4.3. Kinetic constant for acetogenesis in mesophilic conditions, for heterogeneous substrate [36].

	LCFA	Propionic acid	Butyric and Valeric acid
μ_{\max}	0,36	0,52	1,2
k_{\max}	6	13	20
K_s	0,4	0,3	0,3
Y	0,06	0,04	0,06
k_d	0,02	0,02	0,2

Hydrogen-Utilising Methanogenesis

The representative reaction for the hydrogen-utilising methanogenesis is:



Bacteria growth rate is expressed by Monod equation (4.6), instead for the death rate of substrate (hydrogen) is utilized equation (4.7). In Table 4.4 kinetic constants are reported.

Table 4.4. Kinetic constant for hydrogen-utilising methanogenesis in mesophilic conditions, for heterogeneous substrate [36].

μ_{\max}	2,1
k_{\max}	35
K_s	$0,025 \cdot 10^{-3}$
Y	0,06
k_d	0,02

Aceticlastic Methanogenesis

In the major methanogenic step, acetate is cleaved to form methane and CO_2 :



The bacteria growth rate, also in this case, is represented by Monod equation (4.6) (in this case S in the acetic acid).

Table 4.5. Kinetic constant for aceticlastic methanogenesis in mesophilic conditions, for heterogeneous substrate [36].

μ_{\max}	2,1
k_{\max}	35
K_s	$0,025 \cdot 10^{-3}$
Y	0,06
k_d	0,02

4.3. Conditions and variables influencing anaerobic digestion

There are several conditions and parameters that must be controlled to enhance microbial activity increasing AD efficiency. Presence of adequate quantities of nitrogen, micronutrients, and water is essential for the anaerobic digestion to generate methane-rich biogas [88]. In particular is very important to maintain optimal conditions for the growth of the methanogens bacteria [89]. The presence of some substances or not suitable parameters could inhibit or limit the process. Stability parameters permit to dimension and manage the AD process. In particular these parameters fix the retention time of the mass into the reactor, the microorganism concentration and the biogas production rate. Feedstock can be defined by UNI EN 10458:2011:

- Total Solids (TS);
- Total Volatile Solids (TVS);
- Chemical Oxygen Demand (COD);
- Biochemical Oxygen Demand after 5 days (BOD₅).

Total Solids (TS) represent dry matter content of a sample and it is obtained with sample drying at 105°C until mass constancy is achieved. TS are the organic matter plus inert fraction. Inert fraction (% of dry matter) is the residual after combustion at 550°C. Organic matter (% of dry matter) is the complement to 1 of the inert fraction and it includes both Volatile Organic Matter, which become gas, and Fix Organic Matter.

The Total Volatile Solids (TVS) are the dry fraction which volatilizes after combustion at 540-580°C. Volatile Matter is about 70-80% of the total organic matter, and in general it is assumed equal to the organic matter, which is defined substrate.

COD represents oxygen quantity necessary for the chemical oxidation of the organic matter.

BOD₅ is the oxygen quantity consumed in 5 days for the biochemical oxidation of the sample.

Some parameters are discussed in the next paragraphs.

4.3.1. Temperature

Temperature has an important role on the anaerobic degradation reactions speed and completeness, and it selects specific bacteria that operate in the corresponding temperature range. There are three major operating ranges defined in anaerobic digestion [35] (Figure 4.2), referred to methanogens bacteria:

- Psychrophilic: 4-15°C;
- Mesophilic: 20-40°C, with optimum value at 35°C;
- Thermophilic: 45-70°C, with optimum value at 55°C.

In any range there is an increase in reaction rate, followed by a decrease with increasing temperature above optimum. Temperature oscillations have to be $\pm 3^\circ\text{C}$.

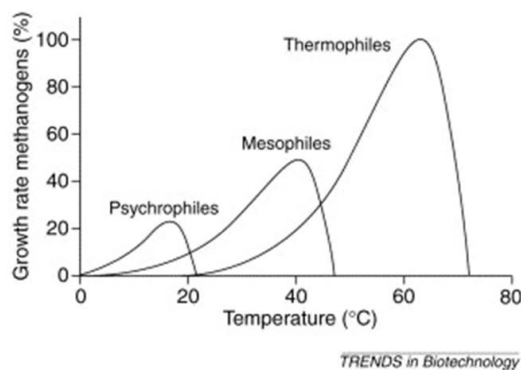


Figure 4.2. Effect of temperature on the growth rate of methanogens

Passing through psychrophilic to thermophilic range there is a decreasing of K_S , and therefore a faster degradation, but thermophilic digestion needs a higher heat input, which makes the process more problematic than mesophilic one.

4.3.2. pH

All bacterial groups depend on pH value, even if the most important effect is on the methanogenic bacteria. Acidogenesis and acetogenesis steps are favoured at acids pH, about 5-5,5, instead methanogenesis is favoured at neutrals pH, with optimum

values between 7 and 7,5 [90] [91]. In general a drop in pH and a rise in the proportion of CO₂ in the biogas are indicators of a disturbance in the digestion process. In such situations, reduction in pH can usually be controlled with the addition of lime [92]. In a real scale plants to prevent instabilities phenomena alkalinity to volatile fatty acids ratio should be controlled [36].

4.3.3. C/N ratio

Carbon to Nitrogen ratio (C/N) in the range of 16:1–25:1 is considered to be optimum for anaerobic digestion [88,93,94]. A high C/N ratio is an indication of a rapid consumption of nitrogen by methanogens and results in a lower gas production. Instead, a lower C/N ratio causes ammonia accumulation and a pH value exceeding 8,5, that is toxic for methanogens. An optimum C/N ratio can be achieved mixing waste of low and high C/N ratio [35].

4.3.4. Retention time

Retention time is the duration for which organic material (substrate) and microorganisms ('solids') must remain together in a digester to achieve the desired extent of degradation. Shorter is substrate retention time required to achieve this objective in an anaerobic reactor, more efficient is the reactor [88]. But to achieve low substrate retention times it is necessary to simultaneously achieve high microorganism retention time. The term commonly used to indicate substrate retention time is Hydraulic Retention Time (HRT). This is the time which an organic material spends in a digester. Solids Retention Time (SRT) is the duration for which active microorganisms reside in a digester.

At any given temperature, the microorganisms present in a digester can only consume a limited amount of food each day. Hence in order to digest a given quantity of substrate is necessary to supply adequate number of microorganisms. The ratio of the quantity of substrate to the quantity of bacteria available to consume that substrate is called the 'food-to-microorganism ratio' (F/M). This ratio is the controlling factor in all biological treatment processes. A lower than adequate F/M ratio will result in a greater percentage of the substrate being converted to biogas [88].

The only way in which F/M ratio can be kept adequately low is to keep high SRT. In conventional low-rate digesters and in the continuously stirred tank reactors (CSTRs) the solids pass out of the digesters at the same rate as the substrate. Afterwards in these systems $HRT = SRT$. Instead in high-rate digesters $SRT \gg HRT$, and typically SRT is about three times higher than the HRT [88].

The average HRT is defined as the ratio between the reactor volume and the feeding flow rate:

$$HRT = \frac{V}{Q} \quad (4.11)$$

Where:

HRT = average hydraulic retention time [d]

V = reactor volume [m^3]

Q = feeding flow rate [m^3/d].

4.3.5. Organic Loading Rate

The Organic Loading Rate (OLR) is the substrate in input at the reactor as a function of the reactor volume unit and of the time.

$$OLR = \frac{Q \cdot S}{V} \quad (4.12)$$

Where:

OLR = is the organic loading rate [kg_{vs}/m^3d]

Q = flow rate [m^3/d]

S = substrate concentration in the flow rate [kg/m^3]

V = reactor volume [m^3]

4.3.6. Mixing

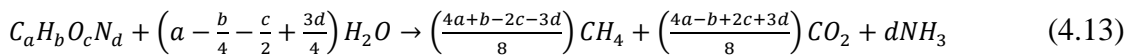
Mixing, within a digester, is required to maintain fluid homogeneity, improving the contact between micro-organism and substrate [35,88,95] Mixing also prevents the

formation of scum and avoids temperature gradients within the digester. However very rapid mixing can disrupt the bacterial community while too slow stirring can cause inadequate mixing [96]. The extent of mixing required is also dependent on the content of the digestion mixture, and in case of co-digestion the different feedstock should be mixed before entering the digester to ensure a sufficient homogeneity.

4.4. Bio-Methane Potential (BMP)

The anaerobic biodegradability evaluation permits to determine the feasibility of the anaerobic digestion process for a certain biomass. To predict biogas production of an organic substance, experimental tests must be done. In real conditions not all the organic content presents in the biomass is converted to biogas. In opportune conditions could be obtained conversions level up to 95% of the theoretical value. The real methane production, defined as Biochemical Methane Potential (BMP) is defined as the gas production that could be observed for a limitless degradation time. In real conditions degradation time is finite and methane production is evaluated by extrapolation of a methane production curve as a function of time. For this reason BMP is estimable only by experimental tests [36].

Sometimes biogas production is evaluated by parametric or semi-empiric formula. Biogas production and composition is related to the organic substrate composition and to its biodegradability in optimal conditions. If the elementary chemical composition of substrate is known, biogas composition is estimable by the following equation [36]:



where can be noticed that methane and carbon dioxide production is predominant relative to other gases.

Biogas production (G_{teor}) per degraded substrate unit (express as VS) is calculated by equation 4.14:

$$G_{teor} \left[\frac{m^3}{kg_{VS}} \right] = \frac{\left[\left(\frac{4a+b-2c-3d}{8} \right) + \left(\frac{4a-b+2c+3d}{8} \right) \right] * 22.414}{12a+b+16c+14d} = \frac{22.414a}{12a+b+16c+14d} \quad (4.14)$$

Theoretical methane volume is calculated as (4.15):

$$G_{teor,CH_4} \left[\frac{m^3}{kg_{VS}} \right] = \frac{\left(\frac{4a+b-2c-3d}{8} \right) * 22.414}{12a+b+16c+14d} \quad (4.15)$$

Methane fraction presents into the biogas is (4.16):

$$p_{CH_4} \left[\frac{m_{CH_4}^3}{m_{biogas}^3} \right] = \frac{G_{teor,CH_4}}{G_{teor}} = \frac{4a+b-2c-3d}{8a} \quad (4.16)$$

This calculation, however, does not consider the non-biodegradable substances into the organic matter. In this way the results can be considered as the upper limit of the methane production.

The best methodologies to know the BMP are based on experimental tests. In general the organic matter is considerate in contact with an inoculum in optimal conditions. The methodologies are a function of the reactor typology (test in BATCH, multi-BATCH, CSTR reactors), the measured component (reaction products, substrate), and the method (constant pressure, constant volume, gas-chromatography, alkalinity and heat for the reaction products, VS, COD, and specific molecules for the substrate).

In general BMP can be expressed by equation (4.17):

$$BMP \left[\frac{l_{CH_4}}{g_{VS}} \right] = \frac{\Sigma V_{CH_4} [l_{CH_4}]}{VS_S \left[\frac{g_{VS}}{l} \right] * V_S [l]} \quad (4.17)$$

where:

V_{CH_4} = produced methane volume;

VS_S = volatile solids in substrate;

V_S = substrate volume.

The measures generally used in laboratories are manometric and volumetric method.

4.4.1. Manometric method

Manometric methods use a constant volume BATCH reactor, in which the pressure, due to the production of the gas in the headspace, is valued by a pressure gauge (Figure 4.3).

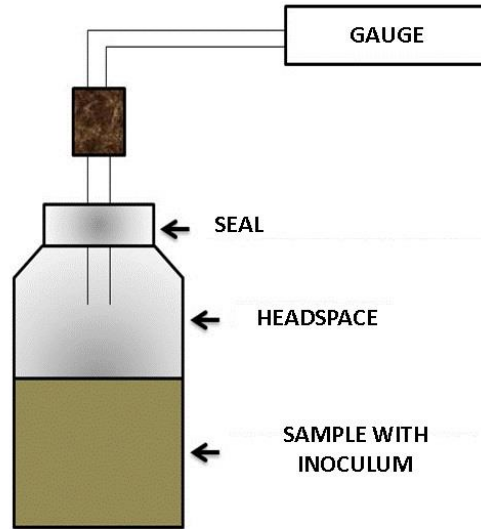


Figure 4.3. Scheme of manometric method.

Generally the produced gas is vented to avoid overpressure in the reactor and all the measures are conducted at constant temperature. Pressure trend over time is converted in biogas volume using the ideal gas law in the headspace [36] (4.18):

$$\frac{\Delta P}{P_{atm}} = \frac{\Delta V}{V_{free}} \text{ from which } \Delta V = \frac{\Delta P}{P_{atm}} * V_{free} \quad (4.18)$$

where:

ΔP = the pressure increase;

P_{atm} = atmospheric pressure;

ΔV = volume of the gas produced;

$V_{free} = V_{reactor} - V_{mix}$ is the volume of the headspace.

To determine BMP methane concentration into the biogas has been known. Biogas composition can be established by gas-chromatography.

4.4.2. Volumetric method

In volumetric methods the pressure is maintained constant, and the produced gas is vented from the reactor and sent to the measurement system. The easier system

consists to connect headspace with a graduated piston or a syringe. Piston motion permits to value the quantity of the produced gas [97]. Another measurement system is based on liquid movement: the gas is sent in a container where it moves a liquid with equivalent volume (eudiometer).

4.5. Laboratory plant

A mini-digester, presents in the CIRDER laboratory, has been used (Figure 4.4 and Figure 4.5). It is composed of:

- BATCH reactor with a volume of 5 l stainless steel;
- Mixing system;
- Water column which permits the entrance of the produced biogas; in this way, as a consequence of the water movement, is possible to evaluate the gas volume;
- pH sensor;
- Temperature sensor;
- Vacuum pump;
- Warmed-up resistance;
- Pressure gauge;
- Air valve;
- Valve and pipe for the gas sample taking. This valve can be manually operated, and it is automatically activated when the pressure into the reactor reaches 0,1 bar.



Figure 4.4. Anaerobic digestion mini-plant.

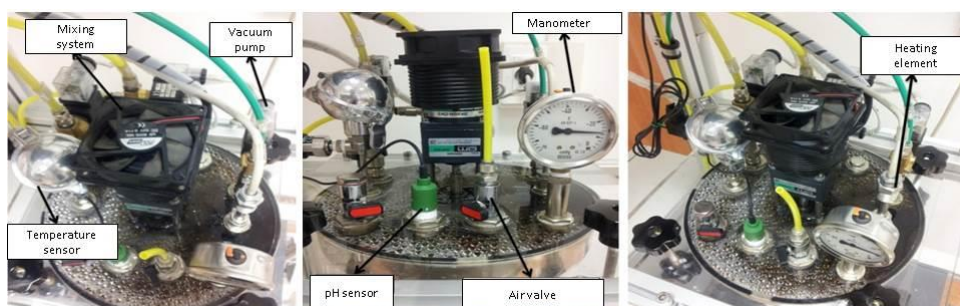


Figure 4.5. Reactor elements.

The gas is extracted through tedlar bags and sent to gas chromatograph AGILENT TECHNOLOGY.

4.6. Experimental tests

Experimental tests to evaluate biogas yield from waste biomass have been done with the mini-digester described above.

For the first tests olive mill solid waste (OMSW) has been used. Olive-mill wastes (OMW) represent a significant environmental problem in Mediterranean area where they are produced in huge quantity and seasonally, thus in short periods of time. One of the most promising processes to exploit OMWs for energy production is anaerobic digestion. In particular OMSWs can be used in co-digestion processes with other biomass. Anaerobic co-digestion technology is increasingly used to simultaneously treat several solid and liquid organic wastes in order to balance the nutrients content, to reduce negative effects of toxic compounds on the process, and, therefore, to increase the biogas yield. Moreover, co-digestion technology contributes to a more efficient use of anaerobic digestion, because multiple streams of wastes can be processed together in a single plant at the same time. The use of OMSW with pit represents economically a very attractive possibility, in particular for the small olive mills.

The other set of tests investigate the biogas production from mixture of Poultry Manure (PM) and Cheese Whey Wastewater (CWW). These tests are part of Rural Development Plan (RDP) project (Reg. 1698/2005 of Lazio 2007/2013), Measure 124: "Cooperation for development of new products, processes and technologies in agriculture, food and forestry: energetic use of agro-industry wastes". The project promotes the innovation of the company through the realization of the activities that envelope new ways for the waste biomass. In the paragraphs below these two experiments are discussed.

4.6.1. Co-digestion tests with Olive Mill Solid Waste

In Mediterranean regions the olive tree cultivation and the olive oil extraction are widespread since thousands of years. Nowadays about 10 million hectares of land in all the world are cultivated with 900 million of olive trees, of which about 98% are in the Mediterranean area [98]. The European Union, from 2007 to 2013, have contributed on average of about 72% of the olive oil world total production. Italy has contributed of

about 22% of the European production with about 6600 olive mills which produce an average of 455 thousands of tons of olive oil per year. Italy represents, in this way, the second European producer after Spain, and it is followed by Greece, Turkey, Syria and Tunisia [99]. The olive oil industry produces huge quantities of wastes which represent a significant environmental problem in Mediterranean area. These wastes are produced in high quantity in a short time, furthermore they are not biodegradable due to the high concentration in organic and phenolic compounds [100,101]. The waste derived by olive mills can be divided in olive mill wastewater (OMWW) and olive mill solid waste (OMSW). The composition and quantity of these wastes depends from the olive oil extraction technology used [100]. In general the OMWW is composed of vegetation water and suspended solid, whereas OMSW is made up by olive pulp, peel, pieces of pit and an oil content [102].

Olive oil extraction can be done through discontinuous (traditional pressing system) or continuous (centrifugation system) processes. The discontinuous pressing system is the oldest and more widespread squeezing method, and it is used in the traditional olive mills. This is a low cost and technically simple method. It produces as by-product OMSW and low quantity of OMWW (40-60 l per 100 kg of olives) [103]. The disadvantages of this system are especially the discontinuity of the process and the high costs of manpower. The OMWW of these kinds of olive mills has however a high COD compared to the other methods. In many countries the traditional pressing system is still used even if it is quite expensive [104]. Continuous extraction processes separate the different phases by centrifugation. They are based on the density difference of the various components of the olive paste, and can operate at two or three phases. In the three-phase system hot water at the centrifugation step is added, and this produces a greater quantity of OMWW [105]. The three-phase systems generate three fractions: OMSW, OMWW and oil with a low quantity of water. The advantages of these systems are the full automation, a better oil quality, and the necessity of smaller spaces; instead the disadvantages are a greater water and energy consumption, a greater OMWW fraction at the output and high installation costs [100]. The three-phase systems are the most widely used, especially in countries that produce high olive quantities. During the last years they became popular also in Italy. To minimize the OMWW volume and to reduce the washing of phenols, two-phase continuous extraction processes have been developed. Using this system the olive paste is divided in two phases: oil and wet

OMSW. The wet OMSW is a semi-solid by-product, a combination of OMSW and OMWW. The two-phase systems are defined ecological because of their high reduction of water consumption, but the resulting residue, which consists of liquid and solid phase, is difficult to manage because the pollutant load is highly concentrated. In the last 10 years this system is become the main system in Spain, where it represents about 90% of the total installation [105].

In Italy there are 6600 olive mills, the three phase system is still the most used with about 46% of the total installation. The pressing system represent 42% of the installation, instead the two-phase continuous system only 2%. However in Puglia, the most important Italian Region for the olives cultivation, 55% of olive mills are continuous cycle [106]. Italy is, therefore, characterized by the presence of many little olive mills that work with traditional process.

In these tests the OMSW, obtained by three-phase system, is examined in order to use it for energy production. It is composed of olive pulp, peel and pieces of pit. This OMSW is characterized by a high C/N ratio ($>34\%$) due to the presence of pieces of pit, a Lower Heating Value (LHV) of about 23 MJ/kg and a high moisture content ($>46\%$). OMSW can be used both in thermochemical conversion processes and in anaerobic digestion to produce biogas [8,18,40,107]. Due to the high moisture content it is not totally convenient to use it in thermochemical processes because it needs to be dried. OMSW can be used, in a very interesting way, in the anaerobic digestion plants, in particular the use in small size biogas production plants, up to 100 kW, is very interesting (D.M. 6 July 2012).

Among the countries that produce primary energy from biogas, first of all there are Germany, United Kingdom and Italy [108]. In Germany the biogas used for the primary energy production is almost totally deriving from digestion plants (87,15% of the total product energy), followed by biogas from sewage sludge (9,95%) and biogas from landfill (2,94%). The situation is totally opposite in United Kingdom and Italy. In the first one the main contribution is given by landfill biogas (84%). In Italy most of the primary energy come from landfill biogas (68,97%) and then from “other biogas” (29,56%).

In Italy the number and the power of bioenergy plants are increasing [7,109]. In particular in 2012 an increase of 81,3% in number, and of 34,6% in power compared to

2011 has been registered. The greater contribute, in terms of number, is given by the biogas plants, in particular those come from agricultural and forestry activities. An increase of 156% in number and 142% in power has been registered. Instead the dominant contribute in terms of installed power is represented by biomass plants, in particular those of urban wastes. In general bioenergy sector contributes at 8% of the total power of the renewable sector [110].

In this work biomass energy characterization has been done and the mini-digester has been used, under mesophilic conditions (38°C), in order to study the biogas yield. The whole process has been carried out under wet conditions, and with a Hydraulic Retention Time (HRT) of 55 days.

The tests concerned two kind of feed:

- OMSW with pit and inoculum,
- OMSW with pit in co-digestion with cattle manure (CM) and cattle slurry (CS).

The inoculum is composed of digested coming from a real plant for biogas production from cattle sewage, taken in a farm. In Table 4.6 and Table 4.7 inoculum and OMSW properties are reported respectively. OMSW to digested ratio was 2:1 on weight. In this way the initial content of Dry Matter (DM) was 24%, therefore this value has been modified to obtain wet conditions.

Table 4.6. Inoculum properties.

Inoculum – Digested from cattle sewage		
pH	8,26±0,3	-
Dry matter	12,2±0,13	[%]
Ashes	3,1±0,08	[% dry matter]
Volatile Solids	94,96±0,08	[% dry matter]

Table 4.7. OMSW properties.

OMSW		
C	51,157±0,041	[%]
H	7,292±0,038	[%]
N	1,478±0,060	[%]
S	0,10	[%]
O	39,973	[%]
C/N ratio	34,61	-
Moisture (wet basis)	45,89±0,83	[%]
Moisture(dry basis)	84,80	[%]
Dry matter	54,12±0,83	[%]

Ashes	4,381±0,183	[% dry matter]
Volatile Solids	93,11±0,183	[% dry matter]
High Heating Value (HHV)	23,110±0,094	[%]
HHV (dry basis)	24,885	[MJ/kg]
Low Heating Value (LHV)	23,382	[MJ/kg]
pH	5,4±0,2	-

In Table 4.8 mixture properties of the first set of test are reported.

Table 4.8. Mixture properties.

Biomass properties				
	Dry matter [%]	Weight [kg]	Ashes [% DM]	Volatile Solids [%DM]
Digested	5,15	1	1,5	5,07
OMSW	54,12	1,867	2,1	51,4
Water	0	1		
Mixture properties				
	Dry matter [%]	Weight [kg]	Initial pH	Volatile Solids [%DM]
Mixture	11,88	3,867	6,51	11,64

In Figure 4.6 trend of volatile solids (VS) is reported. As it is shown there is a decreasing trend due to the use of the VS by the microorganism during the digestion reaction.

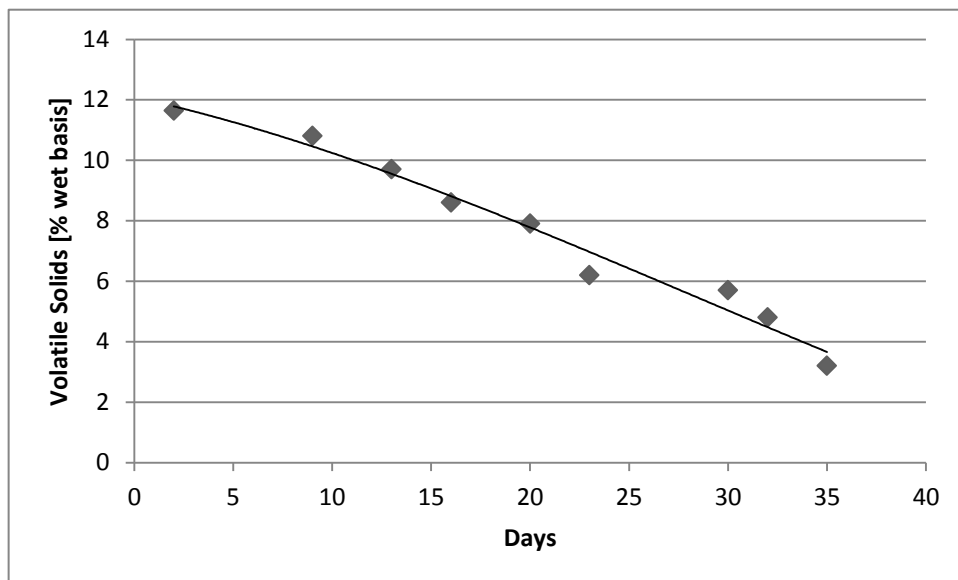


Figure 4.6. Volatile Solids trend (%wet basis).

The trend of the VS can be compared with cumulative production of biogas during the reaction (Figure 4.7). The biogas production increases with decreasing of the VS content in the digestion matrix.

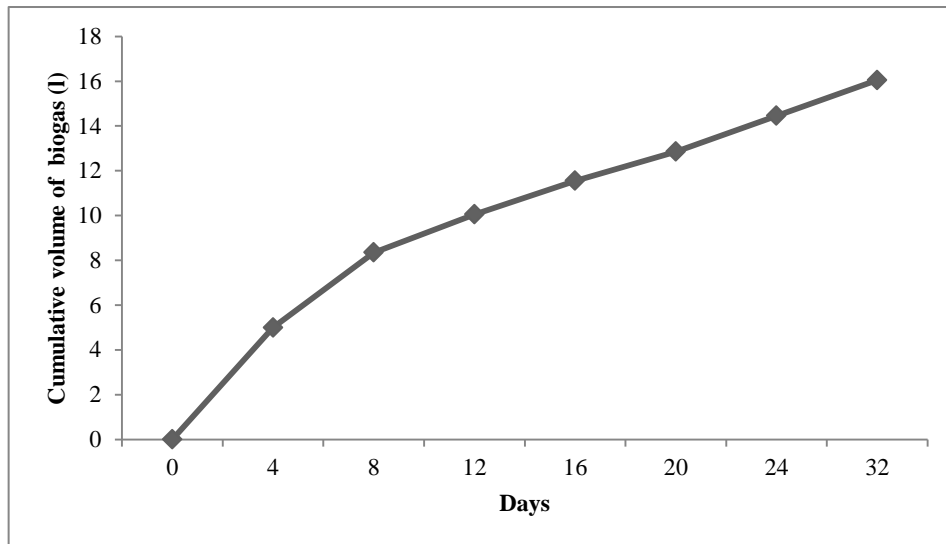


Figure 4.7. Cumulative volume of biogas.

The digestion reaction has been interrupted at Day 32 when the total biogas production had reached 16,05 l. Further the comparison with the cumulative volume of methane into the biogas is congruent with the trend of the VS (Figure 4.8).

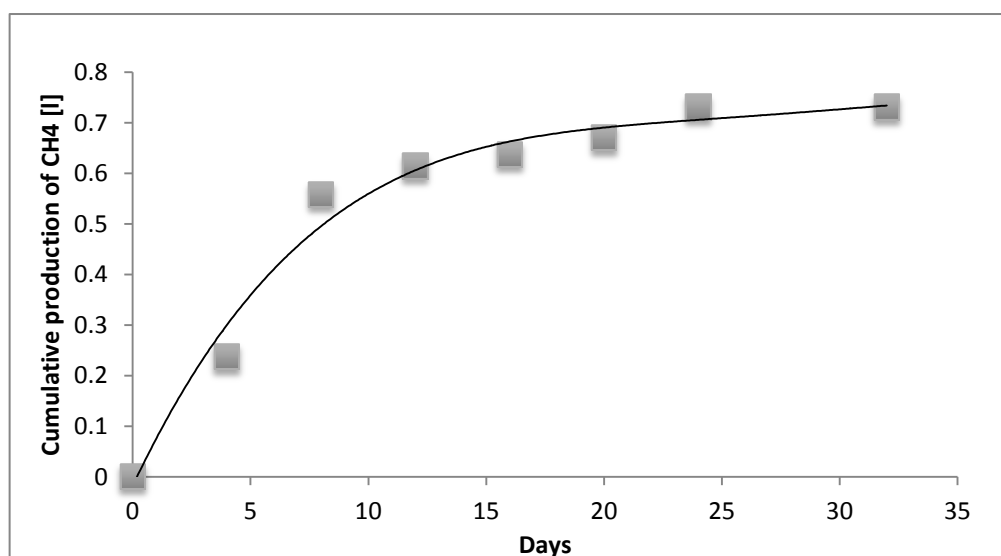


Figure 4.8. Cumulative volume of methane.

When VS tend to a constant value also the methane production tends to stop. Furthermore, as it is possible to see in Figure 4.9, the production of CH_4 has had a very alternating trend and the percentages were very low. For this reason the test has been stopped.

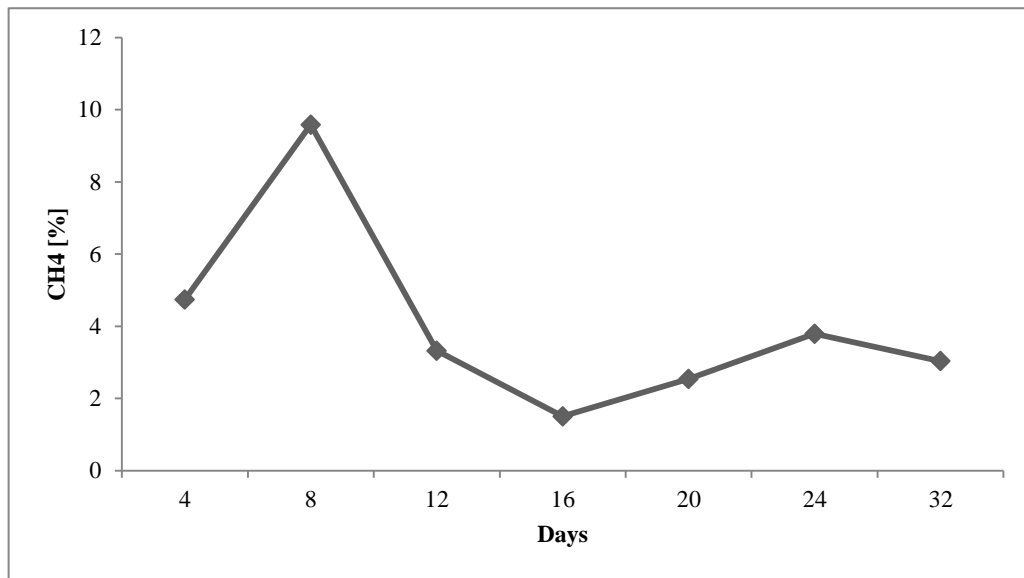


Figure 4.9. Production percentage of methane.

The cumulative volume of methane has reached 0,73 l after 32 days. This percentage is quite low compared to the total biogas production. The BMP is 0,0023 l/g_{vs}.

In Figure 4.10 pH trend is reported. At the beginning of the digestion reaction pH was 6,51; however the trend was very fluctuating, showing that had not occurred a good anaerobic digestion reaction.

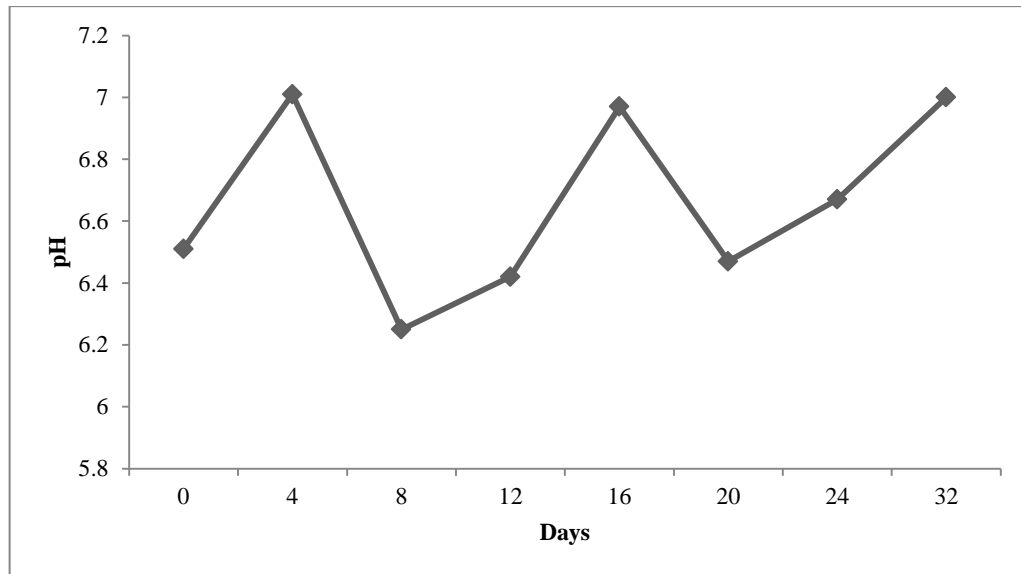


Figure 4.10. Trend of pH.

For all these reasons the test has been interrupted and co-digestion test with OMSW and other substrates have been done. Co-digestion test of OMSW with pit, CM and CS has been done (Table 4.9).

Table 4.9. Biomass properties

Biomass Properties					
	Dry matter [%]	Moisture (wet basis) [%]	Ashes (dry basis) [%]	Organic matter (dry basis) [%]	Weight [kg]
Cattle slurry	1,04	98,96	35,02	61,73	3,1
Cattle manure	18,46	81,54	15,96	75,63	0,2
OMSW	54,12	45,89	4,75	94,07	1
Total					4,3
Mixture properties					
Total dry matter	14 %				
Initial pH	7,07				
Total organic matter on dry basis	93,6 %				
Total organic matter on wet basis	13,03 %				

HRT was 55 days in which the digester has been maintained in mesophilic conditions with a temperature of 38°C. Initial pH, thanks to manure and cattle slurry, was 7,07 and the total organic matter on dry basis was 93,6%. In Figure 4.11 and Figure 4.12 substrate pH trend is reported. In this case pH remains stable during the process, meaning the process is stable.

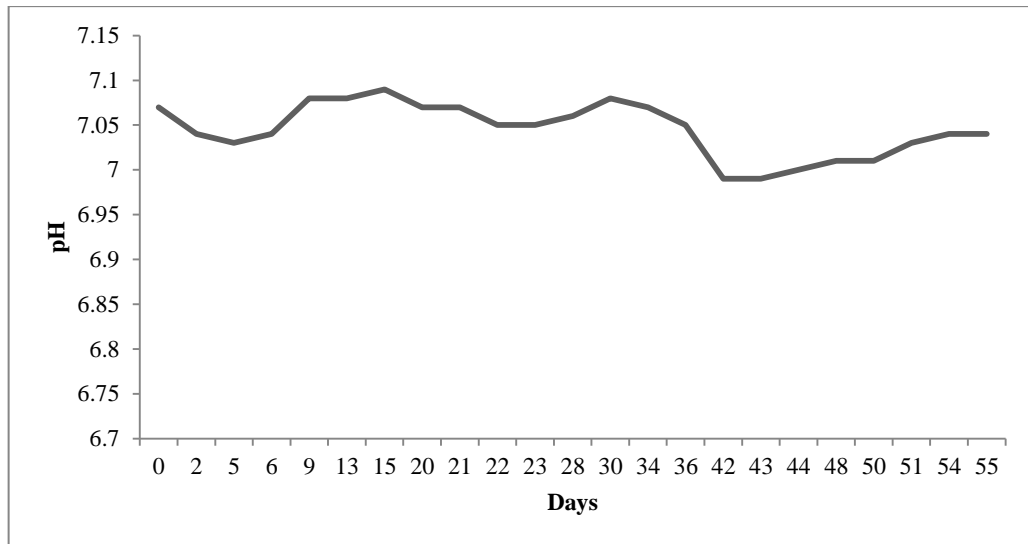


Figure 4.11. pH trend.

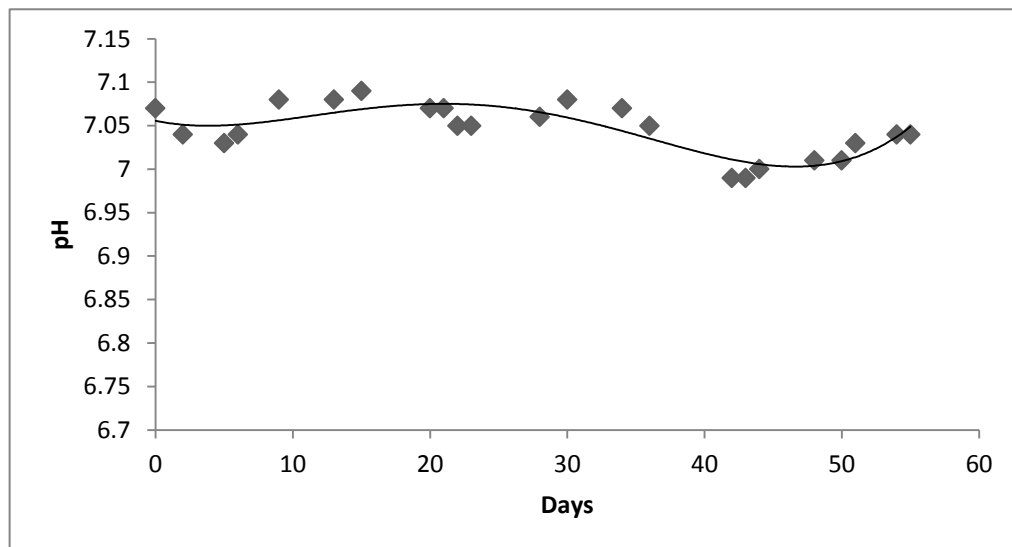


Figure 4.12. Representative points of pH and trend line.

There is an initial pH reduction followed by an increase, which corresponds to the beginning of the phase of the higher methane production. Below the methane percentage into the produced biogas is showed (Figure 4.13).

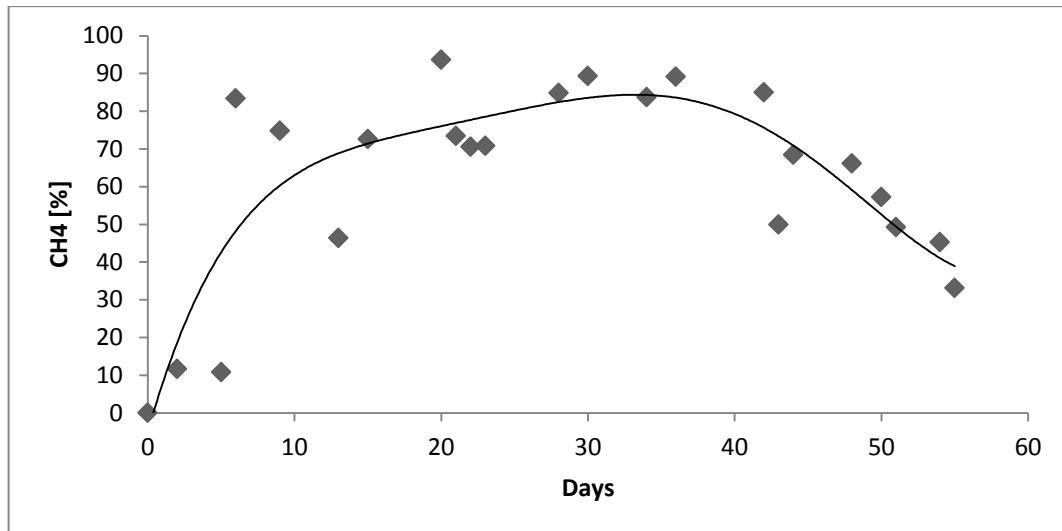


Figure 4.13. Percentage of methane in biogas.

The percentage of methane increases initially, keeping almost constant from day 7 to day 40, and after that it decreases. In Figure 4.14 the cumulative methane production is presented. The production has reached 40,5 l at the day 55.

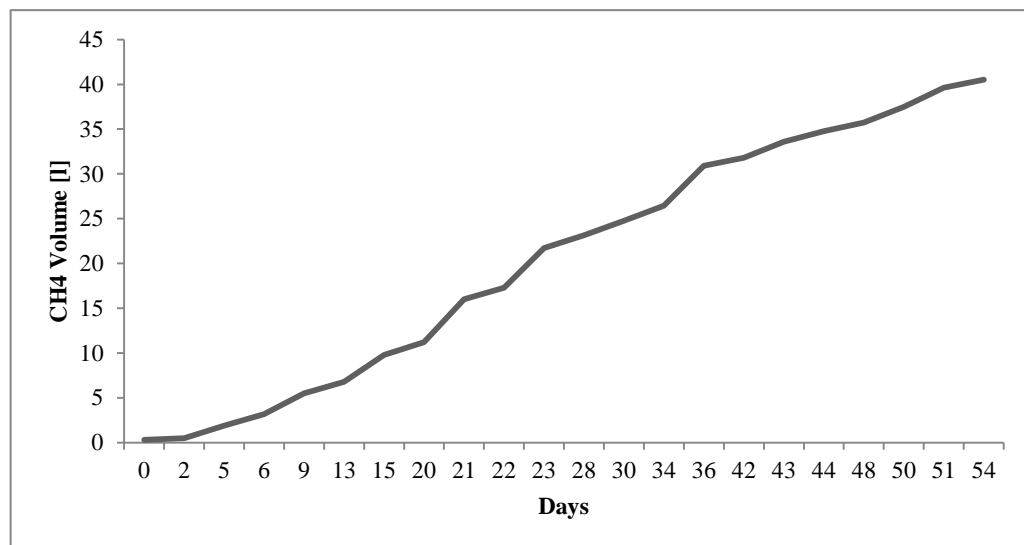


Figure 4.14. Cumulative volume of methane.

The cumulative production of biogas has reached 63 l at the end of the test (Figure 4.15). Therefore the presence of methane into the biogas was 64%.

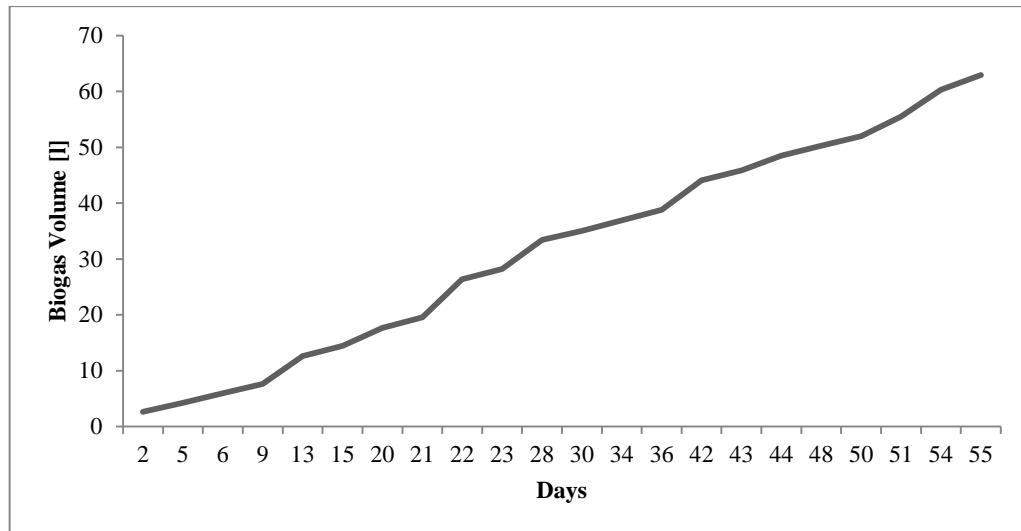


Figure 4.15. Cumulate volume of biogas.

In Figure 4.16 the trend of the VS into the mixture is showed. The time trend of the VS shows a behaviour consistent with that expected: the reduction of the VS increases with test time.

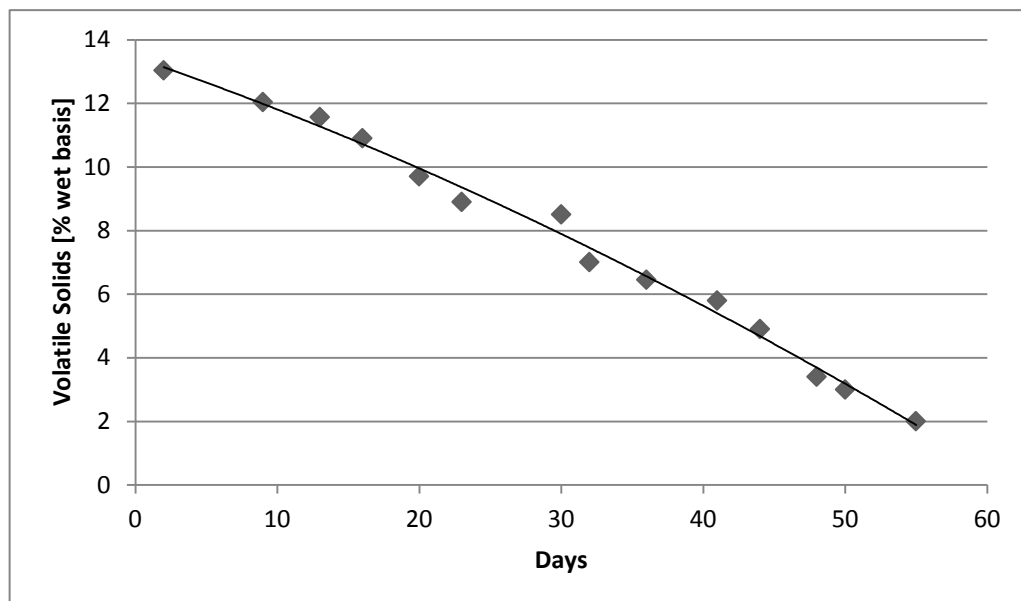


Figure 4.16. VS on wet basis and trend line.

BMP has reached in this case a value of 0,103 l/g_{vs}. Comparing the BMP and the methane average percentage of the two tests (Table 4.10) can be observe as the co-

digestion test of OMSW with pit and manure and cattle slurry has produced better results (0,1034 l/g_{vs} and 64% respectively).

Table 4.10. BMP and methane average percentage in biogas of the two tests

Test	BMP [l/g _{vs}]	Methane average percentage in biogas [%]
Digestion of OMSW without pit and inoculum	0,0023	4,55
Co-digestion of OMSW with pit and manure and cattle slurry	0,1034	64

Therefore from the tests carried out with a batch stirred tank reactor results that OMSW with pit has better performance if used in co-digestion with other substrates. The optimal mixture has been found using 4,65% of CM, 72,10% of CS and 23,25% of OMSW with a Total Solid (TS) content of 14%.

4.6.2. Co-digestion of Poultry Manure and Cheese Whey Wastewater

Cheese factories and poultry farms are agro-industries that represent a considerable share of the European economy with particular interest focused in the Mediterranean region. These industries generate a large amount of liquid and solid wastes, which in many cases are totally unexploited and furthermore dangerous for the environment [111]. Cheese Whey Wastewater (CWW) is a greenish-yellow liquid, which remains in the boiler after the separation of the curds and it can be ovine, buffalo or cow whey as a function of the origin of the milk. Into the whey there are all the soluble elements of the milk that have not participate at the coagulation, and they are in particular lactose, proteins, soluble salts and fats as a function of the curds processing. The whey composition is a function of different factors such as animal species, feeding, the season of the milk production, the kind of cheese and the processing to produce it. Cheese manufacturing industry generate large amounts of CWW, with associated high biological (BOD₅) and chemical oxygen demand (COD) and a BOD₅/COD ratio commonly higher than 0,5 [112]. CWW contains a significant amount of carbohydrates (4-5%), mainly lactose (45-50 g/l), proteins (6-8 g/l), lipids (4-5 g/l), and mineral salts (8-10% of dried extract). CWW also contains significant quantities of lactic (0,5 g/l) and citric acid, non-protein nitrogen compounds and B-group vitamins [113]. Whey obtained by manufacture of hard, semi-hard or soft cheese, is known as sweet whey and

has a pH of 5,9-6,6, while the manufacture of mineral-acid precipitated casein, is known as acid whey, and has a pH of 4,3-4,6 [114]. The CWWs have not dangerous substances (pathogens, heavy metal, virus, etc.) but they have high organic matter content. From the agricultural and environmental point of view some parameters can be incompatible with the diffusion of these wastes on the soil. These parameters are pH, salinity, and some elements concentration, that are under the law limits, but can be used only after some treatments [115]. In particular CWW has an acid pH that after few hours reaches values of about 4. In the dairy industry the CWW is one of the main wastes. These substances are generally not reused, and they represent a pollution source for the watercourses. The possibility to recycle these materials in other one with a higher economic value could be a solution to the environmental problems and at the same time a profit or savings for the dairy industry. For these reasons the CWW should be recycled, transformed and valued [116]. Anaerobic digestion of cheese whey is an excellent method for wastewater treatment, although raw whey is known to be quite problematic to be treated anaerobically due to low bicarbonate alkalinity, high COD concentration and tendency to get acidified very quickly. Supplemental alkalinity is required so as to avoid acidification and subsequently anaerobic process failure [117].

Poultry manure (PM) is rich in nitrogen and phosphorus, therefore, the traditional utilization is to enrich soil and fertilize crops. In some areas, the number of poultry farms is high, therefore, a treatment process of the PM is necessary. Since the good biological degradability of PM, anaerobic digestion is considered to be a good choice to minimize these kinds of wastes and recover bioenergy [118]. However, high content of organic nitrogen, low C/N ratio, undigested protein and uric acid cause the production of the ammonia that inhibits anaerobic process, particularly when digestion is under thermophilic condition. A common method to avoid ammonia inhibition is the dilution of the substrate usually with fresh water. Fresh PM has high concentration of total solid (TS), ranging from 20% to 62,4% [119]; before adding it to a digester, PM must be diluted so that concentration of TS is amount to 0,5-3%, in this way ammonia accumulation is avoided [120]. This on one hand decreases the biogas production per unit of digester volume, on the other hand, it increases the consumption of water and the processing cost for manure discharge. Another method to avoid ammonia inhibition is co-digestion of PM with other substrates. Many biogas plant operators are more willing

to use co-digestion, because this can receive high biogas output with high nutrient content in digestate [121].

The above considerations highlight the difficulty of energy use of the individual waste, and for this reason co-digestion is the best process for the production of electrical and thermal energy from cheese waste and poultry manure.

Availability, characteristics and yields of the waste biomass of two agricultural companies, that are partners into the project, have been analysed, to raise their product values, the competitiveness and the profit, reducing at the same time the environmental impact. The agricultural companies Pacifici and Delrio are part of agricultural and farm chains, in Lazio Region. Delrio company is between Bagnoregio and Bolsena, in the Viterbo Province, where it carries out the whole process of milk and cheese production. The company consists of 60 ha of grazing land for the 370 sheep and the milk is used for the cheese production and the direct sale. The agricultural company Pacifici is in Grotte Santo Stefano, Viterbo municipality, and it consists of 60 ha and a rearing of 34000 laying hens. The wastes biomass of the companies are:

- CWW for a total of about 85 m³ year;
- PM about 1172,5 m³ year.

The samples were analysed and evidence of biogas production were performed in order to verify the feed composition which allowed the maximum yield of biogas. The characteristics of substrates and inoculum are shown in Table 4.11.

Table 4.11. Characterization of substrates and inoculum

Parameter	CWW	PM	Inoculum
C [%]	32,5±0,9	36,8±0,9	34,3±0,7
H [%]	4,4±0,4	5,7±0,4	4,9±0,3
N [%]	5,6±0,8	3,4±0,3	3,8±0,6
C/N ratio	5,8±1,3	10,82±2,9	9,02±1,8
Total Solid [%]	5,88±2,1	78,82±2,3	5,48±1,9
Ashes [% dry matter]	1,54±1,1	38,45±0,9	0,98±0,8
Volatile Solids[%]	5,79±1,08	48,51±0,8	5,15±0,7
COD [g/l]	65±3,1	-	53±2,9
pH	6±0,2	8,7±0,3	7,8±0,12

BMP assays of substrates were carried out using a batch reactor working in mesophilic conditions (37°C) [122]. The trend of temperature, pH and pressure was

continuous measured during the test by means of probes inserted into the reactor and connected to a PLC. BMP tests have been carried out for all the feedings to verify possible problems for the anaerobic digestion process. All experiments were run as triplicate and the mean values of net biogas production and methane content were calculated. The high content of lactic, citric acid and non-protein nitrogen compounds (urea and uric acid) in CWW have produced a quick decrease of pH into the digester. After 24-48 hours by the beginning of the tests, the average pH value was about 4,5. It shows the necessity to use CWW in a co-digestion process with other biomass to reduce the acidification into the reactor due to the ammonia produced in the feeding. Bio-methane tests conducted on PM have confirmed the literature [120,121]; there was no production of biogas due to the process inhibition for the presence of the ammonia. For this reason there is the necessity to use PM in a co-digestion process.

In order to determine the anaerobic biodegradability of different mixtures, three feed with mixing ratio CWW/PM: 3:1, 1:1, 1:3 have been studied. In the feed of reactor the content of TS was less than 10% in weight. The batch reactor was fed with an appropriate amount of substrate mixture and inoculum keeping a TS ratio (TS substrate to TS inoculum) at 1:1 in all setups. A BMP test (control) was conducted on the inoculum, to estimate the volume of methane resulting from anaerobic digestion. The BMP was about 65 ml/g_{VS}. Based on the initial TS contents of CWW, PM and inoculum, a sufficient amount of deionized water was added to reach hemi-solid state anaerobic digestion (HSS-AD) condition [123]. The average Hydraulic Retention Time (HRT) of tests was 35 days. All experiments were run as triplicate and the mean values of net biogas production and methane content were calculated.

The composition analysis of each waste used in this study, i.e. CWW and PM is presented in Table 4.11. Significant differences in the composition were detected, in particular PM presented the highest total solid content (78% in weight) compared to CWW (5,88 % in weight) and consequently a remarkable difference in terms of volatile solids (VS). A mix of CWW and PM has ensured sufficient levels of both nitrogen and alkalinity in the feeding, decreasing high COD concentration and tendency to get acidified very rapidly of the CWW, and high content of organic nitrogen and low C/N ratio of the PM. Table 4.12 shows the properties of the mixture fed into the plant.

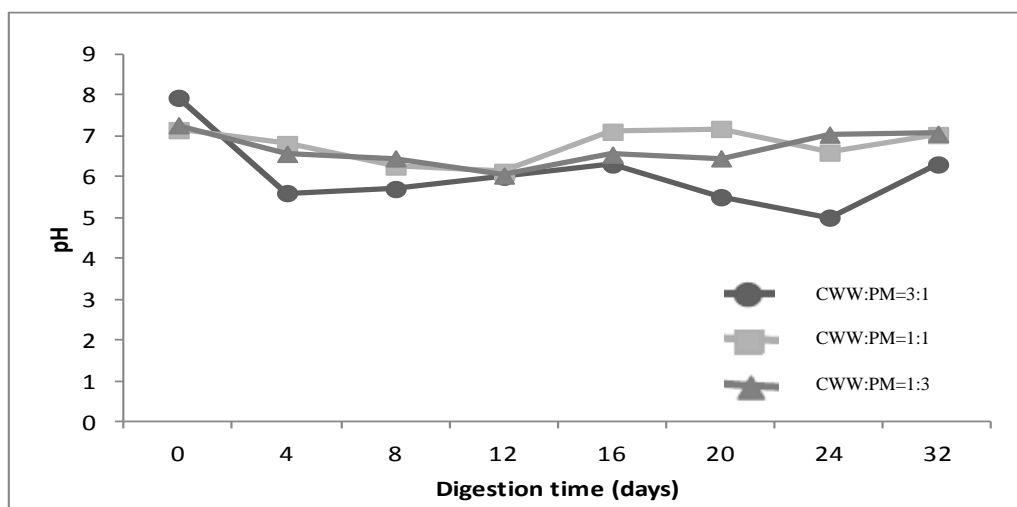
Table 4.12. Properties of the mixtures used.

Parameter	CWW:PM=3:1	CWW:PM=1:1	CWW:PM=1:3
TS (%FM [*])	7,6	8,9	10,2
VS (%TS)	65,89	71,8	75,5
C/N	25,78	22,67	18,84
pH	7,93	7,14	7,26

*FM=Fresh mass

Batch experiments were carried out using different mixtures in order to evaluate optimum mixing ratio (CWW/PM) to reach the maximum biogas yield.

During the test the trend of pH, production and composition of biogas were monitored, as showed in Figure 4.17, 4.18 and 4.19. The trend of pH has been greatly affected by the composition of the starting mixture (Figure 4.17). As regards the feeding with mixing ratio CWW:PM = 3:1, the pH value, after 5 days of the test, reached values of 5,5. For so low pH values the anaerobic digestion process stops and the test was interrupted. The tendency to acidification of CWW was not reduced by mixing it with PM and this caused a sudden drop in pH and a test block. For mixing ratio CWW:PM=1:1 and CWW:PM=1:3 the daily biogas production has had the same trend (Figure 4.18). The biogas production started immediately, increasing until reaching the peak at around day 5, and then quickly decreased. After about 18 days, almost 90% of the experimental biogas yield was obtained. The average content of methane was 65% for ratio 1:1 and 55% for ratio 1:3 (Figure 4.19).

**Figure 4.17. Trend of pH.**

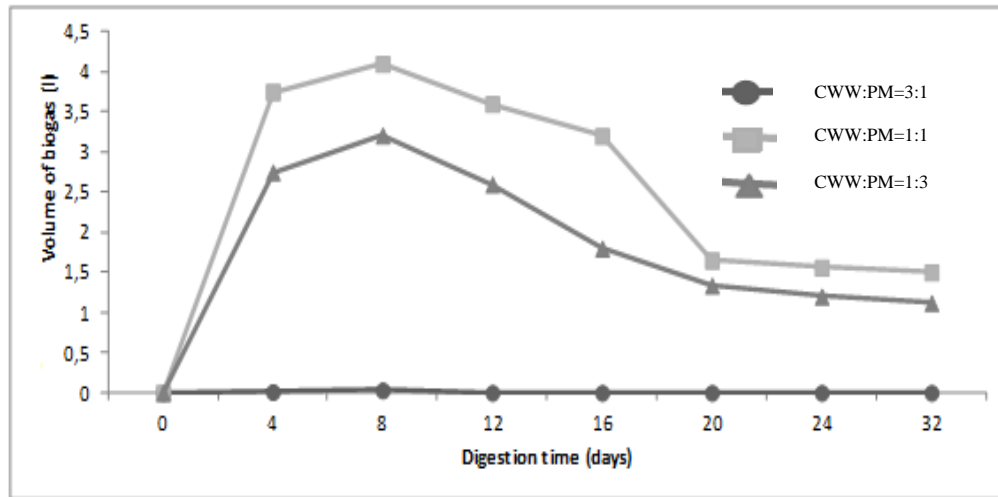


Figure 4.18. Daily biogas production.

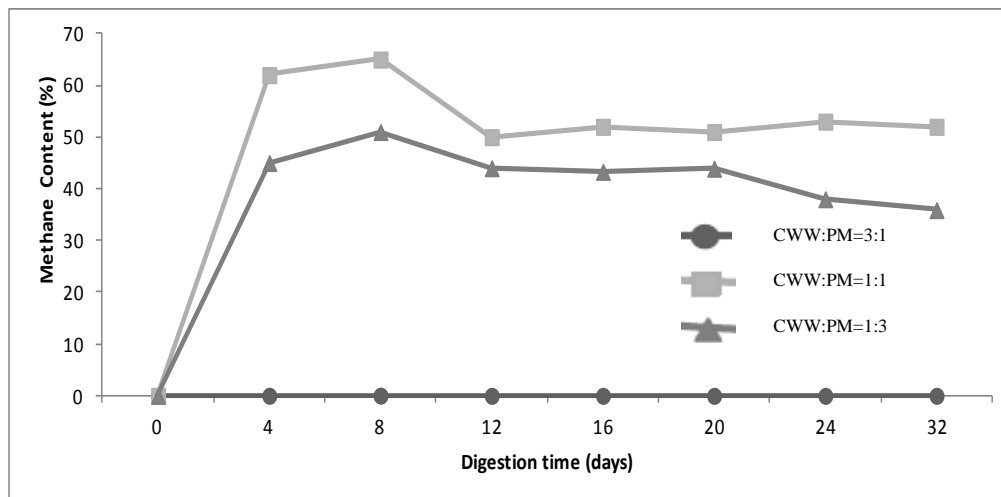


Figure 4.19. Methane content of biogas.

In Figure 4.20 the trend of VS into the mixtures is showed. The time trend of the VS shows behaviour consistent with that expected: the reduction of the VS increases with test time.

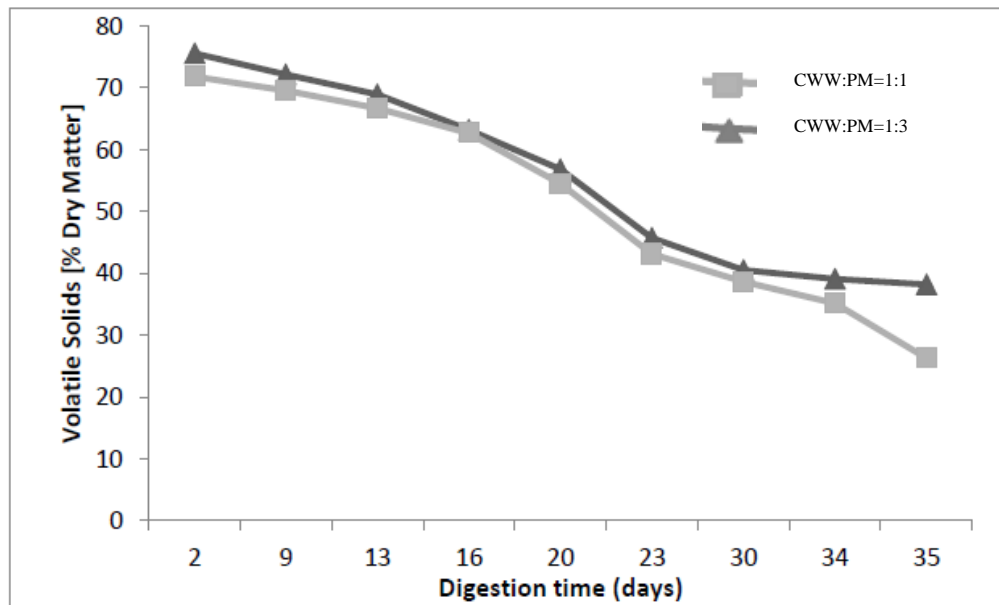


Figure 4.20. VS on wet basis and trend line.

In Table 4.13 the BMP and methane average percentage of the two tests have been reported. The co-digestion test of mixture ratio 1:1 has produced better results, indeed, a TS content of 8,9% of fresh mass and a C/N ratio of 22,67 are suitable conditions for the production of biogas.

Table 4.13. BMP and methane average percentage in biogas of the two tests

Test	BMP [ml/g _{vs}]	Methane average percentage in biogas [%]
CWW:PM=1:1	223	65
CWW:PM=1:3	135	55

In conclusion the use of CWW and PM represents economically a very attractive possibility for farms where they are produced. From the obtained results, the test with CWW:PM ratio of 1:1 permits to produce a greater quantity of methane and at the same time to reduce the acidification trend of CWW, to improve C/N ratio and to reduce the TS fed into the plant. Considering a BMP equal to 223 ml/g_{vs} and the amount of wastes identified into the agricultural companies, a 65 kW anaerobic digestion plant is possible to realise, with an annual production of about 520.000 kWh of electricity.

4.7. AD Model

In this work an anaerobic digestion model has been developed and then implemented in the software AQUASIM 2.0. The model takes into account the specific composition of the feed, as distinguished to proteins, lipids and carbohydrates. The model regards six biological processes: hydrolysis of proteins, lipids and carbohydrates, fermentation of sugar and amino acids, anaerobic oxidation of long chain fatty acids (LCFA), acetogenesis, acetoclastic methanogenesis, hydrogenotrophic methanogenesis and the growth of fermenters, oxidiser, acetogens, aceticlastic methanogens and hydrogenotrophic methanogens bacteria.

The simplified expressions of the biochemical reactions of the model, with their stoichiometry, expressed in COD, and the values of its parameters has been taken from the literature (Table 4.14) [124,125].

Table 4.14. Reactions and constant assumed in the model [124]

<i>Hydrolysis of proteins</i> Proteins (1) → amino acids (1)	$K_H = 0,104 \text{ d}^{-1}$
<i>Hydrolysis of lipids</i> Lipids (1) → long chain fatty acids (1)	$K_H = 0,118 \text{ d}^{-1}$
<i>Hydrolysis of carbohydrates</i> Carbohydrates (1) → sugars (1)	$K_H = 0,146 \text{ d}^{-1}$
<i>Fermentation (with acetate inhibition)</i> Sugar and amino acids (66) → propionate (20) + acetate (35) + hydrogen (11)	$\mu_{\max} = 5,559 \text{ d}^{-1}$ $K_S = 28 \text{ gCOD/m}^3$ $K_I = 604 \text{ gCOD/m}^3$ $Y = 0,043 \text{ gVSS/gCOD}$
<i>Anaerobic oxidation</i> LCFA (34) → acetate (23) + hydrogen (11)	$\mu_{\max} = 0,382 \text{ d}^{-1}$ $K_S = 1,816 \text{ gCOD/m}^3$ $Y = 0,11 \text{ gVSS/gCOD}$
<i>Acetogenesis (with acetate inhibition)</i> Propionate (7) → acetate (4) + hydrogen (3)	$\mu_{\max} = 0,111 \text{ d}^{-1}$ $K_S = 247 \text{ gCOD/m}^3$ $K_I = 181 \text{ gCOD/m}^3$ $Y = 0,018 \text{ gVSS/gCOD}$
<i>Aceticlastic methanogenesis</i> Acetate (1) → methane (1)	$\mu_{\max} = 0,167 \text{ d}^{-1}$ $K_S = 56 \text{ gCOD/m}^3$ $Y = 0,026 \text{ gVSS/gCOD}$
<i>Hydrogenotrophic methanogenesis</i> Hydrogen (1) → methane (1)	$\mu_{\max} = 0,695 \text{ d}^{-1}$ $K_S = 0,13 \text{ gCOD/m}^3$ $Y = 0,018 \text{ gVSS/gCOD}$

Y = biomass yield coefficient. In parentheses () are the coefficients for COD transformation.

Physico-chemical reactions have not been considered in the model as well as inhibition functions, except for the acetate inhibition. Hydrolysis reactions have been

assumed to follow first order kinetic, while Monod equation has been applied to all other reactions. Below are reported their respective rate (4.19), (4.20):

$$r = K_H * C_S \quad (4.19)$$

$$r = \mu_{max} \frac{C_S}{K_S + C_S} C_b \quad (4.20)$$

Where:

K_H = hydrolysis constant;

C_S = substrate concentration;

μ_{max} = maximum reaction velocity;

K_S = saturation constant;

C_b = bacteria concentration.

4.7.1. AD Simulation Result

Anaerobic digestion simulations permit to verify the single process stages and study the bacterial activity, which is difficult to do in experimental test, so that it is possible to check the feasibility and the functionality of the anaerobic digestion process as a function of the input substrate.

A simulation has been carried out with the software AQUASIM 2.0. The HRT has been set at 32 days in mesophilic conditions in a batch reactor as the experimental test.

In particular simulation of the co-digestion test with CWW:PM=1:1 has been carried out, and the mixture characteristics used in the model is showed in Table 4.15.

Table 4.15. Mixture characteristics used in the model

Mixture characteristics	[g/m ³]
Proteins	2740
Carbohydrates	14557
Lipids	3945

The trend of different compounds has been simulated, and the results are reported in Figures 4.21 and 4.22 .

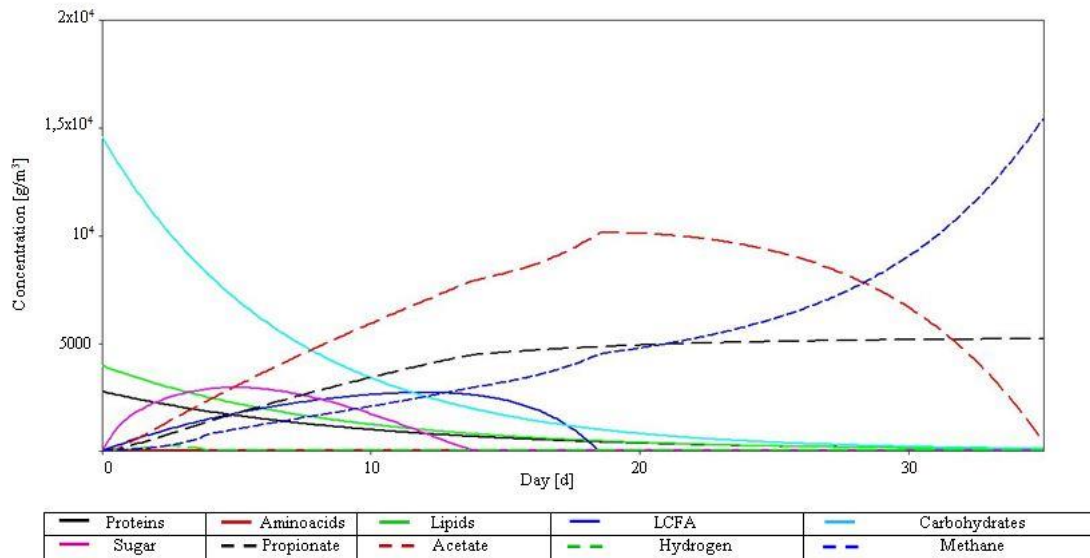


Figure 4.21. Trend of different compounds.

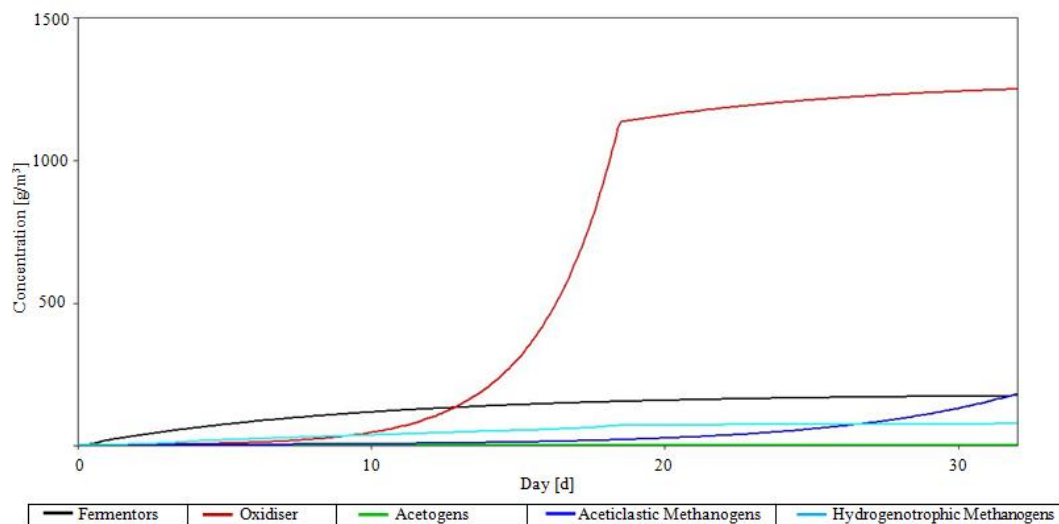


Figure 4.22. Trend of bacteria growth.

The figures show that the decomposition of carbohydrates, proteins and lipids continues up to the end of the simulation.

During the fermentation stage the growth of fermenters can be noticed, with a consequent degradation of sugar up to the day 10, and then it keeps approximately constant. Oxidiser bacteria increase until the day 20 when take place the total decomposition of LCFA and the maximum acetate production. Acetogens maintain a

low concentration and for this reason there is not a high decomposition of propionate, which is more or less constant; probably this trend is due to the acetate inhibition. After the day 20 there is the growth of acetoclastic methanogens with a consequent acetate decrease. Finally hydrogenotrophic methanogens had always a low concentration because there was not a high hydrogen production.

Methane production follows the trend observed in the experimental test, even if the high values are due to the absence into the model of the inhibition functions (except for the acetate) and the chemical-physical reactions. For this reason the model will be further developed and validated with other experimental tests.

Chapter 5. Fusion Energy

5.1. Introduction

Nuclear fusion is considered an essential element of a sustainable and CO₂-free electrical energy source, which will be used to overcome the quick growth of the global energy demand. As a matter of fact global energy demand is expected to double by 2050 due to the combined effect of population increase and energy needs per person in developing countries.

Nuclear fusion will provide a source of energy:

- Environment-friendly: the products of the most promising fusion reaction (D-T, i.e. deuterium and tritium) are only helium and neutrons. No long-term radioactive wastes are generated and with a proper choice of materials for the reaction chamber, induced radioactivity in structural components decays in a relatively short time to values compare to those in carbon-fired plant.

- Intrinsically safe: no chain-reaction is possible, since a very small amount of fuel is needed; in case of damage, accident, or loss of control, fusion reactions and heat generation will very rapidly and automatically switch off.
- Ensuring sustainability and security of supply: the fuel, deuterium and lithium (tritium is produced from lithium in the reactor) are widely available and virtually unlimited (deuterium is abundant in sea water and lithium can be extracted by rocks and ocean water).
- CO₂-free: there is no production of greenhouse gases.

The potential role of fusion in energy production is contextualized by comparisons with the other existing energy options. The comparison shows that the fusion has many attractive features in terms of safety, fuel reserves, and minimal damage to the environment. Furthermore fusion should provide large quantities of electricity in an uninterrupted and reliable manner, thereby becoming an important contributor to the world's energy supply; in fact a nuclear reaction produces one million times more energy per elementary particle than a fossil fuel chemical reaction. Another aspect is the environmental impact. Nuclear power plants produce neither CO₂ nor other harmful emissions [126].

By comparing the energy equivalence of various types of fuel it is clear the reason why, the use of nuclear reactions for energy production, arouses much interest [126]:

$$\begin{array}{ccc} \text{fossil} & \text{fission} & \text{fusion} \\ 106 \text{ tonne oil} = & 0.8 \text{ tonne uranium} = & 0.14 \text{ tonne deuterium} \end{array}$$

Nuclear reactions produce changes in the basic structure of the nuclei of the atoms involved. A nuclear reaction changes atoms of one element into atoms of another (e.g. in fission uranium is changed into xenon and strontium). The energy released per nuclear reaction is always enormous compared to that from a chemical reaction. It is because is the nuclear force rather than the electromagnetic one that causes the reactions. The nuclear force acts over a short range, comparable to a nuclear diameter,

but is much, much stronger than the electromagnetic force over this range. The energy released in a nuclear reaction represents the decrease in nuclear “potential energy”.

It is this difference in mass that is transformed into energy by Einstein’s famous relation $E = mc^2$. Usually the value of E for nuclear reactions is in the range 10–100 MeV.

Fusion reactions consist of generate a nuclear reaction by having two light elements bombard each other, for instance two colliding deuterium nuclei, but two deuterium atoms to undergo a nuclear reaction, their nuclei must be in very close proximity, typically within a nuclear diameter. At these close distances, the inter-particle Coulomb potential produces a strong repulsive force between the two positively charged nuclei, which diverts the particle orbits and greatly reduces the probability of a nuclear reaction. If the deuterium nuclei have sufficiently high energies the repulsive Coulomb force can be overcome. Studies of the nuclear properties of light element fusion indicate that three such reactions may be advantageous for the production of nuclear energy. These involve deuterium (D), tritium (T), and helium-3 (He^3), an isotope of helium. A schematic diagram of the nuclear structure of each of these nuclei is shown in Figure 5.1.

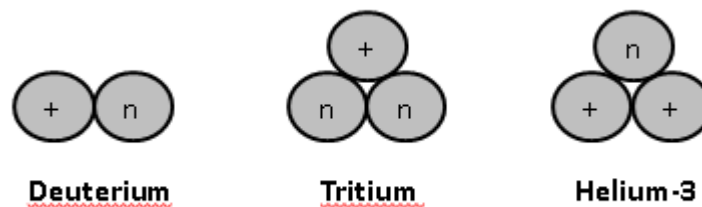


Figure 5.1. Nuclear structure of the basic fusion fuels.

In the next paragraph the main fusion reactions are described.

5.2. Fusion reactions

The D-D reaction

The D–D reaction produces fusion energy by the nuclear interaction of two deuterium nuclei. This is the most desirable reaction in the sense of a virtually unlimited supply of inexpensive fuel, easily extracted from the ocean.

The D–D reaction actually has two branches, each occurring with an approximately equal probability. The relevant reactions are:



Where:

D = deuteron (deuterium nucleus);

T = triton (tritium nucleus);

He³ = Helium-3 nucleus;

n = neutron;

p = proton (hydrogen nucleus).

In terms of energy content the two reactions produce respectively 0,82 and 1,01 MeV per nucleon. Macroscopically this is equivalent to 78×10^6 and 96×10^6 MJ/kg of deuterium. The difficulty of initiating D–D fusion is the reason that this reaction is not the primary focus of current fusion research.

The D–He³ reaction

This reaction fuses a deuterium nucleus with a helium-3 nucleus. The reaction is also difficult to achieve, but less than for D–D. However, it requires helium-3 as a component of the fuel and there are no natural supplies of this isotope on earth, but the end products are all charged particles. From an engineering point of view charged particles are more desirable than neutrons for extracting energy as they greatly reduce the problems associated with materials activation and radiation damage. They also offer the possibility of converting the nuclear energy directly into electricity without passing through a steam cycle. The reaction is:



Where:

α = helium nucleus (${}^4_2\text{He}$).

The energy released per reaction is impressive. The 18,3 MeV corresponds to 3,66 MeV per nucleon, which is macroscopically equivalent to 351×10^6 MJ/kg of the combined D–He³ fuel. The low He³ availability combined with the difficulty of initiating D–He³ fusion are the reasons that current fusion research is not focused around this reaction.

The D–T reaction

The D–T reaction involves the fusion of a deuterium nucleus with a tritium nucleus. It is the easiest of all the fusion reactions to initiate. In terms of energy desirability issues, D–T reactions produce large numbers of neutrons and require a supply of tritium in order to be capable of continuous operation, but there is no natural tritium on earth. Furthermore, the tritium is radioactive with a half-life of 12,26 years. The D–T reaction, nevertheless, produces a significant amount of nuclear energy (Figure 5.2).

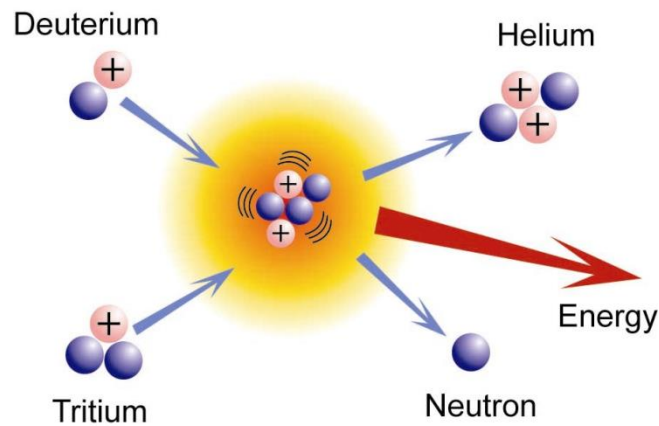


Figure 5.2. Representation of D-T reaction

It can be written as:



The one outstanding problem is the tritium supply. The solution is to breed tritium in the blanket surrounding the region of D–T fusion reactions. The chemical element that is most favourable for breeding tritium is lithium. The nuclear reactions of primary interest are:



Both reactions produce tritium, although the first reaction generates energy and the second one consumes energy. Also natural lithium comprises 7,4% ${}^3\text{Li}6$ and 92,6% ${}^3\text{Li}7$. Even though there is a much larger fraction of ${}^3\text{Li}7$, nuclear data show that the ${}^3\text{Li}6$ reaction is much easier to initiate and as a result this reaction dominates in the breeding of tritium. With respect to the ${}^3\text{Li}6$ reaction, if there were no loss of neutrons, then each n consumed in fusion would produce one new T by breeding with the fusion produced neutron: the breeding ratio would be 1,00. The known reserves of lithium are sufficiently large to last thousands of years so fuel availability is not a problem.

The energy for the D-T reaction corresponds to 3,52 MeV per nucleon and is macroscopically equivalent to 338×10^6 MJ/kg. In spite of the problems associated with tritium and neutrons, the D–T reaction is the central focus of worldwide fusion research, a choice dominated by the fact that it is the easiest fusion reaction to initiate [126].

This reaction has indeed the bigger cross-section (by which depends the reaction probability) at the lowest energy (Figure 5.3).

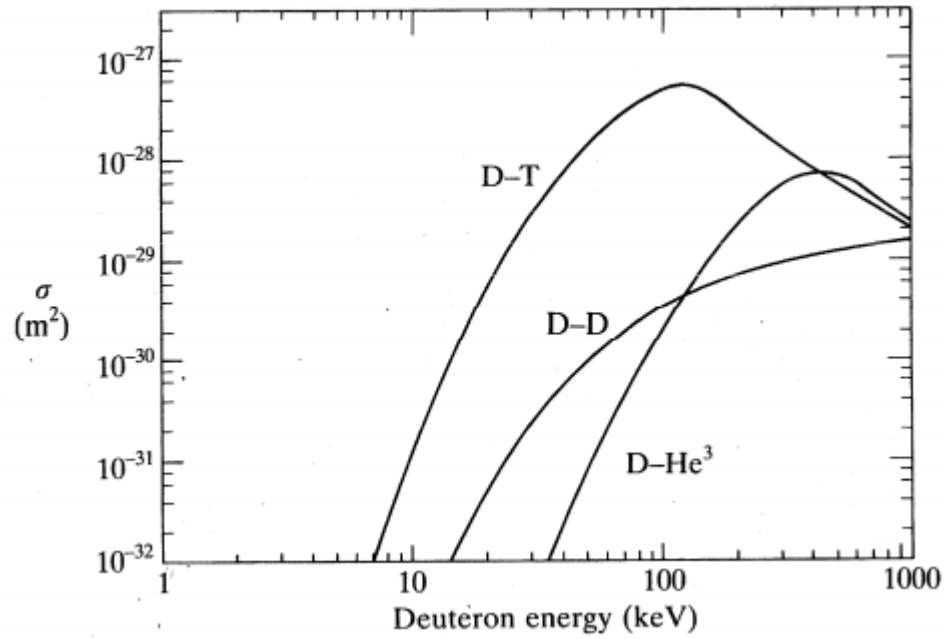


Figure 5.3. Cross-section at different energies for the main fusion reactions.

The produced energy released in the form of produced particles kinetic energy is inversely proportional to the respective masses.

To obtain a significant reaction rate, extremely high temperature (higher than 10 keV) is necessary to achieve (Figure 5.4). These temperatures are higher than the atoms ionization energy (13,6 eV for H), and for this reason fusion reactions take place in a fuel at plasma state (the fourth state of matter). Plasma is an ionised gas, whose atoms have totally or in part lost their electrons, and it is made up by electrons and positive ions.

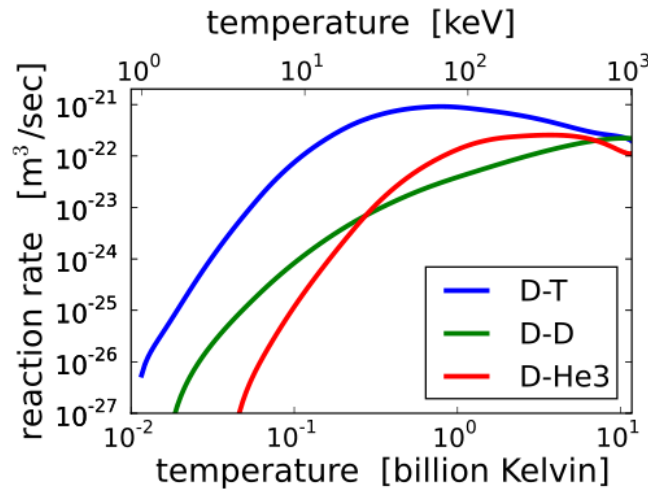


Figure 5.4. Number of reactions per unit time as a function of temperature.

One of the main critical aspects in a fusion reactor is the plasma confinement that tends to escape to the reactor wall.

5.3. Magnetic and Inertial Confinement

To avoid interactions plasma-material with the first wall and, the consequently introduction of impurity and plasma cooling, it must be confined. There are two different approaches:

1. Magnetic confinement (MCNF: Magnetic Confinement Nuclear Fusion);
2. Inertial confinement (ICNF: Inertial Confinement Nuclear Fusion).

Magnetic confinement uses the interaction between charged particles and magnetic fields. The magnetic field produced by a linear solenoid forced the charge particles to rotate around the magnetic field lines and to move along them. To avoid losses at the extremities, the solenoid has to be toroidal. However in this way the field is not uniform: field gradients cause particle drift motions that have to be cancelled by corrective fields. Among the different magnetic configuration the Tokamak (TOroidalnalaya KAmera MAgnitnaya Katushka, i.e. "toroidal magnetic chamber") is the most studied and it is based on the effects of three distinct magnetic fields.

Toroidal field

It represents the main magnetic field and it is produced by toroidal coils placed outside the vacuum chamber (Figure 5.5).

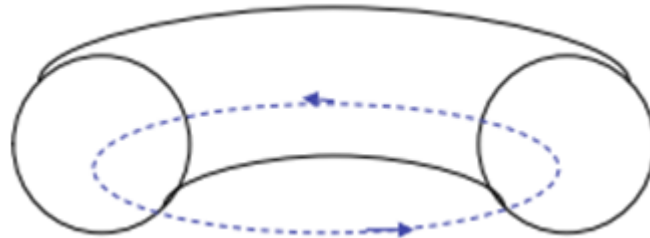


Figure 5.5. Toroidal magnetic field.

Poloidal field

It is generated by the plasma current induced by a central solenoid, and it is necessary to contrast ions drift motions due to the heterogeneity of the toroidal field (Figure 5.6).

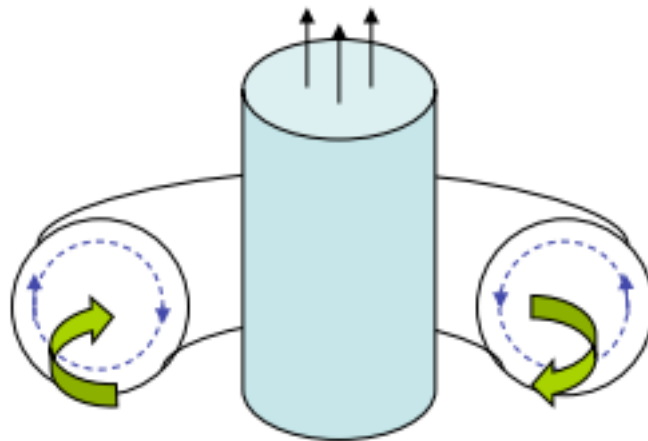


Figure 5.6. Poloidal magnetic field.

These two fields produce magnetic field lines that cover toroidal surface. The particles move along the field lines and therefore on the magnetic surfaces (Figure 5.7).

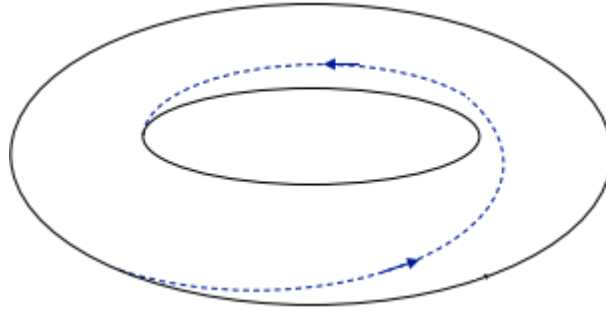


Figure 5.7. Magnetic field lines.

Vertical field

A plasma in a MHD (Magneto Hydro Dynamic) equilibrium cannot be confined only by self-generated current, so is necessary a vertical magnetic field (Figure 5.8) generated by a couple of coils in a symmetrical position compared to plasma, and with current in opposite direction compared to the plasma one.

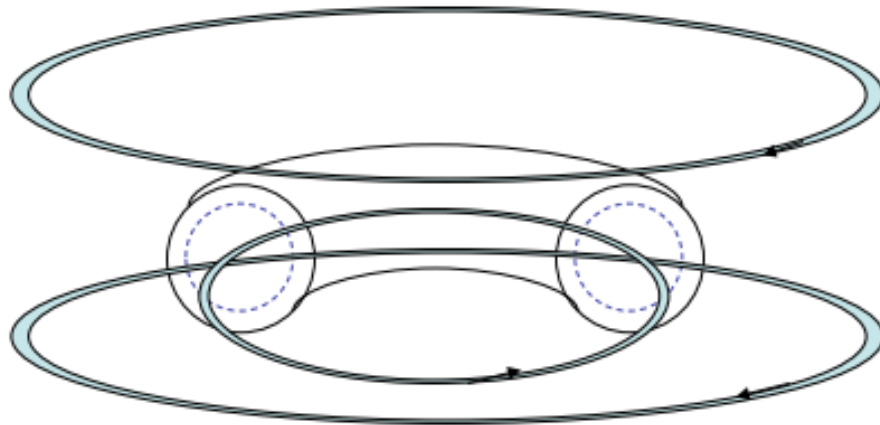


Figure 5.8. Vertical magnetic field.

The combined action of the three fields permits to maintain the plasma position distant from the chamber walls (Figure 5.9).

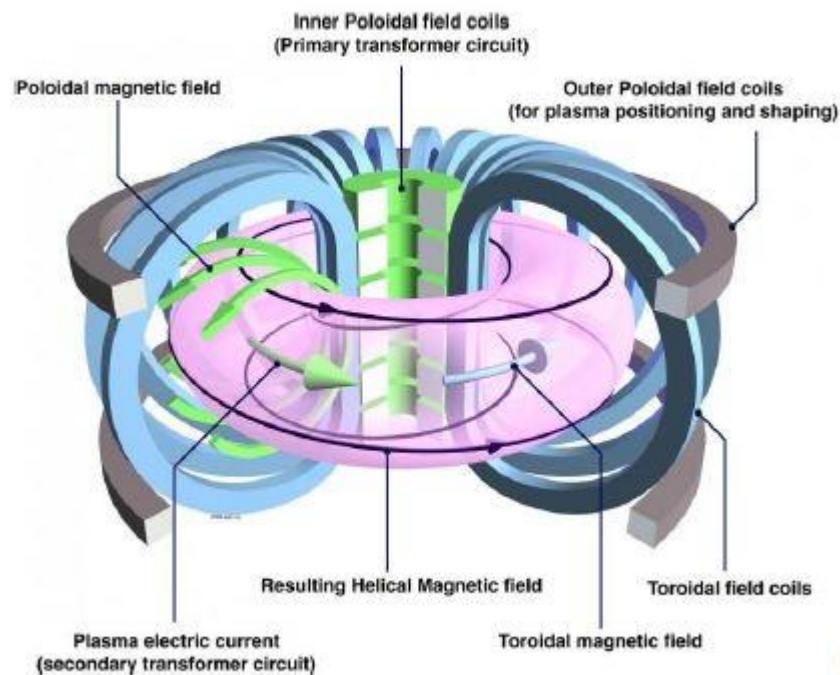
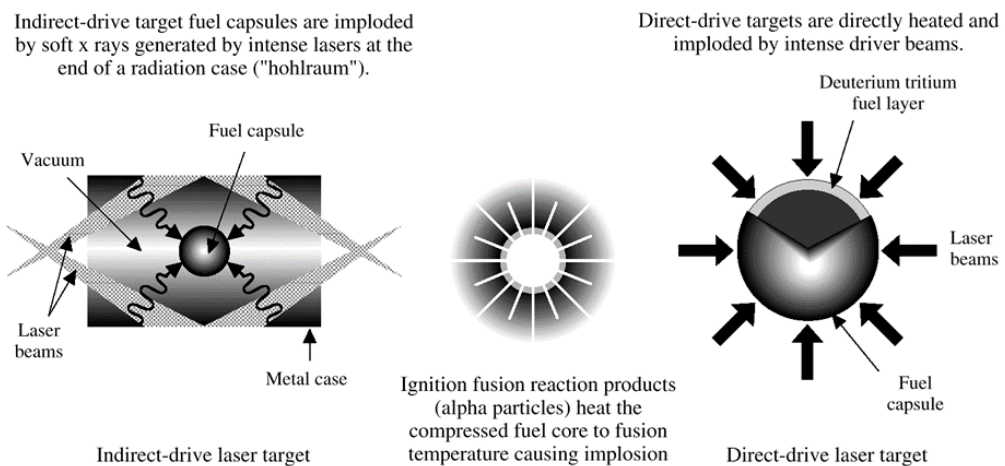


Figure 5.9. Tokamak configuration.

In the inertial configuration the fuel is compressed and heat very quickly by laser rays and force nuclei in so short distance that fusion reactions take place (Figure 5.10).



Source: LLNL 1994a.

Figure 5.10. Inertial confinement.

5.4. ITER and DEMO

ITER (International Thermonuclear Experimental Reactor) is an international scientific experiment, and its goal is the study and the realization of a reactor prototype able to demonstrate the possibility to trigger and sustain fusion reaction. In particular the main goal is to produce, for a relatively long period (hundreds of seconds), a fusion power of 500 MW with a power supplied of 50 MW, reaching in this way a value of 10 times the “quality factor” Q (produced and supplied power ratio).

The plant (Figure 5.11), under construction in Cadarache in the south France, is the last experiment suitable to demonstrate the feasibility of the fusion energy production, like JET (Joint European Torus) in England. JET has reached conditions next to the break-even with the production of 16 MW and a power supplied of 25 MW. The obtained results from these projects will need to realize a new fusion reactors generation for commercial scope, like DEMO, at present in design phase, which will be the first operative fusion power plant.

ITER is composed by different equipment as:

- Coils: 18 superconductors coils for the toroidal field and 6 coils for the poloidal one, a central solenoid, a set of coils that confine, model and control the plasma into the vacuum chamber. Other coils temper the Edge Localized Modes (instabilities at the plasma edge that cause the loss of plasma energy and produce excessive thermal load on the first wall).

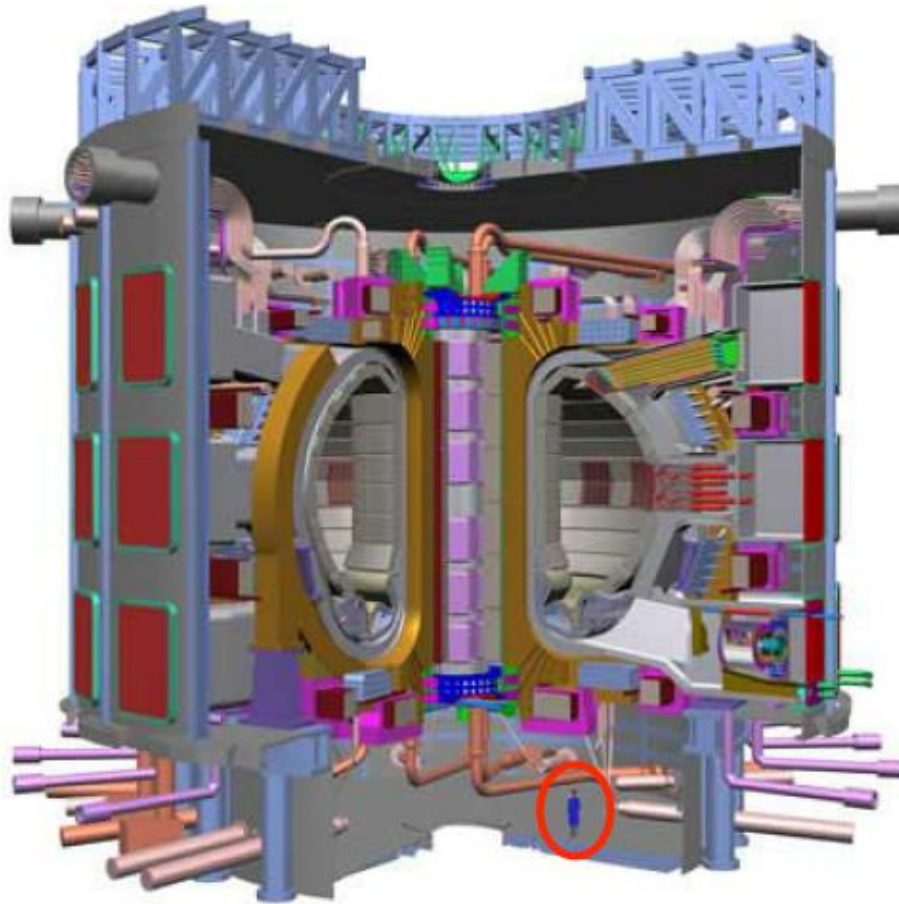


Figure 5.11. ITER reactor.

- Vacuum vessel (VV, vacuum chamber): with a Volume of 1400 m^3 , it is a steel leak proof container, places in a cryostat, where the fusion reaction takes place and it acts as first security barrier. The VV dimension determines the plasma volume: bigger is the chamber, greater is the energy that can be produced.
- Blanket: is a component that is on the VV internal surfaces, to shield the chamber and the superconductor magnets from heat and neutron fluxes. Neutrons kinetic energy is converted in thermal energy and then extracted.
- Divertor: it is one of the main components of ITER. It is located in the lower part of the vacuum chamber, and it is necessary to extract heat, helium residual and other impurities from the plasma.

5.4.1. Thermal load issue

In 2012 EFDA (European Fusion Development Agreement) published the report “Fusion Electricity – A roadmap to the realisation of fusion energy” [127] that defines a program for the production of electric energy by a demonstrative nuclear fusion reactor (DEMO) by the year 2050.

The roadmap defines eight strategic missions to overcome; in particular two projects about the mission “Heat-exhaust system” have as objective the realization of alternative solutions for the disposal of thermal loads:

- “Assessment of alternative divertor geometries and liquid metals PFCs (Plasma Facing Components)”
- “Definition and Design of the Divertor Tokamak Test (DTT) Facility”.

The tokamak confinement [128] is possible thanks to the magnetic field lines that create closed magnetic surfaces. On plasma edge there is a region with a thickness of few centimetres (SOL – Scrape-Off Layer) characterized by open field lines, in which the charges particles (and their energy) are driven from the plasma core to the separatrix (the last closed surface) on the divertor plates (Figure 5.12).

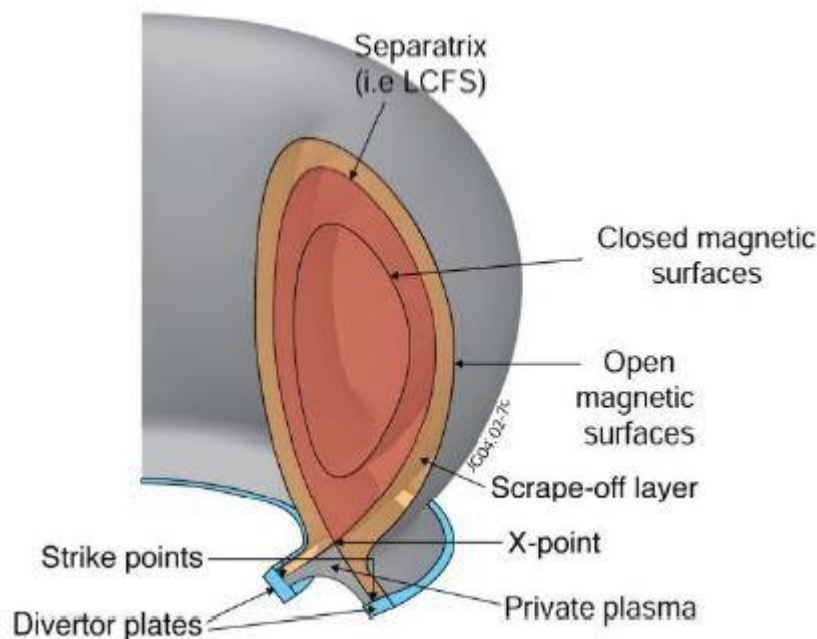


Figure 5.12. Plasma edge: Sol and divertor plates geometry.

The thermal flow parallel to the field lines in the SOL of ITER and DEMO should result greater than on the sun surface (Table 5.1) (Figure 5.13).

Table 5.1. The issue of thermal load on the divertor: P_{SOL} is the total power flowing in the SOL channel, λ_q is the decay length of the heat flow at the outboard midplane, R is the major radius, q_{\parallel} is the heat flow parallel to the magnetic field, q_{pol} is the poloidal component of the heat flow.

	P_{SOL} [MW]	λ_q [mm]	R [m]	q_{\parallel} [GW/m ²]	q_{pol} [GW/m ²]
ITER	~90	~2	~6	~1,8	~0,6
DEMO	~150	~1	~9	~5	~2

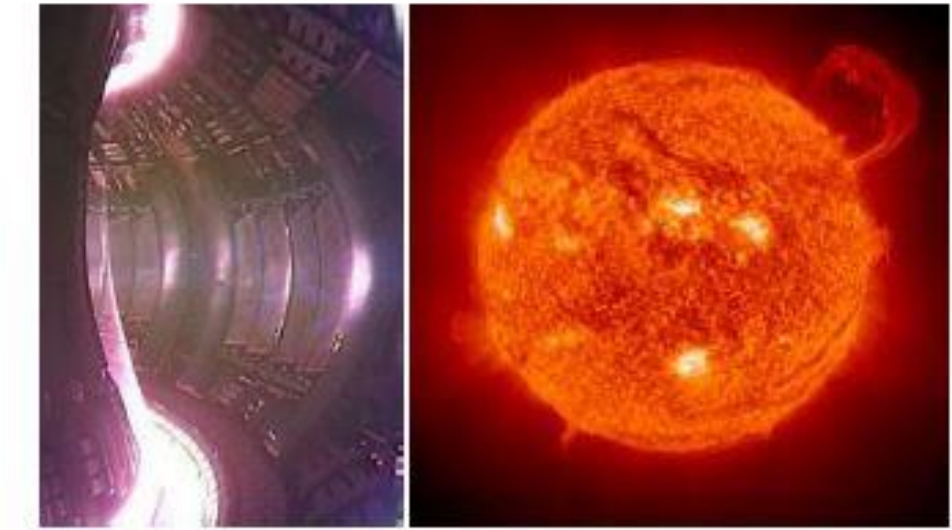


Figure 5.13 The power flux problem on the divertor: geometry is not sufficient to handle a heat flux that is higher on sun surface.

The strategy concerning the thermal loads on the divertor of DEMO is based on:

- Development components capable of withstanding high thermal flows ($>5 \text{ MW/m}^2$);
- Choice of divertor geometry and the field lines expansion;
- Removal of the plasma energy increasing plasma density on the edge and injecting impurities in the SOL region.

To do this must be demonstrate that the possible (alternative or complementary) solutions (e.g. advanced divertor configurations or liquid metals) can be integrated in a DEMO device.

Therefore a program for the definition and the design of DTT (Divertor Tokamak Test) was launched. This tokamak will be used to research alternative solutions for the divertor able to integrate with the specific physic conditions and the envisaged technological solutions in DEMO.

5.5. Divertor Tokamak Test

The alternative solutions tests on DTT shall include advanced magnetics configurations and the divertors in liquid metal like lithium. DTT shall work with high thermal load, flexible divertors and plasma conditions like DEMO. Therefore DTT is characterized by the following parameters: major radius $R = 2,15$ m, aspect ratio $A = 3,1$ ($A = R/a$, where 'a' is the tokamak minor radius), toroidal magnetic field $B_t = 6$ T, plasma current $I_p = 6$ MA and additional power $P_{tot} = 45$ MW.

The DTT scientific program is described in detail in the report “DTT Divertor Tokamak Test facility. Project Proposal” published by ENEA in July 2015 [129]. After the realisation, the machine will achieve the H-mode (operational regimes single null divertor configurations at full performances with the available additional power). In the following phases tests of alternative divertor solutions, including advanced magnetics configurations and liquid metal targets will be done.

DTT will be equipped with a set of external poloidal coils able to guarantee a large set of different magnetic configurations, XD configurations [130], Snow Flakes configurations (SF) [131] and up and down symmetric standard X point configurations (Figure 5.14).

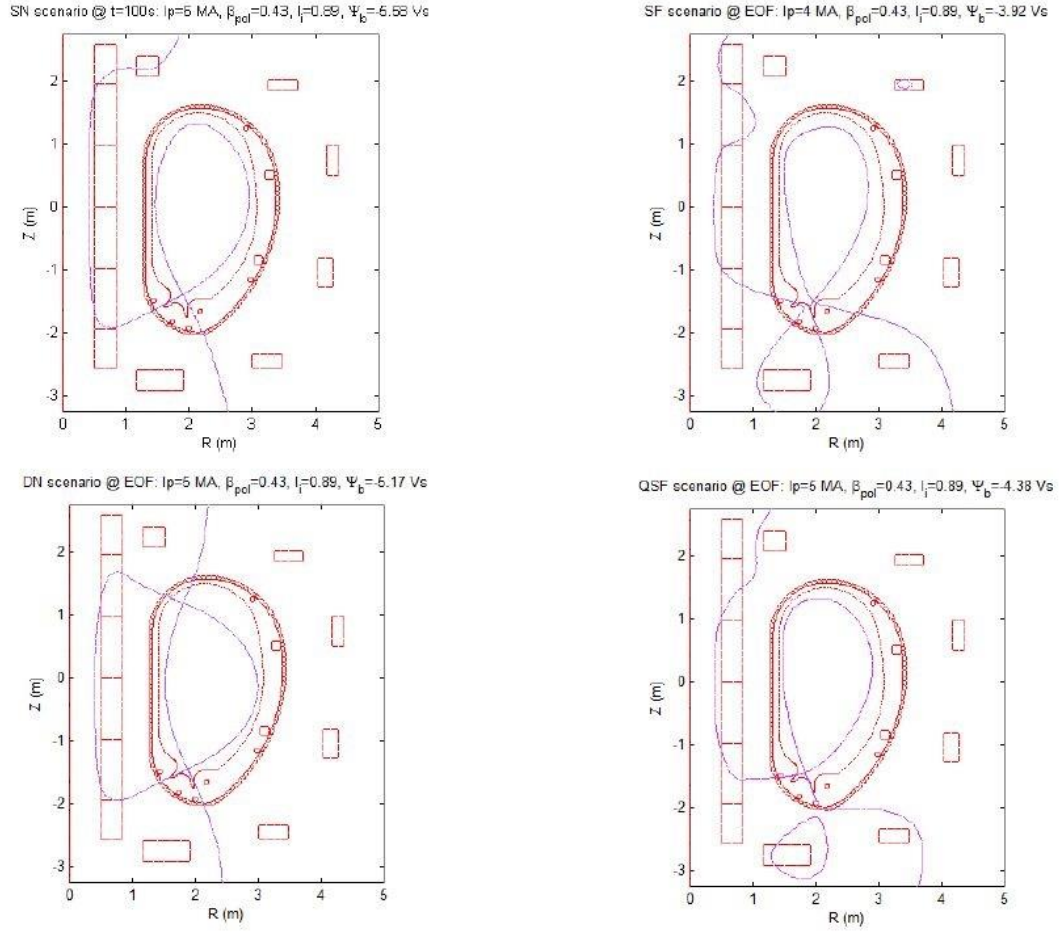


Figure 5.14. Some conventional and alternative magnetic configurations that can be obtained with the DTT poloidal field system.

5.6. Analysis of DTT advanced magnetics configurations

The studies presented in this paragraph concern the analysis of some electromagnetics aspects that can have an influence on the tokamak divertor.

Under the cooperation agreement with the University of Tuscia and the ENEA Frascati Research Centre, simulations on DTT divertor physic have been done with the MAXFEA code [132]. The aim of this work has been to find an optimal divertor magnetic configuration and to test the plasma performances when a liquid metal divertor is used. To optimize the local magnetic configuration, DTT shall a set of internal coils (inside the tokamak vacuum chamber) that can modify a second null of magnetic field B_p generated by the external coils. In this way it is possible to obtain magnetics configurations that allow to have minor thermal loads than the standard magnetics configurations or single null:

- X-Divertor (XD) configurations, characterized by a flaring magnetic flux on the divertor target [130];
- Snow Flakes configurations, characterized by a contracting magnetic flux [131].

The internal coils can be used to control different geometric parameters: the flux expansion, connection length, separatrix distance, X-point distance and the divergence of flux lines on the divertor [133].

In Figure 5.15 magnetic equilibrium, calculated by the MAXFEA code, of the base case, in which the current of the internal coils C1-C4 have been fixed equal to zero, is reported.

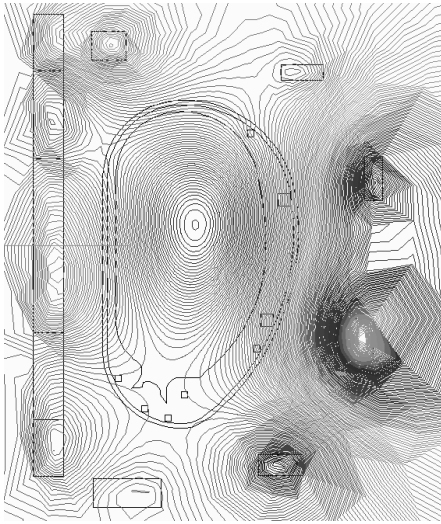


Figure 5.15. Equilibrium calculated with MAXFEA code.

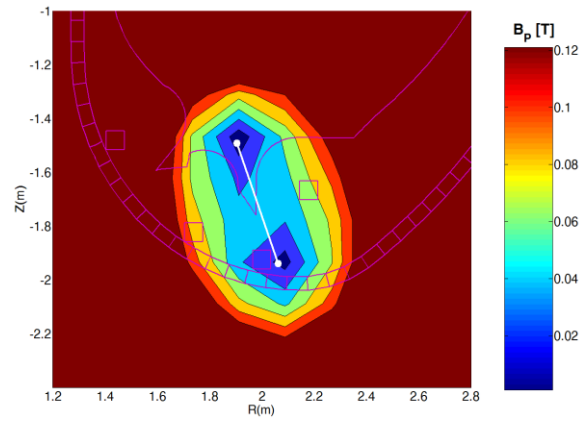


Figure 5.16. Poloidal magnetic field B_p in the divertor region.

In Figure 5.16 the poloidal magnetic field B_p in the divertor region is reported. As it is shown among the two magnetic field nulls there is a region in which the poloidal field increases forming a “hill”. This trend is better shown in Figure 5.17 where B_p value, as a function of the z position along the line x_1 - x_2 joining the two nulls, is reported. The SF^+ configuration is a divertor magnetic configuration where the second null x_2 interacts in a meaningful way with the primary x_1 . A “flat” field around the two nulls is considered as a necessary SF condition, which leads to a thermal load reduction.

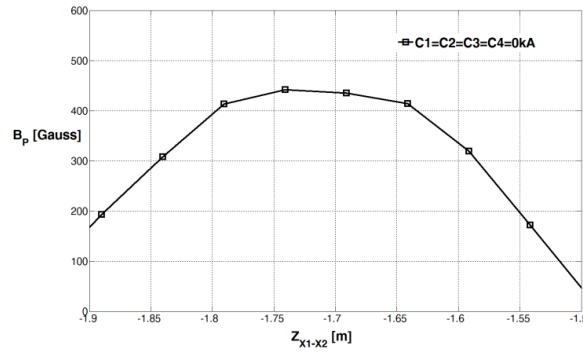


Figure 5.17. B_p as a function of z along the line $x1-x2$.

A possible use of the internal coils C1-C4 is to increase the flat zone (null zone) around the two nulls, acting on the currents as reported in Table 5.2. In Table is also reported the growth rate (parameter that identify the time in which the fusionist plasma escape) for the considered equilibrium. It can be noticed that there is a small effect of the C1-C4 currents on the growth rate than in the case without C1-C4 currents.

Table 5.2. SF^+ equilibrium obtained with MAXFEA with/without C1-C4 currents.

	MAXFEA	MAXFEA
	5 MA SF^+ Scenario – SOF	5 MA SF^+ Scenario – SOF
	C1 = 0kA	C1 = 80kA
	C2 = 0kA	C2 = -33,3kA
	C3 = 0kA	C3 = 0kA
	C4 = 0kA	C4 = 32KA
growth rate (s^{-1})	25	27,7

In Figure 5.18 is reported the poloidal magnetic field B_p in the divertor region for the equilibrium described in Figure 5.15 including internal coils: C1 = 80 kA, C2 = -33,3 kA, C3 = 0 kA, C4 = 32 kA.

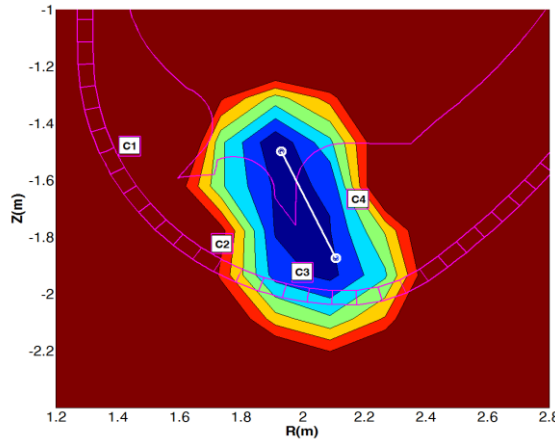


Figure 5.18. Poloidal magnetic field B_p with internal coils currents different from zero.

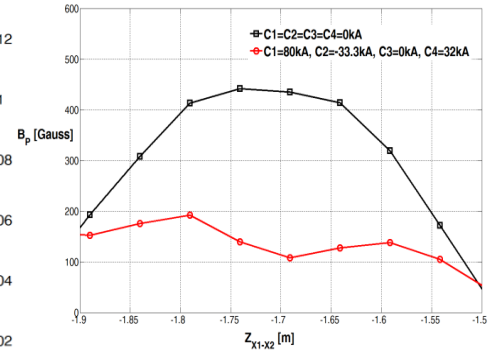


Figure 5.19. Poloidal field as a function of z with/without internal coils.

In Figure 5.19 is reported the poloidal field B_p as a function of z along the line x_1 - x_2 joining the two nulls with and without the internal coils C_1 - C_4 . The poloidal field decreases along z thanks to the internal coils action forming a big null region, that leads a reduction of the high thermal load studied in this work.

Conclusions

Nowadays with the increase of the worldwide energy demand, in addition to a rational use of the fossil energy sources, the development of energy production by non-conventional sources as the biomass, and the research and the development of the thermonuclear fusion have an important role.

During the three years of PhD two different waste biomass conversion processes have been studied: the gasification and the anaerobic digestion. Furthermore, as part of the collaboration agreement between the Tuscia University and the ENEA Frascati Research Center, a work on thermonuclear fusion has been carried out.

The activities showed in this work are part of the simulations activities carried out in the European 7FP UNIfHY project. In particular one of the aims of this work has been to develop and validate experimentally a model capable of predicting the performance of a steam blown fluidized bed biomass gasifier during steady state operation where pine wood was chosen as biomass feedstock. The gasifier model for the simulation receives as input the results of the pyrolysis tests products. Experimental

tests on a bench scale fluidized bed reactor were carried out in the temperatures range adopted for the simulation (750-850°C). The results of the tests include produced gas and tar composition as well gas, tar and char yield. The comparison between the results of the model and those of experiments showed that model is fairly capable of predicting gas composition and production rate

Furthermore during the European project UNIfHY, a system capable to produce pure hydrogen from biomass has been realized and analysed via kinetic and thermodynamic simulations and experimental data. The plant is mainly composed of bubbling fluidized bed gasifier with catalytic filter candles, Water Gas Shift and Pressure Swing Absorption (PSA). Focusing on the hydrogen production, a sensitivity study was carried out varying the steam to biomass ratio and the gasifier operating temperature. The results show that the gas yield increases with the gasification temperature and the S/B ratio. All plant configurations examined assure auto-thermal behaviour of the entire process. Considering the whole plant, hydrogen chemical efficiency always increases with temperature and steam to biomass ratio. The use of the off gas to produce steam allows operating the process without the input of auxiliary fuel. In the simulations the best conditions have been reached at 850°C with a steam to biomass ratio of 2, obtaining a chemical efficiency of 70%.

Another biomass conversion process analysed has been the anaerobic co-digestion which is increasingly used to simultaneously treat several solid and liquid organic wastes in order to balance the nutrients content, to reduce negative effects of toxic compounds on the process, and, therefore, to increase the biogas yield. Moreover, co-digestion technology contributes to a more efficient use of anaerobic digestion, because multiple streams of wastes can be processed together in a single plant at the same time. In this work experimental tests have been carried out considering olive mill solid wastes and cheese whey wastewater.

Olive-mill wastes represent a significant environmental problem in Mediterranean area where they are produced in huge quantity and seasonally, thus in short periods of time. The use of OMSW with pit represents economically a very attractive possibility, in particular for the small olive mills. From the tests carried out with a batch stirred tank reactor results OMSW with pit has better performance if used

in co-digestion with other substrates. The optimal mixture has been found using 4,65% of cattle manure, 72,10% of cattle slurry and 23,25% of OMSW with a Total Solid (TS) content of 14%, reaching a BMP of 0,1034 l/g_{vs} and a methane average percentage production in biogas of 64%.

Also the use of cheese whey wastewater (CWW) and poultry manure (PM) represents economically a very attractive possibility for farms where they are produced. In the dairy industry CWW is one of the main wastes. In fact they are not generally re-used and could represent a pollution source for the watercourses. PM is generally utilized to enrich soils and fertilize crops but, in some areas, the number of poultry farms is high and therefore a treatment process of the PM is necessary. This research is part of the Rural Development Plan (RDP) project, Measure 124.

From the obtained results, among the different studied mixtures the test with CWW:PM ratio of 1:1 permits to produce a greater quantity of methane and at the same time to reduce the acidification trend of CWW, to improve C/N ratio and to reduce the TS fed into the plant. Considering a BMP equal to 223 ml/g_{vs} and the amount of wastes identified into the agricultural companies partner of the project, a 65 kW anaerobic digestion plant is possible to realise, with an annual production of about 520.000 kWh of electricity.

For the anaerobic digestion process would be very important to verify the single process stages and study the bacterial activity so that it is possible to maximise the process yield modifying the input characteristic of the biomass. For this reason an anaerobic digestion model, that takes into account six biological processes, has been developed and simulation with CWW and PM has been carried out. By these is resulted that the model can predict the trend of the methane production and the bacteria growth. A future development will be to improve the model taking into account the physico-chemical reactions and all the inhibition factors.

As part of the collaboration agreement between the University of Tuscia and the ENEA Frascati Research Center, studies about the analysis of some electromagnetic aspects that influence the divertor of the thermonuclear magnetic device in confinement fusion, called tokamak, have been made. The design of a machine called "Divertor Tokamak Test facility " (DTT), has been developed in order to find alternative solutions

to the problem of thermal loads, considered for the divertor in the demonstrative system DEMO, a nuclear fusion power plant that will be able to supply electricity to the grid by 2050. Alternative solutions to be subjected to specific tests in DTT, include, advanced magnetics configurations and the divertors in liquid metal such as lithium. DTT will have to operate with significant thermal loads, flexible divertors and plasma conditions similar to those required for DEMO.

The aim of this study has been to simulate the physics of the divertor in DTT with the use of the MAXFEA code. The purpose of the research was to find an optimal divertor magnetic configuration and tests the performances of plasma with the use of a liquid metal divertor. To optimize the local magnetic configuration, DTT will have a set of internal coils (inside the vacuum chamber of the tokamak) able to change a second magnetic field null generated by the external coils (located out of the vacuum chamber) obtaining magnetics configurations that enable a lower thermal loads compared with the standard magnetics configurations or "*single null*": X divertor-configuration (XD) or Snow Flakes-configurations (SF). The internal coils can be used to control different geometrical parameters whose variation allows a reduction of thermal loads: flows enlargement, length of connection, distance between separators lines, distance between the X-points, or divergence of flux lines on the divertor. By the simulations is shown that is possible to increase the null zone dimensions around the two nulls acting on the currents of the internal coils C1-C4. The poloidal field tends to decrease along z due to the action of internal coils creating a wide null region that will result in a reduction of the high thermal load. Moreover there is a small effect of the currents C1-C4 on the growth rate (a parameter that identifies the time used by the fusionist plasma to escape) compared to the case without C1-C4 currents.

Bibliography

- [1] Monarca D, Colantoni A, Cecchini M, Longo L, Vecchione L, Carlini M, et al. Energy Characterization and Gasification of Biomass Derived by Hazelnut Cultivation: Analysis of Produced Syngas by Gas Chromatography. *Math Probl Eng* 2012;2012.
- [2] Carlini M, Castellucci S, Cocchi S, Manzo A. Waste Wood Biomass Arising from Pruning of Urban Green in Viterbo Town: Energy Characterization and Potential Uses. *Comput. Sci. Its Appl.* 2013, Springer; 2013, p. 242–55.
- [3] Goldemberg J, Johansson TB. World energy assessment: overview: 2004 update. United Nations Publications; 2004.
- [4] International Energy Agency. World Energy Outlook, 2012. OECD/IEA; 2012.
- [5] Orecchini F, Bocci E. Biomass to hydrogen for the realization of closed cycles of energy resources. *Energy* 2007;32:1006–11.
- [6] Bocci E, Di Carlo A, Marcelo D. Power plant perspectives for sugarcane mills. *Energy* 2009;34:689–98.
- [7] Bocci E, Di Carlo A, Vecchione L, Villarini M, De Falco M, Dell’Era A. Technical-Economic Analysis of an Innovative Cogenerative Small Scale Biomass Gasification Power Plant. *Comput. Sci. Its Appl.* 2013, Springer; 2013, p. 256–70.
- [8] Bocci E, Sisinni M, Moneti M, Vecchione L, Di Carlo A, Villarini M. State of Art of Small Scale Biomass Gasification Power Systems: A Review of the Different Typologies. *Energy Procedia* 2014;45:247–56. doi:10.1016/j.egypro.2014.01.027.
- [9] Pari L. Energy production from biomass: the case of Italy. *Renew Energy* 2001;22:21–30. doi:10.1016/S0960-1481(00)00050-1.
- [10] Bocci E. Sistemi a biomasse: progettazione e valutazione economica: impianti di generazione di calore e di elettricità: con software BioSim_1. 0 SIMultiatore economico BIOMassa. Maggioli; 2011.
- [11] European Standard EN 14774-1:2009, Solid biofuel. Determination of moisture content, oven dry method. Part 1: total moisture, reference method. n.d.
- [12] European Standard EN 14774-2:2009, Solid biofuel. Determination of moisture content, oven dry method. Part 2: total moisture, simplified method. n.d.
- [13] European Standard EN 14774-3:2009, Solid biofuel. Determination of moisture content, oven dry method. Part 3: moisture in general analysis sample. n.d.
- [14] European Standard EN 14775:2009, Solid biofuel: Determination of Ash content. n.d.
- [15] European Standard EN 15148 – Solid biofuels – Determination of the content of volatile matter. n.d.
- [16] European Standard EN 15104:2011, Solid biofuels: determination of total content of carbon, hydrogen and nitrogen. Instrumental methods. n.d.

- [17] European Standard EN 14918:2009, Solid biofuels: determination of calorific value. n.d.
- [18] Bocci E, Di Carlo A, McPhail SJ, Gallucci K, Foscolo PU, Moneti M, et al. Biomass to fuel cells state of the art: A review of the most innovative technology solutions. *Int J Hydrog Energy* 2014;39:21876–95.
- [19] Helton Jose' Alves a, *, Cí'cero Bley Junior c , Rafael Rick Niklevicz , Elisandro Pires Frigo b , Michelle Sato Frigo b , Carlos Henrique Coimbra-Arau'jo. Overview of hydrogen production technologies from biogas and the applications in fuel cells 2013.
- [20] Bove R, Lunghi P. Experimental comparison of MCFC performance using three different biogas types and methane. *J Power Sources* 2005;145:588–93. doi:10.1016/j.jpowsour.2005.01.069.
- [21] McPhail SJ, Cigolotti V, Moreno A. Fuel Cells in the Waste-to-Energy Chain 2012.
- [22] (Jack) Guo X, Tak JK, Johnson RL. Ammonia removal from air stream and biogas by a H₂SO₄ impregnated adsorbent originating from waste wood-shavings and biosolids. *J Hazard Mater* 2009;166:372–6. doi:10.1016/j.jhazmat.2008.11.028.
- [23] Hedström L. Fuel Cells and Biogas 2010.
- [24] Rasi S, Veijanen A, Rintala J. Trace compounds of biogas from different biogas production plants. *Energy* 2007;32:1375–80. doi:10.1016/j.energy.2006.10.018.
- [25] Aravind PV, de Jong W. Evaluation of high temperature gas cleaning options for biomass gasification product gas for Solid Oxide Fuel Cells. *Prog Energy Combust Sci* 2012.
- [26] Iaquaniello G, Mangiapane A. Integration of biomass gasification with MCFC. *Int J Hydrog Energy* 2006;31:399–404. doi:10.1016/j.ijhydene.2005.09.010.
- [27] Christensen JM, Jensen PA, Jensen AD. Effects of Feed Composition and Feed Impurities in the Catalytic Conversion of Syngas to Higher Alcohols over Alkali-Promoted Cobalt–Molybdenum Sulfide. *Ind Eng Chem Res* 2011;50:7949–63. doi:10.1021/ie200235e.
- [28] Wang L, Weller CL, Jones DD, Hanna MA. Contemporary issues in thermal gasification of biomass and its application to electricity and fuel production. *Biomass Bioenergy* 2008;32:573–81.
- [29] Warnecke R. Gasification of biomass: comparison of fixed bed and fluidized bed gasifier. *Biomass Bioenergy* 2000;18:489–97. doi:10.1016/S0961-9534(00)00009-X.
- [30] Kunii D, Levenspiel O. Fluidized reactor models. 1. For bubbling beds of fine, intermediate, and large particles. 2. For the lean phase: freeboard and fast fluidization. *Ind Eng Chem Res* 1990;29:1226–34. doi:10.1021/ie00103a022.
- [31] Rapagnà S, Jand N, Kiennemann A, Foscolo PU. Steam-gasification of biomass in a fluidised-bed of olivine particles. *Biomass Bioenergy* 2000;19:187–97. doi:10.1016/S0961-9534(00)00031-3.
- [32] Sarkar N, Ghosh SK, Bannerjee S, Aikat K. Bioethanol production from agricultural wastes: An overview. *Renew Energy* 2012;37:19–27.

- [33] Vivoli FP. Energia dalle biomasse. Tecnologia e prospettive 2008.
- [34] ENEA. RAPPORTO ENERGIA E AMBIENTE ANALISI E SCENARI 2009 2010.
- [35] Monnet F. An introduction to anaerobic digestion of organic wastes. Remade Scotl 2003;1–48.
- [36] Vismara R, Malpei F, Centemero M. Biogas da rifiuti solidi urbani. Palermo Flaccovio Ed 2008.
- [37] Cecchi F, Pavan P, Alvarez JM, Bassetti A, Cozzolino C. Anaerobic Digestion of Municipal Solid Waste: Thermophilic vs. Mesophilic Performance At High Solids. Waste Manag Res 1991;9:305–15. doi:10.1177/0734242X9100900141.
- [38] Bridgwater A. Renewable fuels and chemicals by thermal processing of biomass. Chem Eng J 2003;91:87–102. doi:10.1016/S1385-8947(02)00142-0.
- [39] Vecchione L, Moneti M, Bocci E, Carlo AD, Foscolo P. Steam Gasification of Pine Wood in a Fluidized Bed Reactor: Model Development and Validation at Different Operative Conditions. 21st Eur Biomass Conf Exhib 2013;841–8.
- [40] Di Carlo A, Borello D, Bocci E. Process simulation of a hybrid SOFC/mGT and enriched air/steam fluidized bed gasifier power plant. Int J Hydrog Energy 2013.
- [41] Gil J, Aznar MP, Caballero MA, Francés E, Corella J. Biomass Gasification in Fluidized Bed at Pilot Scale with Steam–Oxygen Mixtures. Product Distribution for Very Different Operating Conditions. Energy Fuels 1997;11:1109–18. doi:10.1021/ef9602335.
- [42] Rapagna S, Jand N, Kiennemann A, Foscolo PU. Steam-gasification of biomass in a fluidised-bed of olivine particles. Biomass Bioenergy 2000;19:187–97.
- [43] Corella GJ, Aznar MP, Caballero MA. Biomass gasification in atmospheric and bubbling fluidized bed: effect of the type of gasifying agent on the product distribution. Biomass Bioenergy 1999;17:389–403.
- [44] Shelley S. Coal gasification comes of age. Chem Eng Prog 2006;102:6–10.
- [45] Hofbauer H, Rauch R, Foscolo P, Matera D. Hydrogen rich gas from biomass steam gasification. First World Conf. Exhib. Biomass Energy Ind. Sevilla Spain, 2000.
- [46] Rapagná S, Provendier H, Petit C, Kiennemann A, Foscolo PU. Development of catalysts suitable for hydrogen or syn-gas production from biomass gasification. Biomass Bioenergy 2002;22:377–88. doi:10.1016/S0961-9534(02)00011-9.
- [47] Rapagnà S, Jand N, Foscolo PU. Catalytic gasification of biomass to produce hydrogen rich gas. Int J Hydrog Energy 1998;23:551–7. doi:10.1016/S0360-3199(97)00108-0.
- [48] Caballero MA, Corella J, Aznar M-P, Gil J. Biomass Gasification with Air in Fluidized Bed. Hot Gas Cleanup with Selected Commercial and Full-Size Nickel-Based Catalysts. Ind Eng Chem Res 2000;39:1143–54. doi:10.1021/ie990738t.
- [49] Van Paasen SVB, Kiel JHA, Veringa HJ. Tar Formation in a Fluidised Bed Gasifier. Impact Fuel Prop Oper Cond 2004.

- [50] Simell P, Kurkela E, Ståhlberg P, Hepola J. Catalytic hot gas cleaning of gasification gas. *Catal Today* 1996;27:55–62. doi:10.1016/0920-5861(95)00172-7.
- [51] Choi Y, Stenger HG. Water gas shift reaction kinetics and reactor modeling for fuel cell grade hydrogen. *J Power Sources* 2003;124:432–9. doi:10.1016/S0378-7753(03)00614-1.
- [52] Mondal P, Dang GS, Garg MO. Syngas production through gasification and cleanup for downstream applications — Recent developments. *Fuel Process Technol* 2011;92:1395–410. doi:10.1016/j.fuproc.2011.03.021.
- [53] Delgado J, Aznar MP, Corella J. Biomass gasification with steam in fluidized bed: Effectiveness of CaO, MgO, and CaO-MgO for hot raw gas cleaning. *Ind Eng Chem Res* 1997;36:1535–43.
- [54] D’Orazio A, Rapagnà S, Foscolo PU, Gallucci K, Nacken M, Heidenreich S, et al. Gas conditioning in H₂ rich syngas production by biomass steam gasification: Experimental comparison between three innovative ceramic filter candles. *Int J Hydrog Energy* 2015;40:7282–90. doi:10.1016/j.ijhydene.2015.03.169.
- [55] Savuto E, Di Carlo A, Bocci E, D’Orazio A, Villarini M, Carlini M, et al. Development of a CFD model for the simulation of tar and methane steam reforming through a ceramic catalytic filter. *Int J Hydrog Energy* 2015;40:7991–8004. doi:10.1016/j.ijhydene.2015.04.044.
- [56] UNIQUE Cooperative Research Project, Contract N.211517 7FP n.d. www.uniqueproject.eu (accessed May 2, 2013).
- [57] Foscolo PU, Gallucci K. Integration of particulate abatement, removal of trace elements and tar reforming in one biomass steam gasification reactor yielding high purity syngas for efficient CHP and power plants. 16th Eur. Biomass Conf. Exhib., 2008.
- [58] Heidenreich S, Nacken M, Foscolo PU, Rapagna S. Gasification apparatus and method for generating syngas from gasifiable feedstock material. App. 12/598,508, 2008.
- [59] Yu Q, Brage C, Chen G, Sjöström K. Temperature impact on the formation of tar from biomass pyrolysis in a free-fall reactor. *J Anal Appl Pyrolysis* 1997;40–41:481–9. doi:10.1016/S0165-2370(97)00017-X.
- [60] Narváez I, Orío A, Aznar MP, Corella J. Biomass Gasification with Air in an Atmospheric Bubbling Fluidized Bed. Effect of Six Operational Variables on the Quality of the Produced Raw Gas. *Ind Eng Chem Res* 1996;35:2110–20. doi:10.1021/ie9507540.
- [61] Kinoshita CM, Wang Y, Zhou J. Tar formation under different biomass gasification conditions. *J Anal Appl Pyrolysis* 1994;29:169–81.
- [62] Devi L, Ptasinski KJ, Janssen FJ. A review of the primary measures for tar elimination in biomass gasification processes. *Biomass Bioenergy* 2003;24:125–40.
- [63] Di Carlo A, Bocci E, Zuccari F, Dell’Era A. Numerical Investigation of Sorption Enhanced Steam Methane Reforming Process Using Computational Fluid Dynamics Eulerian- Eulerian Code. *Ind Eng Chem Res* 2010;49:1561–76.

- [64] D’Orazio A, Di Carlo A, Dionisi N, Dell’Era A, Orecchini F. Toluene steam reforming properties of CaO based synthetic sorbents for biomass gasification process. *Int J Hydrog Energy* 2013.
- [65] Sisinni M, Di Carlo A, Bocci E, Micangeli A, Naso V. Hydrogen-Rich Gas Production by Sorption Enhanced Steam Reforming of Woodgas Containing TAR over a Commercial Ni Catalyst and Calcined Dolomite as CO₂ Sorbent. *Energies* 2013;6:3167–81.
- [66] Rapagnà S, Jand N, Foscolo PU. Catalytic gasification of biomass to produce hydrogen rich gas. *Int J Hydrog Energy* 1998;23:551–7. doi:10.1016/S0360-3199(97)00108-0.
- [67] Momirlan M, Veziroglu TN. The properties of hydrogen as fuel tomorrow in sustainable energy system for a cleaner planet. *Int J Hydrog Energy* 2005;30:795–802. doi:10.1016/j.ijhydene.2004.10.011.
- [68] Balat M. Potential importance of hydrogen as a future solution to environmental and transportation problems. *Int J Hydrog Energy* 2008;33:4013–29. doi:10.1016/j.ijhydene.2008.05.047.
- [69] Jain IP. Hydrogen the fuel for 21st century. *Int J Hydrog Energy* 2009;34:7368–78. doi:10.1016/j.ijhydene.2009.05.093.
- [70] Dunn S. Hydrogen futures: toward a sustainable energy system. *Int J Hydrog Energy* 2002;27:235–64. doi:10.1016/S0360-3199(01)00131-8.
- [71] Kothari R, Buddhi D, Sawhney RL. Comparison of environmental and economic aspects of various hydrogen production methods. *Renew Sustain Energy Rev* 2008;12:553–63. doi:10.1016/j.rser.2006.07.012.
- [72] UNIfHY Collaborative Project, Project ID 299732 7FP n.d. <http://www.unifhy.eu>.
- [73] Foscolo PU, Gallucci K. Integration of particulate abatement, removal of trace elements and tar reforming in one biomass steam gasification reactor yielding high purity syngas for efficient CHP and power plants. 16th Eur. Biomass Conf. Exhib., 2008.
- [74] Di Carlo A, Bocci E, Naso V. Process simulation of a SOFC and double bubbling fluidized bed gasifier power plant. *Int J Hydrog Energy* 2012.
- [75] Nikoo MB, Mahinpey N. Simulation of biomass gasification in fluidized bed reactor using ASPEN PLUS. *Biomass Bioenergy* 2008;32:1245–54. doi:10.1016/j.biombioe.2008.02.020.
- [76] Darton RC. Bubble growth due to coalescence in fluidised beds. *Trans Inst Chem Engrs* 1977;55:274.
- [77] Orecchini F, Bocci E, Di Carlo A. Process simulation of a neutral emission plant using chestnut’s coppice gasification and molten carbonate fuel cells. *J Fuel Cell Sci Technol* 2008;5.
- [78] Rep M. Deliverable 3.1-PSA UNIT DESIGN AND CONSTRUCTION, UNIfHY Project. n.d.
- [79] Fercher E, Hofbauer H, Fleck T, Rauch R, Veronik G. Two years experience with the FICFB-gasification process. 10th Eur. Conf. Technol. Exhib. Biomass Energy Ind., 1998, p. 280–3.

- [80] Rapagnà S, Gallucci K, Di Marcello M, Matt M, Nacken M, Heidenreich S, et al. Gas cleaning, gas conditioning and tar abatement by means of a catalytic filter candle in a biomass fluidized-bed gasifier. *Bioresour Technol* 2010;101:7123–30.
- [81] Gökaliler F, Göçmen BA, Aksoylu AE. The effect of Ni:Pt ratio on oxidative steam reforming performance of Pt–Ni/Al₂O₃ catalyst. *Int J Hydrog Energy* 2008;33:4358–66. doi:10.1016/j.ijhydene.2008.05.068.
- [82] Shen L, Gao Y, Xiao J. Simulation of hydrogen production from biomass gasification in interconnected fluidized beds. *Biomass Bioenergy* 2008;32:120–7. doi:10.1016/j.biombioe.2007.08.002.
- [83] Lv P, Yuan Z, Ma L, Wu C, Chen Y, Zhu J. Hydrogen-rich gas production from biomass air and oxygen/steam gasification in a downdraft gasifier. *Renew Energy* 2007;32:2173–85. doi:10.1016/j.renene.2006.11.010.
- [84] Koroneos C, Dompros A, Roumbas G. Hydrogen production via biomass gasification—A life cycle assessment approach. *Chem Eng Process Process Intensif* 2008;47:1261–8. doi:10.1016/j.cep.2007.04.003.
- [85] Angelidaki I, Ellegaard L, Ahring BK. A comprehensive model of anaerobic bioconversion of complex substrates to biogas. *Biotechnol Bioeng* 1999;63:363–72. doi:10.1002/(SICI)1097-0290(19990505)63:3<363::AID-BIT13>3.0.CO;2-Z.
- [86] Batstone DJ, Keller J, Angelidaki I, Kalyuzhnyi SV, Pavlostathis SG, Rozzi A, et al. The IWA Anaerobic Digestion Model No 1(ADM 1). *Water Sci Technol* 2002;45:65–73.
- [87] Eastman JA, Ferguson JF. Solubilization of Particulate Organic Carbon during the Acid Phase of Anaerobic Digestion. *J Water Pollut Control Fed* 1981;53:352–66.
- [88] Abbasi T, Tauseef SM, Abbasi SA. Anaerobic digestion for global warming control and energy generation—An overview. *Renew Sustain Energy Rev* 2012;16:3228–42. doi:10.1016/j.rser.2012.02.046.
- [89] Abbasi T, Tauseef SM, Abbasi SA. *Biogas energy*. vol. 2. Springer Science & Business Media; 2011.
- [90] Daisy A, Kamaraj S, others. The impact and treatment of night soil in anaerobic digester: a review. *J Microb Biochem Technol* 2011;3:43–50.
- [91] Verma S. *Anaerobic digestion of biodegradable organics in municipal solid wastes*. Columbia University, 2002.
- [92] Fricke K, Santen H, Wallmann R, Hüttner A, Dichtl N. Operating problems in anaerobic digestion plants resulting from nitrogen in MSW. *Waste Manag* 2007;27:30–43. doi:10.1016/j.wasman.2006.03.003.
- [93] Yen H-W, Brune DE. Anaerobic co-digestion of algal sludge and waste paper to produce methane. *Bioresour Technol* 2007;98:130–4.
- [94] Siddiqui Z, Horan NJ, Anaman K. Optimisation of C: N ratio for co-digested processed industrial food waste and sewage sludge using the BMP test. *Int J Chem React Eng* 2011;9.
- [95] Karim K, Hoffmann R, Klasson KT, Al-Dahhan MH. Anaerobic digestion of animal waste: effect of mode of mixing. *Water Res* 2005;39:3597–606.

- [96] Ward AJ, Hobbs PJ, Holliman PJ, Jones DL. Optimisation of the anaerobic digestion of agricultural resources. *Bioresour Technol* 2008;99:7928–40.
- [97] Owen WF, Stuckey DC, Healy Jr. JB, Young LY, McCarty PL. Bioassay for monitoring biochemical methane potential and anaerobic toxicity. *Water Res* 1979;13:485–92. doi:10.1016/0043-1354(79)90043-5.
- [98] Sesli M, Yegenoglu D. RAPD-PCR analysis of cultured type olives in Turkey. *Afr J Biotechnol* 2009;8.
- [99] International Olive Oil Council. [Http://www.internationaloliveoil.org/](http://www.internationaloliveoil.org/) n.d. <http://www.internationaloliveoil.org/>.
- [100] Roig A, Cayuela ML, Sánchez-Monedero MA. An overview on olive mill wastes and their valorisation methods. *Waste Manag* 2006;26:960–9. doi:10.1016/j.wasman.2005.07.024.
- [101] Fountoulakis MS, Dokianakis SN, Kornaros ME, Aggelis GG, Lyberatos G. Removal of phenolics in olive mill wastewaters using the white-rot fungus *Pleurotus ostreatus*. *Water Res* 2002;36:4735–44. doi:10.1016/S0043-1354(02)00184-7.
- [102] Doymaz I, Gorel O, Akgun NA. Drying Characteristics of the Solid By-product of Olive Oil Extraction. *Biosyst Eng* 2004;88:213–9. doi:10.1016/j.biosystemseng.2004.03.003.
- [103] Niaounakis M, Halvadakis CP. Olive Processing Waste Management: Literature Review and Patent Survey 2nd Edition. Elsevier; 2006.
- [104] Azbar N, Yonar T. Comparative evaluation of a laboratory and full-scale treatment alternatives for the vegetable oil refining industry wastewater (VORW). *Process Biochem* 2004;39:869–75. doi:10.1016/S0032-9592(03)00193-6.
- [105] Dermeche S, Nadour M, Larroche C, Moulti-Mati F, Michaud P. Olive mill wastes: Biochemical characterizations and valorization strategies. *Process Biochem* 2013;48:1532–52. doi:10.1016/j.procbio.2013.07.010.
- [106] ISMEA. Istituto dei Servizi per il Mercato Agricolo e Alimentare (ISMEA). <Http://www.ismea.it> n.d. <http://www.ismea.it>.
- [107] Vecchione L, Moneti M, Di Carlo A, Bocci E. Biomass waste shells analysis and advanced gasification tests. *Green Build Mater Civ Eng* 2014;55.
- [108] Eurobserv'er. Biogas Barometer 2012.
- [109] Villarini M, Bocci E, Moneti M, Di Carlo A, Micangeli A. State of Art of Small Scale Solar Powered ORC Systems: A Review of the Different Typologies and Technology Perspectives. *Energy Procedia* 2014;45:257–67. doi:10.1016/j.egypro.2014.01.028.
- [110] GSE. Rapporto Statistico 2012- Impianti a FER 2012.
- [111] Dareioti MA, Vavouraki AI, Kornaros M. Effect of pH on the anaerobic acidogenesis of agroindustrial wastewaters for maximization of bio-hydrogen production: A lab-scale evaluation using batch tests. *Bioresour Technol* 2014;162:218–27. doi:10.1016/j.biortech.2014.03.149.

- [112] Prazeres AR, Carvalho F, Rivas J. Cheese whey management: A review. *J Environ Manage* 2012;110:48–68. doi:10.1016/j.jenvman.2012.05.018.
- [113] Venetsaneas N, Antonopoulou G, Stamatelatou K, Kornaros M, Lyberatos G. Using cheese whey for hydrogen and methane generation in a two-stage continuous process with alternative pH controlling approaches. *Bioresour Technol* 2009;100:3713–7. doi:10.1016/j.biortech.2009.01.025.
- [114] Bylund G. Dairy Processing handbook. Tetra Pak Processing Systems. Sweden 1995.
- [115] Marwaha SS, Kennedy JF. Whey—pollution problem and potential utilization. *Int J Food Sci Technol* 1988;23:323–36. doi:10.1111/j.1365-2621.1988.tb00586.x.
- [116] Zafar S, Owais M, Saleemuddin M, Husain S. Batch kinetics and modelling of ethanolic fermentation of whey. *Int J Food Sci Technol* 2005;40:597–604. doi:10.1111/j.1365-2621.2005.00957.x.
- [117] Lo KV, Liao PH. Digestion of cheese whey with anaerobic rotating biological contact reactors. *Biomass* 1986;10:243–52. doi:10.1016/0144-4565(86)90001-6.
- [118] Nie H, Jacobi HF, Strach K, Xu C, Zhou H, Liebetrau J. Mono-fermentation of chicken manure: Ammonia inhibition and recirculation of the digestate. *Bioresour Technol* 2015;178:238–46. doi:10.1016/j.biortech.2014.09.029.
- [119] Bruni E, Ward AJ, Kjøcks M, Feilberg A, Adamsen APS, Jensen AP, et al. Comprehensive monitoring of a biogas process during pulse loads with ammonia. *Biomass Bioenergy* 2013;56:211–20. doi:10.1016/j.biombioe.2013.05.002.
- [120] Bujoczek G, Oleszkiewicz J, Sparling R, Cenkowski S. High Solid Anaerobic Digestion of Chicken Manure. *J Agric Eng Res* 2000;76:51–60. doi:10.1006/jaer.2000.0529.
- [121] Abouelenien F, Fujiwara W, Namba Y, Kosseva M, Nishio N, Nakashimada Y. Improved methane fermentation of chicken manure via ammonia removal by biogas recycle. *Bioresour Technol* 2010;101:6368–73. doi:10.1016/j.biortech.2010.03.071.
- [122] Carlini M, Castellucci S, Moneti M. Anaerobic co-digestion of olive-mill solid waste with cattle manure and cattle slurry: analysis of bio-methane potential 2014.
- [123] Li Y, Zhang R, Liu X, Chen C, Xiao X, Feng L, et al. Evaluating Methane Production from Anaerobic Mono- and Co-digestion of Kitchen Waste, Corn Stover, and Chicken Manure. *Energy Fuels* 2013;27:2085–91. doi:10.1021/ef400117f.
- [124] Gelegenis J, Georgakakis D, Angelidaki I, Mavris V. Optimization of biogas production by co-digesting whey with diluted poultry manure. *Renew Energy* 2007;32:2147–60. doi:10.1016/j.renene.2006.11.015.
- [125] Ristow NE, Hansford GS. Modelling of a falling sludge bed reactor using AQUASIM. *Water Sa* 2001;27:445–54.
- [126] Freidberg JP. Plasma physics and fusion energy. Cambridge university press; 2007.
- [127] EFDA. Fusion Electricity - A roadmap to the realisation of fusion energy 2012.

- [128] Wesson J, Campbell DJ. Tokamaks. vol. 149. Oxford University Press; 2011.
- [129] http://fsn_fusphy.frascati.enea.it/DTT_ProjectProposal_July2015.pdf n.d.
https://www.google.it/webhp?sourceid=chrome-instant&ion=1&espv=2&ie=UTF-8#q=http%3A%2F%2Ffsn-fusphy.frascati.enea.it%2FDTT_ProjectProposal_July2015.pdf (accessed January 26, 2016).
- [130] Kotschenreuther M, Valanju P, Covele B, Mahajan S. Magnetic geometry and physics of advanced divertors: The X-divertor and the snowflake. *Phys Plasmas* 1994-Present 2013;20:102507.
- [131] Ryutov DD. Geometrical properties of a “snowflake” divertor. *Phys Plasmas* 1994-Present 2007;14:064502.
- [132] Barabaschi P. The MAXFEA code. *Plasma Control Tech. Meet. Naka Jpn.*, 1993.
- [133] Calabrò G, Xiao BJ, Chen SL, Duan YM, Guo Y, Li JG, et al. EAST alternative magnetic configurations: modelling and first experiments. *Nucl Fusion* 2015;55:083005. doi:10.1088/0029-5515/55/8/083005.

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