



Corso di dottorato di ricerca in Ingegneria Industriale e  
dell'Informazione

Ciclo XXX

**A PRELIMINARY STUDY TO PRODUCE  
SOLAR CARBON**

Dottorando  
Marco Citossi

Supervisore  
Prof. Marina Cobal

Anno 2018



# Acknowledgments

First of all, I would like to express my sincere gratitude to my advisor, Prof. Marina Cobal, for the continuous support during my PhD study and related research, for her patience, motivation, and immense knowledge. His guidance helped me in every moment of my research and during the writing of this thesis. I could not have imagined having a better advisor and mentor. My sincere thanks then go to Prof. Hans Grassmann, Prof. Marta Boaro, and Dr. Andrea Pizzariello, who offered me the nice opportunity to join their team as intern, and who gave access to their laboratory and research facilities. Without their precious support, it would not have been possible to complete this research.







# Abstract

Nowadays, the energy demand is growing everywhere at a very high rate, and renewable energies are considered the only possibility to face the future depletion of fossil fuels, natural gas and oils, up to now widely used, and the pollution and health problems related to the use of these traditional energy sources. Goal of this research is to exploit solar pyrolysis because of its potential to provide an efficient, environmentally acceptable, and cost-effective method for the exploitation of a totally renewable energy source, and the characterization of an innovative class of biochars derived from solar pyrolysis. A simple and innovative prototype for biomass pyrolysis is presented, together with some experimental results. The setup allows to pyrolyze a selected and local agro-waste biomass using only the thermal solar energy provided by a system of reflecting mirrors (Linear Mirror II). The chemical characterization of biomasses which were thermally treated using the Linear Mirror II without any help from other thermal auxiliary sources, is discussed in detail. Solar carbon produced has a porous (and graphitic) structure and chemical composition suggest that as activated carbon could be a very versatile material also for catalysis. Activated carbon also enhances soil fertility and allow a more sustainable use of some soils.





## **Riassunto**

Oggigiorno il fabbisogno energetico sta crescendo ovunque ad un tasso molto elevato, e le fonti di energia rinnovabile sono l'unica possibilità per fronteggiare la fine dei combustibili fossile, del gas naturale e degli olii fino ad oggi ampiamente utilizzati, nonché i problemi di inquinamento e di salute derivanti dall'uso di queste fonti energetiche tradizionali.

L'obiettivo di questa ricerca è quello di sfruttare la pirolisi solare in virtù del suo potenziale nel fornire un metodo efficiente, sostenibile e conveniente per lo sfruttamento di una fonte energetica totalmente rinnovabile, e la caratterizzazione di una tipologia innovativa di biochar ottenuti mediante pirolisi solare. Viene inoltre presentato un semplice ed innovativo prototipo per la pirolisi di biomasse assieme ad alcuni risultati sperimentali. Il prototipo consente di pirolizzare una ben precisa biomassa locale agroalimentare e di scarto utilizzando unicamente l'energia termica fornita dal sole attraverso un sistema di specchi riflettenti (Linear Mirror II). Viene inoltre approfondita la caratterizzazione chimica di queste biomasse pirolizzate solarmente mediante il Linear Mirror II. Le biomasse pirolizzate solarmente hanno una struttura porosa e grafitica e la composizione chimica indica che il carbone solare prodotto è un carbone attivo ed estremamente versatile per numerose applicazioni industriali, della catalisi e come ammendante in agricoltura.



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# Chapter 1

## Introduction

The relation between demand and supply of energy is an excellent measure of the developmental index of a country [1]. Due to the rapid depletion of the fossil fuels, natural gas and oil, there's nowadays a quite serious energy crisis across the world, and the demand for energy is growing everywhere at a very high rate. Being true more or less all over the world, this phenomenon is present also in a very local scenario, like the FVG region (Friuli Venezia Giulia region) in Italy. The energy needs faced here nowadays are huge, energy being critical for almost all economic developments in this region of Italy, ranging from manufacture of goods to irrigation. The research has also shown that the demand of energy will increase in the coming years [1].

On top of the increasing requests of energy, there is also the problem that fossil fuels and other energy sources which provided up to now most of the energy, are not eternal, and they contribute to the global warming through the emission of GHGs. The negative effect of greenhouse gases is not just the global warming but also a lot of health issues across the world.

Since long time, renewable energy sources, like sunlight, wind, geothermal heat, water, sea tides, biomass and biogas, have been proposed – being natural replenished [2] - to solve the energy problem. In addition, they are a cleaner source of energy, which emit a smaller amount of carbon dioxide, which don't affect the ozone layer and the atmosphere unlike the

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non-renewable sources. Renewable energy can meet the power demands such as electrification of homes and industries, heating and cooling of buildings, and powering of vehicles among others [3][4].

Using renewable energies has another a great advantage. They can be found in any geographical area whereas the old traditional sources are just found in a few countries, i.e. fossil fuel is majorly found in the Middle East.

This thesis concentrates mostly on the renewable energy coming from the pyrolysis of biomasses. Pyrolysis has been considered as one of the most effective ways to obtain renewable energy from various types of biomasses including forest residuals, agricultural residues, and the municipal waste. The pyrolysis process involves the breakdown of very large molecules into very small molecules of any substance in presence of burning heat. During pyrolysis, the substance undergoing the processes is subjected under high temperatures and therefore experiences molecular vibrations. At these elevated temperatures and under constant vibrations the substituent molecules begin breaking from each other randomly. This process can be used to make bio-fuels such as bio-diesel from waste agricultural materials [5][6].

The pyrolysis technology is in advance in different countries across the world and it is believed to play a great role in solving the energy issues. With Italy being on the front line in improving the use of renewable energy sources in the country, it is important to evaluate the contribution of solar biomass pyrolysis to the goal set by the European Union in this country.

With the recent developments, such as the production of solar biomasses using pyrolysis, it's possible to generate energy as well as to produce bio-fuels which will be used for powering vehicles[6][7].

The structure of this thesis is the following: after an introduction to the present situation in terms of energy needs at general level, but also looking at the particular situation of Italy and –in more detail – of the FVG region, a review of the available sources is given. Chapter 3 is mostly devoted to the solar renewable energies, focusing on an innovative and revolutionary tool to

concentrate solar light, developed by the Isomorph srl<sup>1</sup>, a spin-off of the University of Udine: the so-called Linear Mirror II. Importance of biomass and solar pyrolysis and the uses of renewable sources in these processes are also discussed, exploring the advantages and disadvantages of a completely solar driven pyrolysis with Linear Mirror II and its applicability in North-East of Italy. While Chapter 4 discusses the different type of biomasses which can be used and describes the pyrolysis process and some of the common devices used to pyrolyze biomasses, Chapter 5 shows the results of a study of chemical characterization of wheat straw before and after the pyrolysis process, and a first design for a device for pyrolyzing biomasses using exclusively the Sun energy is presented, together with some preliminary measurements. Chapter 6 concentrates in studying several local biomasses, performing their detailed and in-depth characterization before and after pyrolyzation using the Linear Mirror II, to compare their properties and select the best ones to be used. Finally, Chapter 7 draws the conclusions and gives the future plans of work.

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<sup>1</sup> <http://www.isomorph.it>

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# Chapter 2

## The Perfect Storm: toward Renewables

In this Chapter, an overview is given of the origin and effects of the big energetic crisis which hit our society, as well as of the different renewable energies sources present in Italy and all over the world.

### 2.1 The Energy Crisis

Renewable energy is energy that is collected from renewable resources, which are naturally replenished on a human timescale, such as sunlight, wind, rain, tides, waves, and geothermal heat [2].

Prior to the development of coal in the mid 19th century, nearly all energy used was renewable.

The oldest known use of renewable energy, in the form of traditional biomass to fuel fires, dates from 790,000 years ago. Use of biomass for fire did not become commonplace until many hundreds of thousands of years later, sometime between 200,000 and 400,000 years ago [8]. Probably the second oldest usage of renewable energy is harnessing the wind in order to drive ships over water. This practice can be traced back some 7000 years, to ships in the Persian Gulf [9] and on the Nile [10]. Moving into the time of recorded history, the primary sources of traditional renewable energy were

human labor, animal power, water power, wind, in grain crushing windmills [9], and firewood, a traditional biomass.

More than two hundred years ago however, the world experienced an energy revolution that initiated the so-called Industrial Age. The driving force of this revolution was ordinary black coal, which is an energy-rich hydrocarbon that supplanted wood as the primary fuel. Having black coal allowed scientists, innovators and industrialists to process steel, propel steamships, and energize machines [3]. A century later, the industrialized world's need for energy had already increased in an unpredictable way. As a consequence, and thanks to their versatility and high quality, petroleum and natural gas soon were added to coal as principal fuels. Fifty years later, scientists understood how to use uranium to fuel nuclear reactors and provide therefore atomic energy.

Today, cheap energy is at the base of our society. But relying on resources like coal, oil, natural gas, or uranium to supply our growing energy demands is a risk, since these fuels are limited, and their use put into a serious danger our health and environment. Beside contributing to the global warming, burning fossil fuel releases chemicals and particulates that can cause cancer, brain and nerve damage, birth defects, lung injury, and breathing problems. The combustion of hydrocarbons pollutes the air and water, and brings acid rain and smog. Nuclear energy as well has never been economically successful when all costs are factored in, and fear of disasters like the Chernobyl or Fukushima reactors have virtually shut the industry down in the U.S., Europe and Japan [4].

Coal, which is the most abundant of the carbon-based fossil fuels, currently provides more than 20% of the world's primary energy requirements: however, it won't last forever, and health and environmental costs limit its potential as an acceptable fuel in the future [13]. Burning coal currently accounts for more than 40% of all annual global carbon emissions [14].

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If one looks at the top ten most air-polluted cities in the world - nine of them are in China, and one in India - it can be seen that - all heavily use coal. Atmospheric scientists have tracked large dust clouds of particulates and sulfur from Asia to the United States west coast. Using coal simply because it is there and it will be there for many years still to come, it would be a big mistake: burning coal has become a global problem [4][11] for all the health dangers associated with processing coal into electricity.

Petroleum currently accounts for 40% of the world's energy, but many geologists anticipate an oil supply crisis sometime within the next two decades when global demand will exceed supply [15].

In 1950, the U.S. was producing half the world's oil, while nowadays they are producing less than half of their needs. America produced about 260 billion barrels; only one country, Saudi Arabia, had more. Although the U.S. is now the world's third largest producer, about 65% of the known oil has been already burned. It is noticeable that U.S. has 4% of the world's people but makes use of 25% of the world's oil. If the Chinese annually consumed oil at the same per capita rate as Americans, there would be none available for anyone else [11][16]. Economists like to point out that the world contains enormous caches of unconventional oil that can substitute for crude oil as soon as the price becomes competitive [1][17]. It is true that resources of heavy oil, tar sands, and shale deposits exist in large quantities. But the industry will be hard-pressed for the time and money needed to ramp up production of unconventional oil quickly enough to forestall an economic crisis.

Coal, natural gas, and uranium are alternative non-renewable energy resources to cheap oil, but each has advantages and limitations, and none is as versatile as petroleum. The replacement of oil will require a mix of energy sources, including clean renewable energy such as solar and wind power. This adjustment will involve substantial reorganization of the world's economic structure and significant lifestyle changes in the industrialized countries.

Natural gas (methane) is advertised by energy suppliers as an abundant clean fuel for the twenty-first century, and it burns cleaner than coal or oil. But this resource is also nonrenewable, and the U.S. has only 3.5% of the world's total natural gas reserves-enough to last about sixty-five years. More than 70% of the world's known natural gas reserves are located in the politically risky Persian Gulf and former Soviet Union. After 2020, the bulk of the world's supplies of both oil and natural gas will be centered there [1][14].

Natural gas provides 27% of the energy used today<sup>2</sup>. Similar to their consumption of oil, Americans consume more than their share of natural gas; in 1997, the U.S. used 28% of the world's total production. Consumption in the U.S. and Canada is expected to grow 50% by 2020, enforced in part by the Clean Air Act Amendments of 1990, which are designed to reduce acid rain, toxic emissions, and urban air pollution. Compared to the combustion of oil and coal, natural gas combustion is relatively benign as a contributor to air pollution [15].

Nuclear energy presents similar problems to those associated with non-renewable fossil fuels. The planet's supply of uranium is limited. Worse, the radioactive waste byproducts are a lethal long-term danger to the environment. In 1999, nuclear energy provided about 17% of the world's electricity [4], but the health and environmental costs of using atomic energy have become serious obstacles to the industry. Disposal of radioactive waste has proven to be a much greater problem than originally estimated. Nuclear power does not contribute to air pollution and greenhouse gas emissions, but a good solution to safely storing tons and tons of radioactive waste, a nuclear byproduct that remains dangerous to all life-forms for thousands of years, remains elusive.

In the 1950s and 1960s, atomic energy was thought to be an unlimited and soon-to-become cheap solution to the pollution problems generated by fossil fuels.

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<sup>2</sup> 2017 Communication from Energy Use Administration

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Today instead, the idea to support fission nuclear energy does not belong to U.S. nor to Europe [11][18]. Nobody wants a nuclear reactor in their backyard. Fears are reinforced by the numbers which have been made public: at least 4,365 people who took part in the Chernobyl cleanup have died in the Ukraine [12].

## **2.2 Renewable energies**

As stated earlier, renewable energy is obtained from renewable or natural resources that do not deplete but are renewed continuously. Energy from these resources is obtained either directly or indirectly from the suns solar energy or heat that is generated below the earth's surface. Renewable energy sources include, biofuels, geothermal energy, solar energy in form of heat and light, wind, ocean, hydropower energy.

Non-renewable energy sources are mainly found at few specific locations worldwide compared to the renewable sources which are located in large geographical areas. Some of the benefits of using renewable energy are, increase in energy efficiency, reduction of climate change, energy security and high economic benefits [19]. Recent studies in literature [20] proof that those who emit greenhouse gas (GHG) are responsible for damages that are as a result of the emission that causes climatic changes. Development of technology that uses renewable sources would decrease the use of non-renewable sources which act as liabilities when used.

Renewable energy often provides energy in four important areas: electricity generation, air and water heating/cooling, transportation, and rural (off-grid) energy services [21].

From what said above, it is clear that renewable energy will play a major role in the energy industry of the twenty-first century and beyond. British Petroleum, Royal Dutch/Shell, and other companies are investing heavily in renewable sources of energy. Industry experts realize that these alternative energy systems not only help reduce greenhouse gas emissions, but they predict that over the next half century, renewables may grow to supply half



the world's energy. Successfully generating electricity by harnessing the perpetual power of the Sun and wind is not only technologically feasible, it is already a reality. Solar power relies on the energy produced by nuclear fusion in the Sun. This energy can be collected and converted in different ways, such as simple water heating for domestic use or by the direct conversion of sunlight to electrical energy using mirrors, boilers, or photovoltaic cells. The technology is improving and the economics are getting more competitive. Photovoltaic modules don't generate electricity at night, but they can be used to produce hydrogen in the daytime, which can then be stored. The media and industry claim that renewable energies are not yet economically competitive with fossil fuels. Perhaps not, but when one considers the health and environmental costs associated with burning coal and oil, the price of renewable energy becomes more attractive. No renewable energy system will single-handedly replace oil, but together they will become a very important part of the energy mix of the future [14]. According to a report, REN21's 2016 [14], 19.2% of the global energy consumption in the year 2014 resulted from the use of renewable sources of energy and 23.7% of renewables generated electricity in the year 2015. 8.9% of the energy consumption is from traditional biomass, heat energy from geothermal and modern biomass amounts to 4.2% of the energy consumption, while hydroelectricity and electricity from wind, geothermal, solar and biomass amounts to 3.9 % and 2.2 % respectively. The amount of capital invested in renewable energy technologies in the year 2015b amounted to US\$ 286 billion. Major countries like china and USA invested much on the use of wind, solar, hydro and biofuels [14]. Solar photovoltaics is the largest renewable energy employer out of the 7.7 million jobs created by renewable energy sources [14]. More than 50% of all the installed electricity capacity was from renewable energy sources as of the year 2015 [22]. A minimum of 30 countries worldwide have renewable energy contributing more than 20% of their total energy. Countries worldwide are foreseen to grow their renewable sources of energy markets in few decades to come [23].

Other places and countries generate all their electric power from renewable energy, examples being Norway and Iceland, while other countries are also aimed at achieving a target of 100% renewable energy in the near future (see Figure 2.1). Denmark is an example of such countries that have decided the total supply of energy for heating/cooling, mobility and generation of electricity to be sourced 100% from renewable sources by the year 2050 [24].

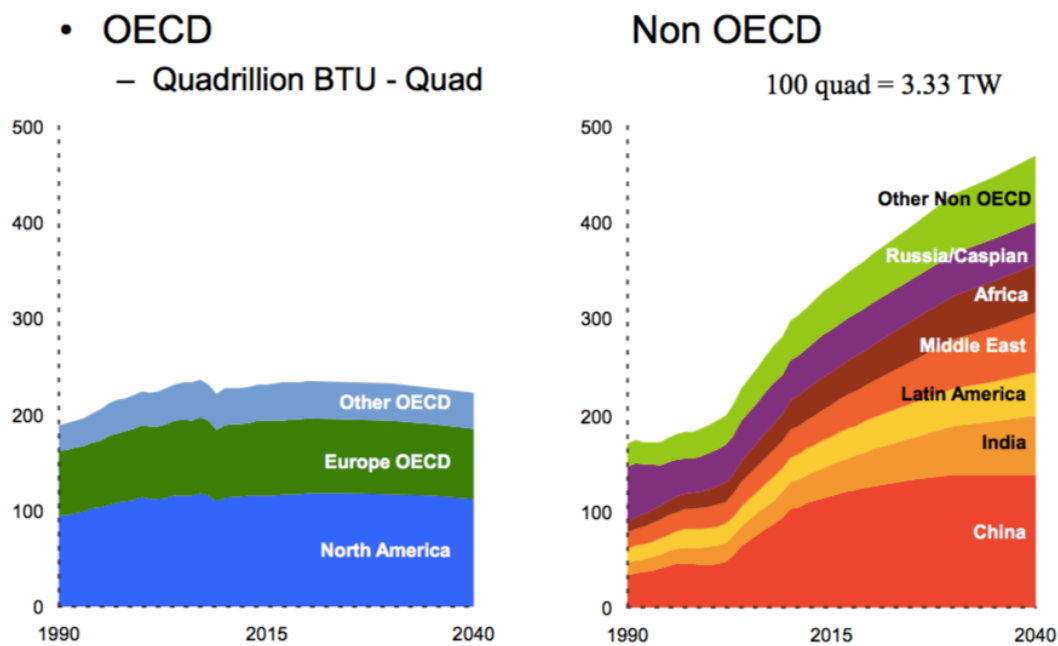


Figure 2.1: Energy Demand from 1990 to 2040.

### 2.2.1 Renewable energy sources

In the following, the main renewable sources of energies are listed and examined, commenting on their use across the world.

#### *Wind Energy*

Humans have been harnessing the wind for thousands of years, and are now cleanly producing electricity with it. Air flowing through turbines or spinning blades generates power that can be used to pump water or generate

electricity. Wind energy is now the world's fastest growing energy source and has become one of the most rapidly expanding industries[25].

### ***Hydroelectric Energy***

Hydroelectric power is another source of renewable energy. The potential of hydropower has been already exploited and that the construction of new big plants has today stopped in order to not harm the environment [10]. Fisheries and other wildlife habitat have been severely impacted on many dammed rivers. Most of the world's hydroelectric dams are historically recent, but all reservoirs eventually fill up and require very expensive excavation to become useful again. At this time, most of the available locations for hydroelectric dams in the U.S. are already developed.

### ***Geothermal Energy***

Geothermal energy left over from the original accretion radioactive decay seeps out slowly everywhere, everyday. In certain areas, the geothermal gradient (increase in temperature with depth) is high enough to exploit for the generation of electricity [26]. Another form of geothermal energy can be tapped from the planet's surface. Soil maintains a relatively constant temperature throughout the year and can be used with heat pumps to warm a building in winter or cool a dwelling in *summer*. This form of energy can lessen the need for other power to maintain comfortable temperatures in buildings, but it cannot be used to produce electricity.

### ***Solar Energy***

This is the energy harnessed from the Sun's radiation using variety of technologies. The solar energy technologies include solar thermal electricity, solar heating, solar architecture, solar photovoltaic and artificial photosynthesis [2][27]. The solar technologies have been characterized into either active solar or passive solar depending on the way they harness, convert and transmit the solar energy. Active solar technologies involve the use of concentrated solar power, photovoltaic systems and solar water

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heating to capture the solar power [2]. Passive energy technologies involve selecting materials that can capture energy easily, orienting buildings to the Sun and designing spaces that can naturally circulate air.

The International Energy Agency has said that the development of inexhaustible, affordable and clean solar energy has long-term benefits for the whole world. It will increase energy security via reliance of inexhaustible, indigenous sources and independent resource. The utilization of solar energy will also lead to availability of sustainable energy, reduced pollution and low cost of mitigating climates changes. Every hour, the sunlight that reaches the earth surface can meet the world energy demand for a whole year. This shows the great potential vested on solar energy and is awaiting exploitation.

The earth receives at least 174PW from the incoming solar radiation at upper atmosphere. 30% is approximately reflected back to the space while the rest of the energy is absorbed by land masses, water bodies and the clouds. Spectrum of solar energy at the surface of earth is mostly spread via visible and infrared ranges with some small parts across the near ultraviolet [10].

The other factor that affects the solar energy is land availability because the amount of energy that can be harnessed from the sun depends on the space available. Roof tops are one of the suitable places where the solar panels can be installed for collecting electricity to use in homes. The other place that is conducive for solar panels is empty land where no businesses are being carried around. With availability of clear space where the installation can be done, a lot of energy can be captured from the sun on daily basis.

Solar energy alone accounts for 10% of the electricity being used in Italy. This makes Italy the country with the highest use of solar energy in the whole world [19].

### **2.2.2 Renewable energy status in Italy**

The renewable energy status in Italy has always experienced continuous development over the last few years and the trend will definitely continue over the future.

In Italy, interesting incentive schemes have been implemented to encourage the development of renewable energy production. At the end of 2014 Italy became the world's fourth largest country by installation of PV, above USA at that time [14][28]. In the recent years, Italy has grown its use of renewable energy and many other countries are still being motivated to doing the same.

Hydroelectric power is the most common renewable energy source in Italy in terms of production though all the 8,047 municipalities have also employed other renewable sources. Other sources apart from hydropower that contributes heavily are bioenergy, geothermal power and wind power. The primary consumption of renewable energy in Italy had grown to 14.6 Million tons of equivalent oil by the year 2013 [28].

Italy has implemented generous incentive schemes to encourage the development of renewable energy production. Its largest scheme incentivized solar PV production and led Italy from a low base of installed PV in 2010 to become the world's fourth largest country by installations by the end of 2014, ahead of the USA at that time [19][28]. All sources of renewable energy have grown in Italy during recent years (see Table 2.1) and many continue to receive incentives.

Due to the renewable energy targets set by the National Renewable Energy Action Plan, NREAP [28], for 2020 the use of renewable energy in Italy will scale up very fast. The National Renewable Energy Action Plan was approved by the Italian Ministry for Economic Development in 2010 to help in implementing the directives from European Union about the renewable energy targets. The plan aims to generate 17% of total energy being used in Italy from renewable energy sources before or by 2020 [28].

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By the year 2010, the energy generated from renewable energy sources in Italy was 13%. Today, in the year 2017, the energy being used in Italy from renewable energy is over 17%. The 2020 target has already been reached and surpassed by our country, and other countries as well have surpassed this target, like Croatia, Bulgaria, Czech Republic, Romania, Sweden, Finland and Hungary. Generally, Italy is at the center of the achievement when it comes to the proportion allocated to every European Nation to generate power from renewable energy sources. More specifically, Italy is now the world leader in solar energy [28].

There're major reasons for reliance on biomass as energy source in Italy. The first is linked to the cost-effectiveness of the biomass pyrolysis raw materials which puts it up in the competition with other renewable energy sources. The other reason is the availability of the raw materials such as wood required for biomass pyrolysis, given for example the low level of use of the forests in Italy and the results of implementing opportunities to enhancing the active forests management. This would reduce unemployment in Italy and also boost income in rural areas [28].

Table 2.1: Different amount of renewable energy in Italy

<b>Renewable Energy Source</b>	<b>Amount of Power (GW)</b>
Wind power	9.1
Bio Energy	4.2
Solar Power	18.9
Hydro Power	18.5
Geothermal	0.8
<b>Total</b>	<b>51.5</b>

The following are the four main goals for the National Energy Strategy (NES) [29]:

1. Significantly reduce the energy cost gap for businesses and consumers. The NES intends to do this by bringing the prices down with respect to the European standard target by 2020.

2. Achieve the environmental and exceed the decarbonisation targets set by the European Union in the 2020 Energy Package and Climate Change document. Therefore, push all the energy policies target to improve and boost the Italian decarbonisation and environmental standards which have already reached the world's best level. The policy decisions also ensure that Italy remains as a global example on these targets.
3. Ensure and assure security of supply. The NES aims at reducing dependency on imports especially in the gas sector. Italy needs, most notably, to boost its ability to instantly respond to important events and as well facilitate the process of cutting down the energy imports into the nation which cost around 62 euros per year.
4. Foster economic growth on sustainability measures. The NES targets to foster the economic growth of the country by ensuring constant development in the energy sector. The body considers local and international opportunities that would lead to continuous growth in the energy sector. The development of energy sector will in turn result in economic growth in the country.

### **2.2.3 Renewable energy status in the North-East of Italy, FVG region**

This thesis is concentrated to the development of a setup to pyrolyze the biomasses, and in particular the otherwise unused local biomasses produced in FVG region. This region has an energy plan aimed at discovering and exploiting the available local energy source. The plan is aimed of course at reducing the over reliance on fossil fuels and their consumption. In particular, the Regional Energy Plan (REP) [30] steers the improvement of the regional energy system and strives to improve its efficiency as well as to reduce the GHGs. The Regional Energy Plan oversees the advancement of energy production from the renewable energy sources and the minimization of energy consumption in industry, transport, residential sectors and services

and striving also to improve their energy efficiency [30]. In the Figure 2.2 and Table 2.2 is possible to see the electricity production in MWh in FVG region until 2011 [31].

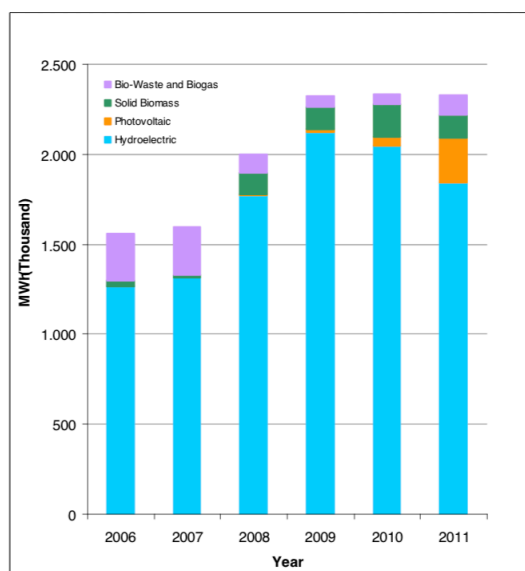


Figure 2.2: Electricity production in FVG region until 2011 (Source: TERNA and GSE).

Table 2.2: Electricity production in MWh in FVG region from 2006 to 2011.

<b>RES Production</b>	<b>2006 MWh</b>	<b>2007 MWh</b>	<b>2008 MWh</b>	<b>2009 MWh</b>	<b>2010 MWh</b>	<b>2011 MWh</b>
<b>Hydroelectric</b>	1264500	1315300	1773900	2123000	2049400	1854000
<b>Photovoltaic</b>	-	2000	5600	18100	44000	246100
<b>Solid Biomass</b>	34884	11628	116280	124000	184500	127400
<b>Bi-waste and biogas</b>	255816	267444	104652	57000	56700	107100
<b>Total</b>	1555300	1596372	2000432	2322100	2334600	1325600

The condition of renewable energy sources in this region highlights a very limited contribution to the overall national energy production. The breakdown is as follows; 5.2% of the energy is generated through



thermoelectric, 2.3% of the energy is generated through hydroelectric plants, 2.2% through geothermal gases, 0.7% through fuels. Wood biomasses are widely used for house warming and heating. Another source of renewable energy is given by solar energy photovoltaic modules which provide electricity and water heating for private use. Generally, 45% of the energy generated in this region is derived from hydroelectric power plants while the other 55% is derived from the use of biomasses. In order to achieve its goals, the Regional Energy Plan focuses on the following seven priorities:

1. Energy efficiency: this would contribute to achievement of the energy policy aims and specific objectives. Reducing the regional energy costs due to the savings made in fuel consumption would also reduce the environmental impact coming from the carbon dioxide and other emissions made from fossil fuels.
2. Competitive gas market, as in the Hub Southern Europe. Italy aims to create competitive and internal liquid market which is a part of other EU countries. It's predicted that over the coming years, Europe will be importing gas and therefore aims to be a door for gas entry into Europe from the south. This plan will definitely favor the Italian economy by ensuring security of supply and strengthening infrastructure as well as market liquidity.
3. Renewable Energy sustainable development. It's remarkable that Italy has already surpassed the 2020 target that was set by the European Union back in 2010 [21]. The promotion of renewable energy will boost the green environment objective by reducing emissions from the fossil fuels and other non-renewable energy sources. It's of great significance to curb high expenditures on electricity bills and in turn direct the expenditure towards technologies and sectors that have very high value to the country.

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4. Development of electricity market and electricity infrastructure. These sectors are on the verge of great transformation as determined by a number of economic changes.
  5. Restructuring the fuel distributor sector and refining industry. The refining industry has been made difficult by the decrease in demand due to economic crisis and also by the increase in economic competition from other countries. The country needs to be transformed in such a way the technology is improved and its competitiveness is also boosted.
  6. Domestic hydrocarbons sustainable production. Italy has always over relied on imported fossil fuels and also it has large reserves for gas and oil. Therefore, it's important for the country to take advantage of these particular resources as far as their benefits in economic growth and employment is concerned. However, close attention should be accorded to this sources due to their environmental impact. The government doesn't want to therefore pursue the shale gas projects.
  7. System of governance modernization. An efficient and effective governance system has to be developed in order to facilitate all the above goals and specific objectives. Italy acknowledges that their objectives are cumbersome and much longer than their counterpart countries and therefore needs close attention incorporating the best decision-making procedures.

# Chapter 3

## Solar Thermal and Linear Mirror II

Photovoltaic alone, cannot substitute completely the fossil fuels [23]. However, photovoltaic systems are not the only ones that can be used to convert solar energy into electricity. When solar energy is captured in the form of high thermal energy temperature, this can then be easily converted into energy mechanics through a conventional thermodynamic cycle.

In this Chapter, an overview is given of the main solar thermal power systems on the market. Their characteristics, performances and limitations are shown and compared. An innovative solar system, developed by Isomorph srl, a spin-off of the University of Udine, is then presented: the Linear Mirror II.

### 3.1 Solar thermal systems

Solar thermal technology uses the sun's energy, rather than fossil fuels, to generate low-cost, environmentally friendly thermal energy. This energy is used to heat water or other fluids, and can also power solar cooling systems. Solar thermal systems differ from solar photovoltaic systems, which generate electricity rather than heat. However, the heat from a solar thermal system can then be used to produce also electricity.

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In solar thermal power generation systems, there is collection and concentration of sunlight to produce heat at high temperature. In all solar thermal power plants, there are collectors that are used to gather energy from the Sun [32]. These collectors consist of two main parts: reflectors, typically mirrors which capture and direct sunlight onto the second element: a receiver. To achieve high yields of the thermodynamic cycle, it is necessary that the thermal energy is made available at high temperature. Flat solar collectors do not allow to produce fluids with temperatures above about 100°C [32], so one needs to use concentration systems, such as lenses, mirrors and parabolas.

There is then a heat transfer fluid that is normally heated and made to circulate in these systems and generate steam. This steam is essential for the production of electricity by driving the turbine and generator [10].

Solar energy is emitted from the Sun at an apparent temperature of about 5780 K with a surface power density of about 60-65 MW/m<sup>2</sup>, while at the ground level the maximum power density is of the order of 1000 W/m<sup>2</sup>.

Sunlight has two components, the "direct beam" that carries about 90% of the solar energy (depending on the local latitude), 900 W/m<sup>2</sup> direct out of 1000 W/m<sup>2</sup> total [33] and the "diffuse sunlight" that carries the remainder – the diffuse portion is the blue sky on a clear day, and is a larger proportion of the total on cloudy days. Reflected radiation describes sunlight that has been reflected off of non-atmospheric things such as the ground. For example asphalt reflects about 4% of the light that strikes it and a lawn about 25% [33].

As the majority of the energy is in the direct beam, maximizing collection requires the Sun to be visible to the solar concentrators for as long as possible. A **solar tracker** is a device that orients the payload (solar panels, parabolic troughs, Fresnel reflectors, lenses or the mirrors of a heliostat, see the following subsection) toward the Sun.

The optics in concentrated solar applications accept the direct component of sunlight light and therefore must be oriented appropriately to collect

energy. Tracking systems are found in all concentrator applications because such systems collect the sun's energy with maximum efficiency when the optical axis is aligned with incident solar radiation. For example, trackers that have accuracies of  $\pm 5^\circ$  can deliver greater than 99.6% of the energy delivered by the direct beam plus 100% of the diffuse light. The Sun travels (0.25 degrees per minute) \* (1440 minutes) = 360 degrees in a single day, but from the perspective of any fixed location the visible portion is 180 degrees during an average 1/2-day period (more in spring and summer; less, in fall and winter). Local horizon effects reduce this somewhat, making the effective motion about 150 degrees. A tracker that only attempts to compensate for the east-west movement of the Sun is known as a single-axis tracker.

Due to the tilt of the Earth's axis, the Sun also moves through 46 degrees north and south during a year. The same set of panels set at the midpoint between the two local extremes will thus see the Sun move 23 degrees on either side. A tracker that accounts for both the daily and seasonal motions is known as a dual-axis tracker. Generally speaking, the losses due to seasonal angle changes is complicated by changes in the length of the day, increasing collection in the summer in northern or southern latitudes. This biases collection toward the summer, there is considerable argument within the industry whether the small difference (few %) in yearly collection between single and dual-axis trackers makes the added complexity of a two-axis tracker worthwhile [34].

Some solar thermal power plants are capable to store thermal energy, allowing a balance of energy demand between daytime and nighttime, storing summer heat for winter heating, or winter cold for summer air conditioning.

**Thermal energy storage** is achieved with widely differing technologies. Depending on the specific technology, it allows excess thermal energy to be stored and used later, at scales ranging from individual process, building, multiuser-building, district, town, or region. Most practical active solar heating systems provide storage from a few hours to a day's worth of energy collected. However, there are a growing number of facilities that use

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seasonal thermal energy storage, enabling solar energy to be stored in summer for space heating use during winter [35][36]. The Drake Landing Solar Community in Alberta, Canada, has now achieved a year-round 97% solar heating fraction, a world record made possible only by incorporating a storage system [37][38].

Storage media include water or ice-slush tanks, masses of native earth or bedrock accessed with heat exchangers by means of boreholes, deep aquifers contained between impermeable strata; shallow, lined pits filled with gravel and water and insulated at the top, as well as eutectic solutions and phase-change materials

Solar thermal power plants can occur also as hybrid systems. Hybrid systems use other fuels for example natural gas to generate energy to compensate for solar energy at times when solar absorption is low.

## **3.2 Traditional concentrating solar power systems**

There are different types of traditional solar thermal systems (CSP). A short review is given in the following paragraphs.

### **3.2.1 Linear concentrating systems**

In these systems, there are many collectors (long, rectangular, curved (U-shaped) mirrors) forming a field of collectors arranged in rows, which are parallel and arranged in a north-south orientation. This orientation is vital for obtaining a maximum collection of solar energy. With this configuration, mirrors are in a position to capture the sun from east to west throughout the day continuously concentrating the sunrays onto the receivers. These are tubes that run the length of the mirrors. The concentrated sunlight heats a fluid flowing through the tubes and sent to a heat exchanger to boil water in a conventional steam-turbine generator to produce electricity

There are two major types of linear concentrator systems: parabolic trough systems, where receiver tubes are positioned along the focal line of each

parabolic mirror, and linear Fresnel reflector systems, where one receiver tube is positioned above several mirrors to allow the mirrors greater mobility in tracking the sun.

### ***Parabolic troughs systems***

The linear concentrating systems that are mostly used, apply parabolic trough collectors. The receiver tube is attached on the mirror body. A parabolic trough collector has a long parabolic-shaped reflector that focuses the sun rays on a receiver pipe located at the focus of the parabola, as shown in Figure 3.1.

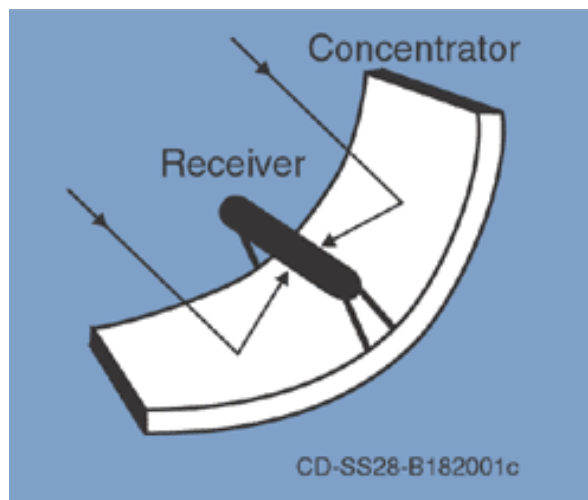


Figure 3.1: Parabolic Trough System schematic diagram

Figure 3.2 illustrates a linear concentrating system using a parabolic trough collector, while an image of a typical parabolic trough plant is given in Figure 3.3.

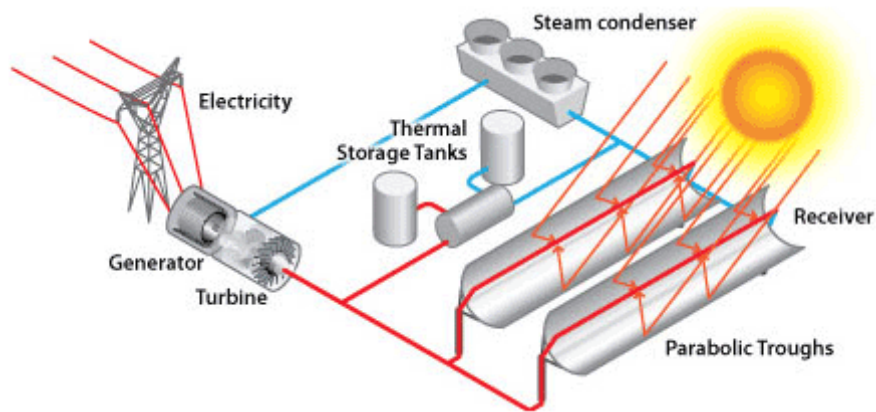


Figure 3.2: Linear concentrating system with a parabolic concentrator.

As the sun tilts, the collector tilts as well to keep sunlight focused on the receiver as the sun moves from east to west throughout day. A parabolic trough concentrator can focus the sunlight from 30 times to 100 times its normal intensity because of its parabolic shape on the receiver tube [39].



Figure 3.3: Parabolic trough power plant.

The receiver tube is located along the focal line of the trough [40]. This arrangement helps to a higher temperature of 750°F for operations purposes. The fluid that is used for heat transfer flows in and out of the field made of solar mirrors and enters where it is used to generate steam. This thermal energy storage system uses a principle that states that excess heat collected in the solar field is sent to a heat exchanger and warms the heat transfer fluid going from the cold tank to the hot tank. When needed, the heat from the hot



tank can be returned to the hot tank fluid and sent to the steam generator (a sketch of the system is given in Figure 3.4).

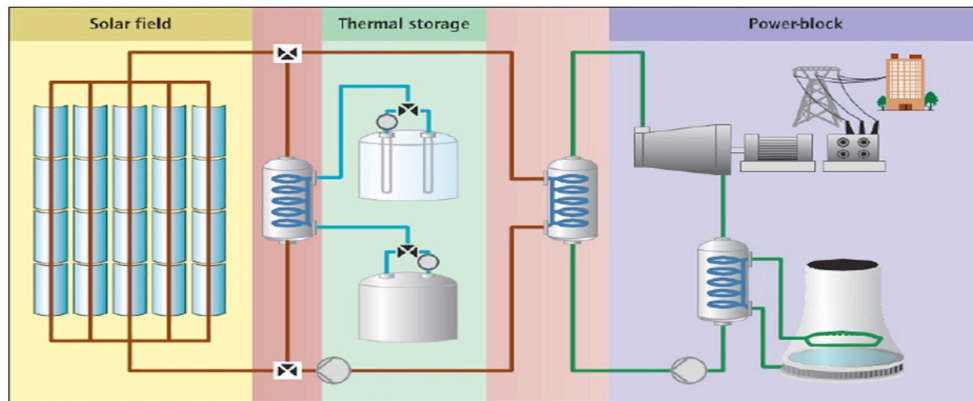


Figure 3.4: Thermal energy storage system in a parabolic trough concentrator.

In a year the solar energy that is converted to electricity, can be up to a mean value of 15% annually. In current parabolic systems, synthetic oil, as well as molten salts are used as transfer fluids.

Troughs systems are considered – in between the traditional systems - to be the most effective and mature technology. This technology is applied in most current projects because some of them contain important thermal storage capacities [40]. An example is the Solar Energy Generating System (SEGS), located in California which consists of nine plants.

One of the plant which was the first to be started, has been in operation since 1984, and the last plant to be built started operations in 1990. The SEGS plant forms one of the largest solar thermal electric power plants existing nowadays, with an energy output of 354 MW. There are many others parabolic trough solar power projects which have been implemented around the world. The major systems in the United States after SEGS include:

- Mojave Solar Project with an output of 280 MW and located in Barstow, California
- Solana Generating Station with an output of 280 MW located project in Gila Bend, Arizona
- Genesis Solar Energy Project with an output of 250 MW in Blythe, California.

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Other important plants in Europe are:

- Solaben Solar Power Station with an output of 200 MW in Spain
- Solnova Solar Power Station with an output of 200MW in Spain
- The Andasol solar power station with an output of 150 MW (Europe's first commercial plant to use parabolic troughs), in Andalusia, Spain.

### ***Linear Fresnel reflectors***

This technology is similar to the one used in the parabolic trough systems, as seen in Figure 3.6, since mirrors which are slightly curved or flat reflect light from the sun on a receiver tube which is placed above the mirrors.

These reflectors use the Fresnel lens effect, which allows for a concentrating mirror with a large aperture and short focal length [41], and they have the ability to concentrate the energy from the sun to about 30 times normal intensity (see Figure 3.5 and Figure 3.6).

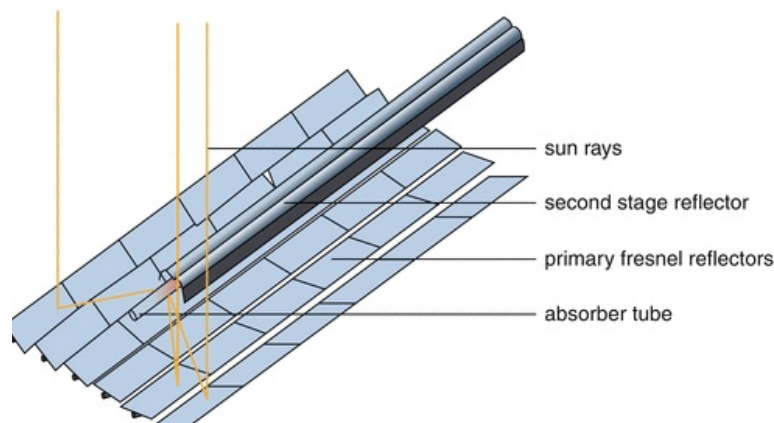


Figure 3.5: Fresnel reflectors scheme.

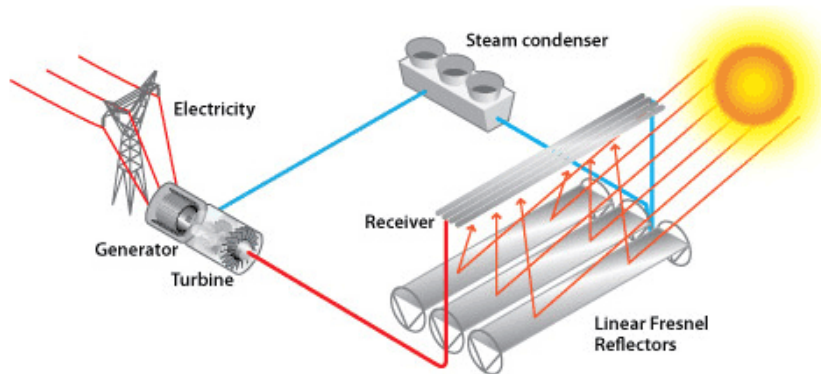


Figure 3.6: Linear Fresnel reflectors system.

A design which has been recently developed is known as “Compact Linear Fresnel Reflectors” (CLFR). This technology uses two parallel receivers for each row of mirrors (see Figure 3.7). Thanks to this arrangement, one needs a less extended surface with respect to the one needed using parabolic troughs to produce a given energy output. Puerto Errado 1 (Figure 3.8) was the first CLFR plant to be build, in Spain in March 2009. Its capacity was rated to be 1.4 MW. The success of this plant motivated the design of a PE 2, a power plant with a capacity of 30 MW constructed in Spain in 2012, which is the world's largest Fresnel power plant in operation. Recently in California a power plant with capacity 5 MW has been constructed as well.

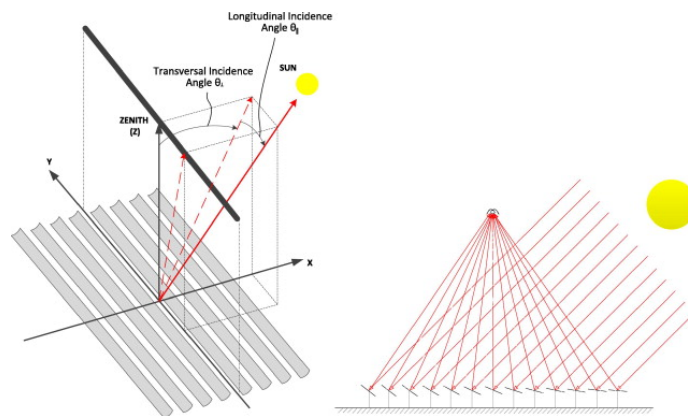


Figure 3.7: Linear compact Fresnel System.



Figure 3.8: Puerto Errado I plant.

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### 3.2.2 Solar power towers

These are central receiver systems which concentrate the sun rays on top of a fixed tower. This allows this type of system to reach higher temperatures and efficiencies than linear systems do [42]. Towers are used to generate saturated or super-heated steam using different media as heat transfer fluids. Some power towers use air or water as the heat-transfer fluid. In some advanced designs, molten nitrate salt is used since it has a higher heat transfer and capability to store energy. The capability to store thermal energy allows the system to produce electricity during rainy weather or in evening.

A solar power tower system uses a large field of flat, sun-tracking mirrors called heliostats (see Figure 3.9 and Figure 3.10) to reflect and concentrate sunlight onto a receiver on the top of a tower. Sunlight can be concentrated as much as 1,500 times [42].

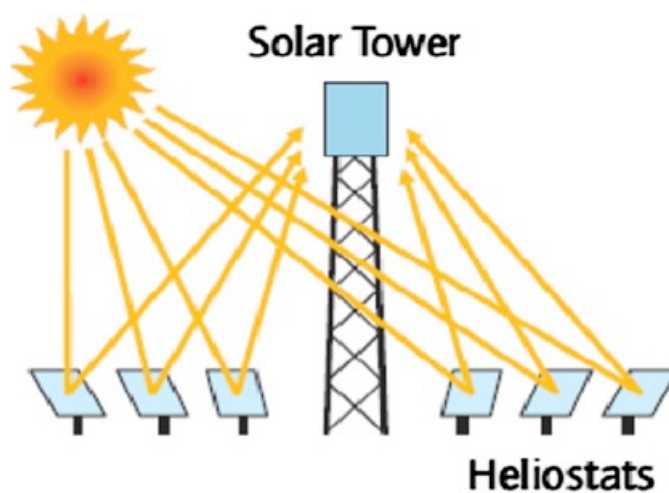


Figure 3.9: Solar Tower system.



Figure 3.10: Solar tower plant.

There are three major solar power tower system in the United States:

- Ivanpah Solar Power Facility: a 392 MW project located in Ivanpah Dry Lake, California
- Crescent Dunes Solar Energy Project: a 110 MW project located in Nevada
- Sierra Sun Tower: a 5 MW two-tower project located in the Mojave Desert in southern California

The major systems in Europe are instead:

- PS20 solar power tower a 20 MW project located in Spain
- Gemasolar s 17 MW project located in Spain
- PS10 solar power tower 11 MW project located in Spain
- Jülich Solar Tower a 1.5 MW project located in Germany
- Greenway CSP Mersin Solar Tower Plant in Turkey

### 3.2.3 Solar dishes/engines

In these systems, the sunrays are concentrated on a focal point which is moving together with the dish tracking the sun, offering the highest optical efficiency on much smaller capacities. This has allowed them to compete with the larger systems and they are often used for mass production of energy. As a result, benefit from economies of scale has been realized [41]. These systems require to be cooled using water and they tend to be less compatible with thermal storage.

A dish is used which is similar to a very big satellite dish made of flat, small mirrors to minimize cost. Solar dish/engine concentrators are made to face

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the sun and concentrate the energy from the sun at the focal point of the dish (see Figure 3.11 and Figure 3.12). Concentration ratio in solar dish collectors is higher than in linear concentrating systems [41][43]. In solar dish collectors, the working fluid has a temperature which is usually higher than 750 °C. The equipment that is used to generate power with solar dish concentrators is usually put at the focal point of the dish.

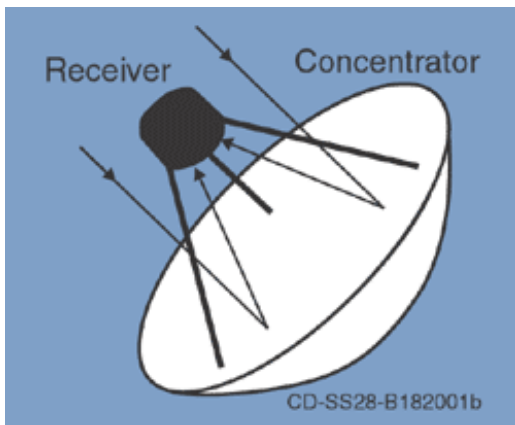


Figure 3.11: Left: Solar dish concentrator. Right: Solar dish system.



Figure 3.12: Solar dish array (by Solar System Ltd)

An ideal example of heat engine used in dish/engine systems is the Stirling engine. Here the fluid heated is used to move pistons and therefore mechanical power is created. The mechanical power obtained is then applied in running a generator which produces electricity.

### 3.3 Performance of traditional CSP Plant Design

CSP plant in general, require a lot of direct solar radiation to be able to generate electric power [44]. This fact has limited the concentrated solar power to be installed mainly in dry and hot regions which are constantly exposed to continuous solar radiations. The traditional CSP is required to have a Direct Normal Irradiance, DNI level of 2000 kWh/m<sup>2</sup>/year or even more for the system to be economically stable.

The CSP plants located in areas where there's relatively high DNI will definitely have Lower Levelized Cost of Energy, LCOE<sup>3</sup>. Those located in regions with relatively low DNI will in vice versa have high LCOE. Globally there're particular regions in the world that have relatively high DNI such as the Middle East, North Africa, South Africa, Western United States, Australia and South American parts. The resources are available in almost all parts of the world including Italy but may not be fully utilized until the costs for installing them begins to decline substantially.

#### 3.3.1 Solar Field Sizing, Capacity Factors, Thermal Storage and Solar Multiple

There are several parameters that determine the design and sizing of optimal plants. Two of the most important ones are certainly the thermal energy storage system and the purposes of the plant [18].

The thermal storage of energy increases the plant's capacity factor though it has an equivalent increase in cost. The cost normally increases due to the

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<sup>3</sup> The **levelized cost of electricity (LCOE)** is a measure of a power source which attempts to compare different methods of electricity generation on a consistent basis. It is an economic assessment of the average total cost to build and operate a power-generating asset over its lifetime divided by the total energy output of the asset over that lifetime. The LCOE can also be regarded as the average minimum cost at which electricity must be sold in order to break-even over the lifetime of the project [45].

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need to buy, install and maintain the energy storage components such as batteries.

It can be said that much depends on the specific design of the project and whether the storage system will be used to increase the capacity factors or shift generation of electricity.

They also have reduced operating and maintenance costs for every kWh. The solar multiple is another parameter that must be considered when optimizing a solar thermal plant design for any application. Solar multiple can be defined as the ratio of the solar plant field (the system of solar collectors) to the size that would be utilized to reach the full potential of electricity capacity at the design point [45]. Solar Multiple should be between 1.3 and 1.4 for the energy to be utilized well through the year.

### **3.4 Comparison of CSP technologies**

Parabolic trough collector plants are the most developed of all commercially operating plants (about 90% of the installed power). Solar power tower (about 10%), Fresnel reflector and dish concentrators (still marginal) require less land as compared to parabolic trough concentrator in order to produce a given energy output, but are expensive to buy and maintain compared the first one [18].

One aspect of thermodynamic solar technology is the availability of water, both for the periodic cleaning of the mirrors, but especially for the cooling of the steam cycle condenser. This might be a big limit for desert applications, which are the ideal environment for their installation.

Water requirements are of high importance for those locations with water scarcity, e.g., in most of the deserts. Like any other thermal power plants, water is required in CSP for the purpose of cooling and condensing process. Different concentrators require varying amount of water. For example, parabolic trough concentrators require about 3000 l/MWh similar to linear Fresnel reflectors plants. Less water is required in solar parabolic trough



plant compared to parabolic trough concentrators. Surrounding air is used to cool parabolic dish collector's dishes; therefore, they do not require cooling water.

Cooling with dry air is an effective process. This has been proven by plants under construction in North Africa. Installing dry cooling on parabolic trough concentrators plants located in hot deserts is known to reduce the annual production of electricity by 7%. Another effect is the increase in the cost of the electricity produced.

The efficiency reduction caused by dry cooling is lower in solar parabolic trough. When hybrid wet and dry systems are installed for cooling purposes, water consumption is reduced while the performance penalty is minimized [39]. Operation of hybrid systems uses only dry cooling in the winter when cooling needs are lower, then switch to combined wet and dry cooling during the summer.

Another criticism which can be moved to CSP system is that the deserts – which are thought to be the best places to host these systems - have a very important cooling function in the climate of our planet. In particular:

- Each m<sup>2</sup> of hot desert surface radiates up to 600W of heat
- Since the air over the desert is very dry, this radiation gets emitted away from the planet into the Universe.

But water vapor is a greenhouse gas even worse than CO<sub>2</sub>: humid air in the desert interrupts the cooling function of the desert [40].

The Noor 1 plant<sup>4</sup> uses 1.7 million m<sup>3</sup>/year of water or 4.6 kg of water/ kWh (producing electricity with a diesel generator: 1 kg of CO<sub>2</sub> /kWh). In addition, it burns 19 tons of Diesel per day.

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<sup>4</sup> CSP project in **Ouarzazate** Phase I (called **Noor 1 CSP**):

[https://www.nrel.gov/csp/solarpaces/project\\_detail.cfm/projectID=270](https://www.nrel.gov/csp/solarpaces/project_detail.cfm/projectID=270)

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### 3.5 An innovative system: The Linear Mirror II

As seen in the previous section, a problem of the CSP is often the cost. However, solar energy concentration in principle is a very simple technique and should therefore be cheap. A m<sup>2</sup> of reflecting surface to concentrate the Sun, costs about ca. 30 €, and collects about 1000 kWh of energy per year, for a value of about 100 Euro. The system should then be repaired back in three months [46].

The Linear Mirror II is a particularly simple solar concentrating device that has become available very recently and has been developed by Isomorph srl, physics research company [46]. The Linear Mirror has two particular advantages: 1) its construction is very simple, since its multiple reflecting surfaces are connected to each other by mechanical links, and operated all together by means of only three small motors; 2) the sunlight is concentrated on a target mounted in a fixed position which can be on the ground, unlike for instance the heat exchanger of a parabolic dish. This allows for a wide variety of different applications. The Linear Mirror II (see Figure 3.13) has a maximum thermal power of 9 kW and usually it is used to concentrate sunlight onto a suitable target. It consists of an array of 4 × 2 mirrors, which follows the Zenith and the Azimuth positions of the Sun by means of three motors [47][48]. Each of these mirrors contains four segments with a slight relative inclination of 2°, resulting in a light concentration, which varies through the day. The mirrors are all connected to each other by bars and levers of different lengths. The absorber is in a fixed position (see Figure 3.14).



Figure 3.13: The Linear Mirror II device.

A more detailed discussion of the Linear Mirror II principle of function can be found in [46]. The Linear Mirror II is now a regular industrial product, which has been tested and certified with the “Solar Keymark” certificate [49] and can benefit of economic incentives which makes it quite convenient. The first system has been mounted in 2014 at the Hotel “Al Cavaliere”, Pordenone (Italy), providing 9 kW of thermal power and heating water at 100 °C also in winter.



Figure 3.14: The Linear Mirror II, with the absorber.

The Linear Mirror II is not mounted horizontally, therefore it works well also at the European latitude and in winter. Besides that, a traditional CSP system should have a surface of about 30 m<sup>2</sup>, to be compared with the Linear Mirror II absorber surface of 0,5 m<sup>2</sup>. The absorber is heated 20 times faster having this small surface and it has much smaller losses.

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Up to now this system has been used to produce heating and hot water, but in the future, it could provide energy for all the applications of the solar energy like:

- Solar cooling
- Process heat
- Steam machine

This system looks very promising, simple and cheap, and this is why it has been chosen to start a study for a system which is capable to produce “solar carbon” by means of pyrolyzation of biomasses, as explained in the next chapters.

# Chapter 4

## Biomasses and Pyrolysis

In this Chapter, an overview is given on biomasses and their use, with a special attention to their status and use in the FVG region. Some of the processes which allows their chemical conversion are described, and in particular the so-called pyrolysis.

### 4.1 Biomass

The term *biomass* is an industry term to indicate organic matter, like trees, plants and agricultural and urban waste which, combusted, can produce energy which can be used for heating, electricity generation, and transport. The plants absorb the sun's radiation, in this way storing energy from the sun [50]. When the biomass is burned, the energy stored inside the plants is released as heat, and this steam runs a turbine to make electricity, or provides heat to industries and homes.

Biomass energy can also be converted to biofuels or biogas.

There are two main types of biofuels; ethanol and biodiesel. Ethanol is type of alcohol obtained by fermenting biomass with high carbohydrate content. To reduce emissions and cost, biofuels are added to fossil fuels. In flexible vehicles 85% ethanol can be mixed with petrol. Biodiesel is a concoction of alcohol with vegetable oil, animal fat or recycled cooking grease. In its pure form is used to run diesel engines.

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Biogas is an energy source obtained from the decomposition of organic matter in the absence of air

The following are examples of biomass energy and their uses:

- Wood processing wastes – Burned to produce electricity, heat buildings and process heat in industries
- Waste materials from agriculture – Converted to liquid biofuels such as ethanol and biodiesel. With some small changes to engine, the biodiesel from biomass can be used to run automobiles.
- Yard, wood and food waste in garbage – converted to biogas in landfills and burned to generate electricity.
- Human sewage and animal manure – it's usually converted to biogas which is then burned as fuel.

Burning biomass is considered as a renewable energy source in the EU and UN legal frameworks, since - for example - plant stocks can be replaced with new growth and waste residues will always exist – in terms of scrap wood, mill residuals etc.

For biomass to be effective at reducing greenhouse gas emissions, it must be produced in a sustainable way. Biomass production involves a chain of activities ranging from the growing of feedstock to final energy conversion. Each step along the way can pose different sustainability challenges that need to be managed. New technologies – including pollution controls and combustion engineering – have advanced to the point that any emissions from burning biomass in industrial facilities are generally less than emissions produced when using fossil fuels (coal, natural gas, oil)..

Increasing the use of biomass in the EU can help diversify Europe's energy supply, create growth and jobs, and lower greenhouse gas emissions. In 2012, biomass and waste accounted for about two-thirds of all renewable energy consumption in the EU [14].

The larger sources of biomass for bioenergy feedstocks are: forests, agriculture, and waste. However, non-forest conservation lands, such as grasslands and savannahs, and alga culture (cultivation of algae) are also potential sources. Biomass materials can be divided into two broad categories: woody and non-woody (Figure 4.1, [51]). While forests provide only woody materials, agriculture sources provide both woody and non-woody biomass for bioenergy production (Figure 4.2).

Forest-based wood constitute the majority of biomass used in production of bioenergy but grassland- and agriculture-based biomass materials are likely to play a bigger role in the future. Agricultural systems are the source of four types of biomass materials: sugars, starches, non-woody lignocellulosic materials and woody lignocellulosic materials.

Starches and sugars are a small portion of plant matter which is mostly done of cellulose, hemicellulose and lignin. Cellulose and hemicellulose are made up of chains of sugars. Advanced bioethanol technology can break down these chains into fermentable sugars. As a result, ethanol can be produced from nearly any plant material. Cellulose and hemicellulose can be readily used in thermal and thermochemical conversion processes. Eventually, grasslands and agricultural systems are a vast and important potential source of feedstocks for every bioenergy product and end-use. Agriculture-based biomass materials come from annual commodity crops like corn and soybeans, residues collected after harvest of annual crops grown for food or feed, and perennial crops such as grass and tree crops.

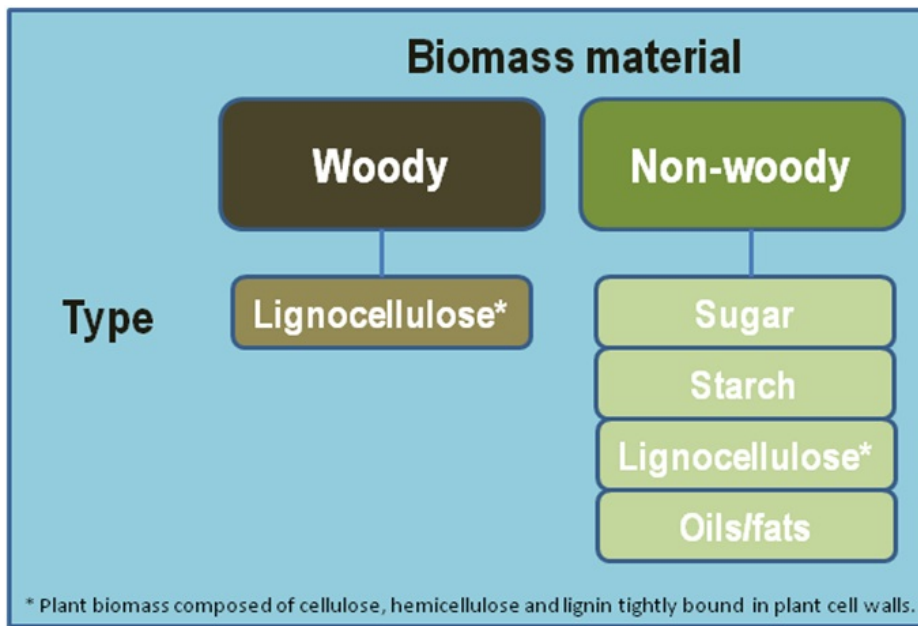


Figure 4.1: Two broad categories of biomass materials, and four composition types.

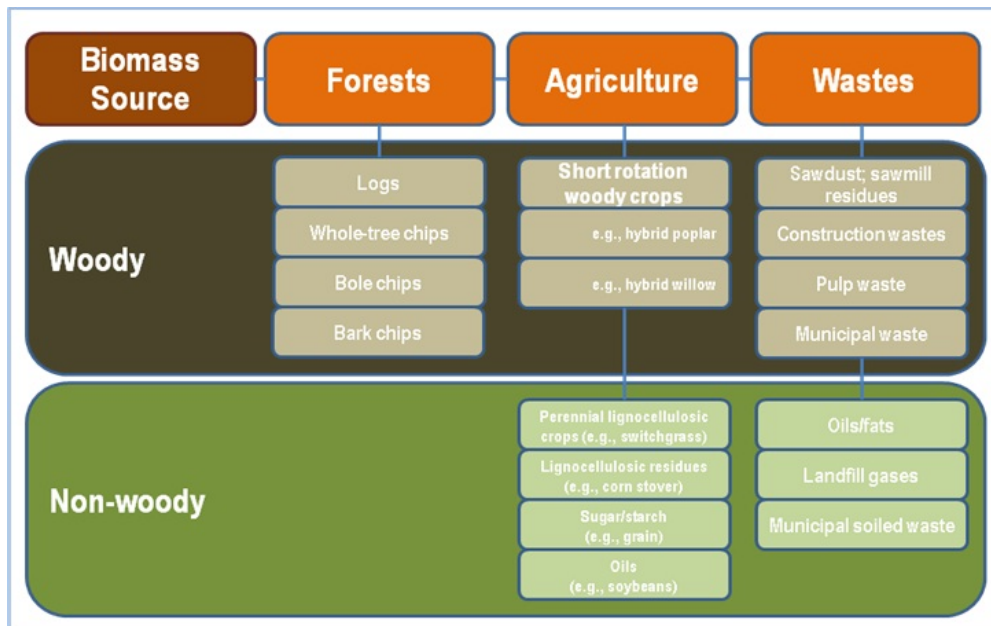


Figure 4.2: Sources and types of biomass materials for conversion into bioenergy.



## 4.2 Chemical conversion

Converting biomass into other forms can be done using various chemical processes. Most of these processes are Fischer-Tropsch synthesis, methanol production, olefins (ethylene and propylene) and involve gasification, which is very expensive and technically risky.

Since biomass is harder to compress in a pressure vessel than char or any liquid, the gasification of biomass is done at atmospheric pressure. This causes combustion of biomass and the production of a mixture of carbon monoxide, hydrogen and methane [52]. The gas produced could be used for internal combustion engines or for substitute furnace oil heat applications. This process is more interesting than ethanol or biomass production because it can convert solid waste in a mixed gas, very useful as fuel [53].

## 4.3 Biomasses in Italy and FVG region

Italy is dedicated to reducing its fossil fuel consumption and in turn reduce its carbon footprint by implementing the Italian action plan that targets 17% of the total energy generated be from renewable sources. By 2012, 750 MW of electric power was being produced from biogas sources [28][29]. This steady increase in the number of biogas plants (anaerobic digestion plants) has been due to energy laws implemented from 2004- 2007 which waived an all-inclusive feed-in tariff for electricity production.

In FVG region, which is an autonomous part of Italy, a similar energy plans have been adopted. This has led to the increase in biomass energy production for both industrial and domestic use. The forest coverage in FVG region (FVG) is given by 300,000 hectares which translates to 41% of the total FVG area [30]. Forest as a resource in FVG was traditionally used to satisfy human needs such as wood, paper, soil erosion deterrent, mitigation of climate change among others, but with the ever-increasing cost of fossil fuel, the resource is being viewed as a source of energy. In order to maintain

the FVG forests as an energy source, sustainability and forest management must be observed to ensure the resource is renewable. The energy plan stipulates that with proper utilization and increased efficiency of the plants, the resource can serve for many generations.

An energy assessment conducted in FVG illustrated that with current number of animals and agriculture residue in the region, biogas can be produced which would replace 2.6% of the energy and 10% of the electricity consumption in the region. In Table 4.1 some of the statistical data of biomasses and their energy production are reported.

Table 4.1: Statistical data of some biomasses and their energy production implications.

Agriculture	Cornstalk	Straw	Animal waste	Total
Area (ha)	73846	15974	-	-
By products (t/year)	406153	74949	2416102	2897204
Biogas (N) Mm <sup>3</sup> /year	126	22	38	187
Energy potential (TJ/year)	2430	429	777	3636
Share of energy potential (%)	67	12	21	100

## 4.4 Pyrolysis

Biomass conversion into energy or chemical involves thermochemical technologies such as combustion, pyrolysis, gasification and high-pressure liquefaction. In the past decade, the interest has been grown for thermochemical conversion of biomass and urban wastes for upgrading the energy through more easily handled fuels and charcoal.

This thesis focuses on the use of thermo-solar energy for biomass pyrolysis which is the thermochemical process with the highest flexibility in terms of the yield and composition of the products [50]. Pyrolysis is a thermochemical process through which organic materials decompose into small elements with release of energy at very high temperatures and in the absence of oxygen. This process involves physical phases and spontaneous

change in the chemical composition of a substance or material and it's irreversible [16][50]. The word Pyrolysis can be broken into two distinct Greek components “pyro” meaning fire and “lysis” meaning separation.

The pyrolysis process involves the breakdown of very large molecules into very small molecules of any substance in presence of burning heat. During pyrolysis, the substance is kept at very high temperatures and therefore experiences molecular vibrations. At this elevated temperature and under constant vibrations the substituent molecules begin breaking from each other randomly. This process can be used to make bio-fuels such as bio-diesel from waste agricultural materials.

Many years ago, around 5000 years ago in Italy and also in Middle East, pyrolysis was commonly being used to produce charcoal [10][50]. The process was also used famously for manufacturing tar to caulk boats in Egypt. Since then, the use of pyrolysis has continued to widen and broaden based on different technologies and utilization. Biomass preparation is a very significant factor for an effective operation of pyrolysis since all the types of pyrolysis requires to have a feedstock sizing for an efficient heat transfer [54].

The two main processes used for converting biomass into useful fuels are the biochemical and thermochemical. The biochemical process has efficiencies ranging between 30 and 55wt. % while the thermochemical process has a conversion efficiency that lay between 40 and 70wt. % [55]. The thermochemical processes may include the pyrolysis, gasification, combustion and liquefaction. Besides transforming the biomasses into bio-energetics, these processes may also be used in manufacturing and making products for petrochemical industries.

The process of biomass pyrolysis is normally used to produce bio-oils, bio-fuels, chars and biogas on different types of pyrolysis. The main advantage of pyrolysis is the inherent ability in it to produce over 60wt. % of bio-oil from the biomass. However, pyrolysis requires the provision of an external or outward energy input in order to achieve the operating temperatures [50].

The temperatures for pyrolysis ranges between 3500 °C to 7000 °C. Between these temperatures it's possible for liquid products to be formed. The energy being used is derived from either a renewable or non-renewable energy source but it should have a negative impact on the surrounding environment [50].

#### 4.4.1 Pyrolysis products

The main products obtained from pyrolysis are bio-oil, gas and char. However, the outcome strongly depends on the temperatures inside the reactor, and pyrolysis can take place at different temperatures [27][56]. At very high temperatures there is formation of more liquid byproducts and gases than at low temperatures. The biomass pyrolysis may therefore be grouped as follows:

- a) At low temperatures- production of charcoal.
- b) High heating rate, low temperatures, short gas prevailing time process- production of liquids.
- c) Low heating rate, high temperatures and long gas prevailing time- production of fuel gases.

Table 4.2: Different products of pyrolysis

<b>Condition</b>	<b>Process</b>	<b>Products</b>
<b>Below 3000 °C</b>	Water elimination, free radical formation and depolymerisation	Formation of CO, CO <sub>2</sub> , charred residual and carbonyl
<b>Between 3000 °C to 500 °C</b>	Breaking of glycosidic linkages	Laevoglucose, anhydrides and oligosaccharides to the formation of tar fractions
<b>Above 5000 °C</b>	Dehydration , fission of sugar units and rearrangement	Formation glyoxal, acrolein, acetalhyde which are components of carbonyl
<b>Above 5500 °C</b>	A combination of all the above processes	A combination of all the above compounds
<b>Condensation</b>	Unsaturated products cleaving to the char	Highly reactive char residues

#### 4.4.2 Biomass pyrolysis setup

The use of solar thermal energy in biomass pyrolysis has been proved to be effectual and has continually attracted great interest. There are three main types of biomass pyrolysis setups [56]:

1. Resistively Heated Filament:

where a small sample is rapidly brought to pyrolyzing temperatures by placing them onto a pyrolysis filament, made of materials of high electrical resistance and wide operating range (i.e. iron or platinum).

2. Inductively Heated Filament: Curie-pt. Pyrolyzer:

here, the electrical current is induced onto a wire made of ferromagnetic metal by use of magnet or high frequency coil [56]. Due to Continual induction of current the wire begins to heat until it reaches a temperature at which it is no longer ferromagnetic. When the wire becomes paramagnetic, no further current may be induced in it. It is then heated to pyrolysis temperature in milliseconds.

3. Furnace Pyrolyzer.

In this type of pyrolyzer (Figure 4.3), a metal or quartz sample tube is wrapped with heating wire and thermally insulated. The furnace pyrolyzer has a much larger sample chamber than the filament pyrolyzers.

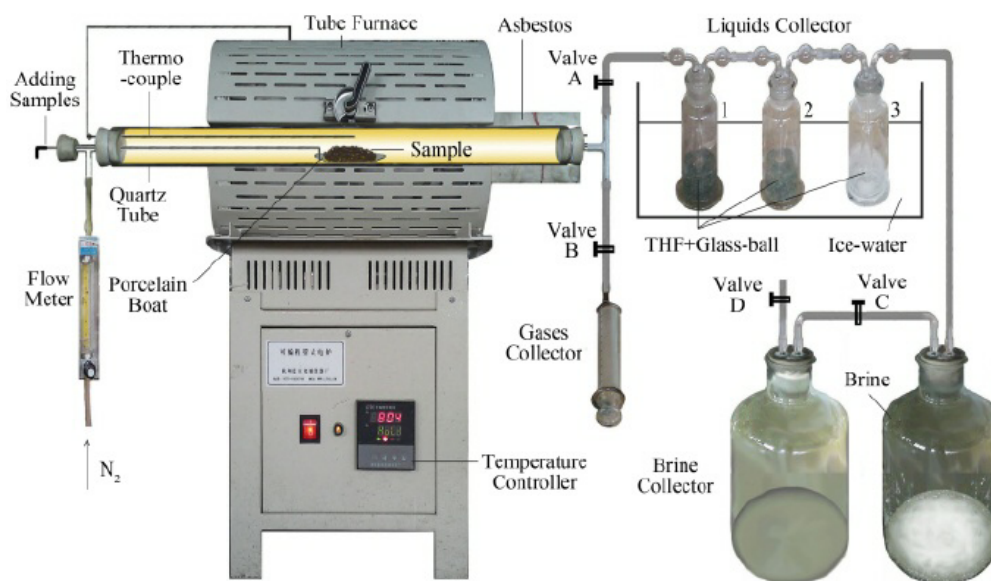


Figure 4.3: A sketch of a furnace pyrolyzer setup.

### 4.4.3 Types of pyrolysis reactors

There are different types of pyrolysis reactors that are in use due to different technologies and inventions. The following are some of the reactors:

#### ***Fixed bed reactor***

This type of pyrolysis reactor can be used to produce charcoal where the biomass feedstock is partly gasified using air [50][56]. A company known as Bio-Alternative in Italy operated a fixed downdraft bed gassier of height 3m and diameter 1m with an apparent biomass through put of 200kg/h. The products obtained from this process are viscous tar, charcoal and gas with the yield being maximized at the production of charcoal. For beech wood and fir, the charcoal yield achieved are in the area of 300wt%.

#### ***Fluid bed reactor***

This pyrolysis reactor is common and well known. It was first applied for biomass pyrolysis by the likes of Gourtay et al (1987), Kosstrin (1980), and Scott et al (1988) [27]. With a flow rate of 100kg/h, there's yield of tar yields

produced are mainly low for a medium fluid bed reactor. The reason for the low tar yields are due to the crack of vapors in the bed and freeboard of the reactor [54][56]. Therefore, this reactor provides an option of gasifying biomass feedstock and with reduced tar products. The materials used for the reactor should be selected such that it has an optimum catalytic ability to crack tar behavior. When the product desired is tar, the gaseous products are quenched immediately after formation and the materials should also be non-catalytic.

## 4.5 Pyrolysis of biomasses

Pyrolysis of biomasses may be defined as the process of thermal degradation of biopolymers that are present as an organic material with the absence of oxygen.

The energy density of biomass constituents is low compared to that of coal or petroleum-derived fuels. The heat content of biomass, on a dry basis, is significantly lower than that of anthracites, bituminous coals and petroleum. In general, biomass has low energy content per unit mass because of physically adsorbed moisture, up to 50% by weight [50].

Vast quantities of pruned vine shoots, a woody waste product is disposed of. No suitable system for collecting, treating, and utilizing this product has been developed [54]. Numerous ways of potentially making use of pruned vine shoots are being at the technical feasibility testing stage. The attempts have been made to obtain various products using vine shoots as a raw material: active charcoal, pulp for paper making, polyphenols. There have also been many attempts to make use of its absolute energy potential as a lignocellulosic biomass, including compacting to produce solid biofuel and gasification with air.

Corncocks are not as energy dense as the fossil fuels but they have a similar energy density to other biomass feedstock and less energy dense coals. Both are successfully utilized as energy feedstocks around the world. The chemical

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properties and physical characteristics make corn cobs suitable for several methods of energy generation. It was found that corncobs contain 32.3-45.6% cellulose, 39.8% hemicelluloses and 6.7-13.9% lignin [57]. Current technologies can convert the energy contained in the corncob molecular structure. Combustion and gasification can utilize the molecular structure of the cellulose, hemicellulose, and lignin to produce heat energy or synthesis gas. The advantages of using corncobs as a coal alternate include a potentially cleaner emissions stream and the decrease in undesirable emissions and waste ash.

Wood pellets have been extremely popular as a heating fuel during recent years. In general, biomass pellets are a superior fuel when compared to their raw feedstock. Wood pellets have higher mass and volumetric energy content due to pelletization. They are more energy dense, easier to handle and utilize in automated feed systems [17]. These advantages accompanied by sustainable and ecologically properties of the fuel, make wood pellets very attractive for use. Wood pellets are a higher energy density feedstock than wood chips, and therefore reduce the costs of handling, transport and storage. Despite the fact that pellets are more energy intensive to manufacture than wood chips, greenhouse gas emission benefits can be achieved when using them to substitute conventional fossil fuels.

Pyrolysis of a biomass is endothermic process that involves the thermal degradation of the organic matrix under an inert oxygen-free atmosphere resulting in production of liquid bio-oil, solid biochar, and non-condensable gas products. The most important operating parameters affecting the yield of each product are temperature, sweep gas flow rate, heating rate and pressure. Many studies have been done on biomass pyrolysis in conventional reactors concerning product composition at different operating parameters. Conventional pyrolysis requires extra energy inputs obtained by combustion of a non-renewable source which reduces the energy conversion efficiency and increases the pollution release. The drawbacks of traditional pyrolysis



can be avoided using concentrated solar energy that provides the heat necessary for reactions.

Solar energy is directly absorbed by the biomass resulting in fast pyrolysis, producing chemical fuels, tar and char. The temperature is the main process parameter which affects solar-to-fuel energy conversion efficiency and the maximum efficiency of 75% may be achieved at 1500 K. The advantages of using concentrated solar energy in pyrolysis process can be summarized as: i) it enhances the calorific value of feedstock; ii) the by-products of combustion do not contaminate the solar pyrolysis gaseous products; iii) the emission of pollutants to the environment is reduced; iiiii) there is no need for energy-intensive processing of pure oxygen.

The carbon-rich char or “solar carbon” obtained in solar pyrolysis of biomass can be further used as a fuel or decontamination adsorbent. The effects of temperature, heating rate, residence time and pressure on the structure and reactivity of biomass chars have been investigated in numerous studies [17]. The bio-carbon material could be utilized in conventional power plants and solar energy can be stored for long periods of time, without losses. An innovative concept of solar systems for pyrolysis can be used to mitigate the problems of high costs, complexity and environmental threat associated with conventional biomass pyrolysis.

This study presents the results of experiments carried out with the Linear Mirror II, a simple device for concentrating solar thermal energy. The Linear Mirror II is successor of the first generation of multi-purpose device developed in 2011. This industrial product is certified with the “Solar Keymark” [49] certificate and can readily be used for solar cooling, industrial process heat and heating. The device has a very simple and robust construction and its cost is reasonable since it uses only three electrical motors. The total reflecting surface is 13.8 m<sup>2</sup> and a maximum thermal power is 9 kW. The device contains eight single mirrors, and a resulting light concentration is enough to achieve the temperatures of about 250 °C [46]

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[48]. This thesis describes pyrolysis of different feedstock with a device which uses the Linear Mirror II to provide solar energy for necessary reactions.

Pyrolysis may be categorized into two processes as fast pyrolysis and slow pyrolysis. Fast pyrolysis is the common one in terms of use while the slow pyrolysis has not been used so much. Slow pyrolysis takes a long time to completely yield the products expected from the process and gives biochar as the main component of the products, this is undesirable. On other hand, fast pyrolysis yields up to 60% bio fuel and takes a short period of time to complete and also produces only 20% syngas and 20% biochar. This effective pyrolysis process involves the following processes:

1. Open core with fixed bed pyrolysis
2. Cyclonic fast pyrolysis
3. Ablative fast pyrolysis
4. Rotating core fast pyrolysis

The essential features of a fast pyrolysis are:

- It has a carefully controlled reaction process with temperatures around 6000 C in the vaporization phase
- It has both high heating as well as high heat transfer coefficients and rates. Requires a finely and well ground feed.
- The pyrolysis vapors take around 1 sec inside the reactor
- To get the bio-fuels or the bio-oil the products of this process are rapidly quenched.

Table 4.3: Densities for different feeds.

<b>Feedstock</b>	<b>Bulk Density kg/m<sup>3</sup></b>	<b>Heating Value Dry Basis (GJ/t)</b>	<b>Energy density (GJ/m<sup>3</sup>)</b>
<b>Straw</b>	100	20	2
<b>Woodchips</b>	400	20	8
<b>Pyro-oil</b>	1200	25	30
<b>Charcoal</b>	300	30	9
<b>Char-water slurry</b>	1000	15	15
<b>Char-oil slurry</b>	1150	23	26

#### **4.5.1 Gas emission during pyrolysis processes and reducing emission methods**

During the process of pyrolysis of biomass matter, harmful gases and other toxic substances are produced though some are in little quantity.

##### **Carbon dioxide (CO<sub>2</sub>)**

This is a gas that is colorless and odorless that results from the oxidation of carbon. Though biomass is termed as renewable source of energy, it cannot be termed as entirely clean. Combustion of biomass produces CO<sub>2</sub> even during the process of direct burning. For the production of CO<sub>2</sub>, an oxidation reaction of carbon takes place to produce heat and CO<sub>2</sub> gas. The amount of carbon dioxide produced during pyrolysis combustion depends on some parameters like temperature of pyrolysis and time of combustion. Despite having more advantages, when in excess carbon dioxide is one of the main greenhouse gases emitted to the atmosphere. It can cause heating up of the earth's surface an effect commonly called greenhouse effect. Another negative effect is that more amounts of carbon dioxide increases the acidic levels of seas and it can affect a variety of sea organisms.

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Mitigation strategies of CO<sub>2</sub> during pyrolysis is important and desirable in order to reduce its emission to the environment. The major techniques that are more developed in industries are absorption processes in separation of CO<sub>2</sub>. Other techniques that are being used increasingly are adsorption, chemical looping combustion and membrane separation. Some of the factors to consider when choosing the membrane for CO<sub>2</sub> separation are separation factor, CO<sub>2</sub> permeate flux and gas permeability. Zeolite membranes are examples of membranes that have been experimented on in the process of CO<sub>2</sub> separation [50][58].

### **Carbon monoxide (CO)**

Just like CO<sub>2</sub>, carbon monoxide is an odorless and colorless gas that is harmful and toxic to lives. Carbon monoxide is also a greenhouse gas that increases the temperature of the earth's atmosphere leading to global warming effect. Increase in the amount of carbon monoxide in the air also leads to suffocation of the living organism in the earth's surface. If the amount of CO increases in a room to a value higher than 5%, a human being inside the room can end up dead [59].

### **TAR**

This is a natural substance that is mainly obtained naturally from underground or produced from coal, and biomass. During pyrolysis, the formation of tar is mainly caused by incomplete conversion of liquid products. The amount of tar produced is a serious problem for areas of application of the fuel that is produced during that process. Tar condenses at low temperature which leads to blockage of fuel lines and engines. When high amounts of tar is produced, there is a possibility of reduced efficiency of biomass. Tar is also a toxic substance which is harmful to the environment [50][59].

During pyrolysis, tar can be removed from the setup by several methods including;

- Physical removal. This is the method of removing tar by physically scrubbing the condensed tar.
- Chemical removal; during chemical removal, a conversion of tar chemically is applied either by the use of partial oxidation or catalytic cracking. During thermal cracking, the temperature of the tar is raised to a level that end up cracking the tar species to a less problematic species such as methane, hydrogen and carbon monoxide. This process should be done at temperatures of about 1000 degrees Celsius.
- During partial oxidation, oxygen gas is added at different stages of pyrolysis leading to oxidation of tar. (International Journal of Innovative Research in Science, Engineering and Technology) [59]

### **Methane gas**

This is a natural substance that is constituted in high percentage by natural gas. It highly flammable, colorless and odorless. Methane warms up the earth's atmosphere making it a greenhouse gas just like carbon dioxide and carbon monoxide but it is estimated to be 20 times worse than CO<sub>2</sub>. If it is burnt, it releases compounds which are toxic to the atmosphere. Unlike the other gases, methane is one of the major component that is produced in the process of pyrolysis. The quality of methane should be increased to achieve high efficiency during combustion by reducing or removing other gases like CO<sub>2</sub>, carbon monoxide and nitrogen [50].

### **Nitrogen and its compounds**

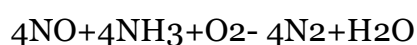
This is a colorless, tasteless and odorless gas that is slightly lighter than air and slightly soluble in water. Nitrogen is found naturally in some compounds that are formed through biological process.

Nitrogen constituted in biomass is mainly in the form of amino acids. During pyrolysis of biomass matter, emissions of nitrogen oxide (NO<sub>x</sub>) and N<sub>2</sub>O are produced. Availability of oxygen during this process promotes formation of NO and HCNO (fulminic acid). Some of these nitrogen compounds like NO<sub>x</sub>

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are harmful to health in such a way that they cause inflammation of airways. On the environment, NO<sub>x</sub> can cause reduced growth and leaf damage to crops. NO<sub>x</sub> can also contribute to the formation of acid rain if it is emitted in excess.

Mitigating the release of NO<sub>x</sub> and N<sub>2</sub>O from pyrolysis is done by application of specific non-catalytic reduction and selective catalytic reduction. These methods help the reaction between NO and ammonia to reduce the emission of NO<sub>x</sub> which constitutes about 95% NO ( ). The reaction that occurs is as follows



The selective non-catalytic reduction is efficient if the concentration of the gas and its flow is stable and a good reaction time. Selective catalytic reduction can work for many different installations [60][61].

## 4.6 Biomass Pyrolysis in FVG region

Pyrolysis finds its applications in FVG. Pyrolysis also known as thermal cracking, cracking, thermolysis or depolymerisation is a chemical reaction. During pyrolysis, there is molecular breakdown of larger molecules into smaller molecules in the presence of burning heat [50]. This process involves physical phases and spontaneous change in the chemical composition of a substance or material and it's irreversible. During pyrolysis, the substance undergoing the processes is subjected under high temperatures and therefore experiences molecular vibrations. At these elevated temperatures and under constant vibrations the substituent molecules begin breaking from each other randomly [50]. This process can be used to make bio-fuels such as bio-diesel from waste agricultural materials. Pyrolysis is the precursor of both the combustion and gasification processes. It occurs naturally in the first two seconds.

In FVG pyrolysis is used to yield biochar, bio oil and gases such as methane, hydrogen, carbon monoxide and carbon dioxide. With pyrolysis

Solid biomass can be converted into an easily stored and transported liquid which can be used to produce heat, oil and chemicals.

The efficiency of pyrolysis process depends on the size of the particles feedstocks. Pyrolysis can either be slow or fast one. Pyrolysis is an alternative to incineration of waste products since the process uses low temperatures. The low temperature resulting from the process enables environmentally – friendly processing of all flammable materials [50].

In FVG, the solid biomass such as agricultural and forest wastes and biogas compose up to the second largest energy source in the region with an apparent percentage share of 13%. The share of solid biomass for this particular region is almost equal to that of the national contribution of the renewable energy sources from biogas and generally the biomass that made up to 11% of the national renewable energy source [30][31].

In the following chapter, the first prototype ever realized able to pyrolyze biomasses with the only use of solar thermal energy is described.

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# Chapter 5

## Solar Pyrolysis with Linear Mirror II

In this chapter, a test with a first prototype setup which uniquely uses solar thermal energy collected and concentrated by the Linear Mirror II to pyrolyze biomasses is described, and the results obtained are discussed.

### 5.1 Solar pyrolysis

In conventional pyrolysis, biomass is heated by burning fossil fuels, consuming part of the processed biomass or with the use of an electrical furnace. Alternatively, concentrated thermal solar energy can be used as heat source. Several are the advantages of a solar driven thermal carbonization: i) it delivers a higher carbonized material output per unit of feedstock because no portion of the feedstock is combusted for process heat; ii) the process is CO<sub>2</sub> neutral and discharge of pollutants in the environment is avoided iii) it offers an efficient way of chemically store the intermittent solar energy in the form of a readily transportable fuel. A number of attempts to perform pyrolysis with solar energy based on different solar concentrating systems have been made [8][48].



Solar pyrolysis can be used for converting biomasses inside an inert atmosphere and it's an endothermic process. The following are the three ways which allow the energy to be transferred to the biomass from solar heat:

1. By employing intermediate fluid
2. By application of direct irradiation to the biomass inside the reactor
3. By application of heat via the walls of the reactor

The thermo-solar system captures solar radiation from a very wide area and then concentrate the heat to a very small area which is then used for heating purposes. The system contains the following main components:

1. Solar collector
2. Solar concentrator
3. Supporting structure

The direct sun-rays are concentrated and reflected to a pyrolytic reactor which is then heated until the desired temperatures for pyrolysis are achieved.

The solar concentrator support is a structure which enables to focus the sun's radiation to a solar collector. In this case, the solar collector is the pyrolytic reactor.

## **5.2 Solar Pyrolysis with the Linear Mirror II**

The scheme of the pyrolysis setup realized for the research developed in this thesis is presented in [48]. The device comprises a stainless-steel retort (100 cm x 44 cm x 46 cm), which rotates around a horizontal axis at a speed of two rotations per minute. A retort is heated by the Linear Mirror II. A secondary reflector is situated in the focal plane of the Linear Mirror II system and deflects the concentrated light (side view), so that the light enters the pyrolysis device from below [48]. Thick mineral wool isolating cloth surrounds the retort, enabling the sunlight entrance. One side of the rotating

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axis of the retort contains a steel tube, throughout the pyrolysis gas and the water vapor release. The retort is positioned at a distance of 5 m in front of the mirror array in a fixed position. Two temperature sensors are used for monitoring: an infrared sensor which measures the temperature of the metal surface of the pyrolysis retort (sensor A) illuminated by the sunlight concentrated by the mirror. A second sensor (PT100) is mounted within the steel tube close to a face of the retort (sensor B) which is not illuminated. The entire system is robust and simple, able to accept bulky moist chopped organic feedstock. The work of this thesis included also a contribution to improve the experimental prototype optimizing the heat transfer from the outer walls to the inside of the retort (with the consequent homogenization of the process temperature). A system to measure the inner and outer temperature in the pyrolyzer chamber using a BeagleBoneBlack Board (BBB) and K-thermocouples has been developed as well (see Appendix B).

Temperature measurements have been conducted in a sunny day. The temperature profiles over time span measured by sensor A (green line) and B (red line) are shown in Figure 5.2. The operating temperature of 500°C measured by sensor A was reached in about 90 minutes. Sensor B measured ambient temperature during the short period of time. After the first ten minutes of the experiment, a steady state temperature of 300°C was reached in about 100 minutes.

When the temperature of 300°C had been measured by sensor B, the heating process accompanied by a strong production of fumes and gases was stopped. The constant temperatures of sensors A and B after 100 minutes indicate that the system had reached an operative thermal equilibrium. The minor decrease of about 50°C of the temperature measured by both sensors after 100 minutes is due to reduced solar intensity in the afternoon. After about 150 minutes the experiment was completed by bringing the reflecting mirrors of the Linear Mirror II system into their park position (not focusing anymore

the sunlight on the pyrolyzer). It can be observed a strong decrease of the temperature measured by sensor A.

A direct measurement of the material temperature was not performed. In order to get an insight into the temperature within the material and consequently on the nature of the material, its HHV<sup>5</sup> has been compared to the reference samples.

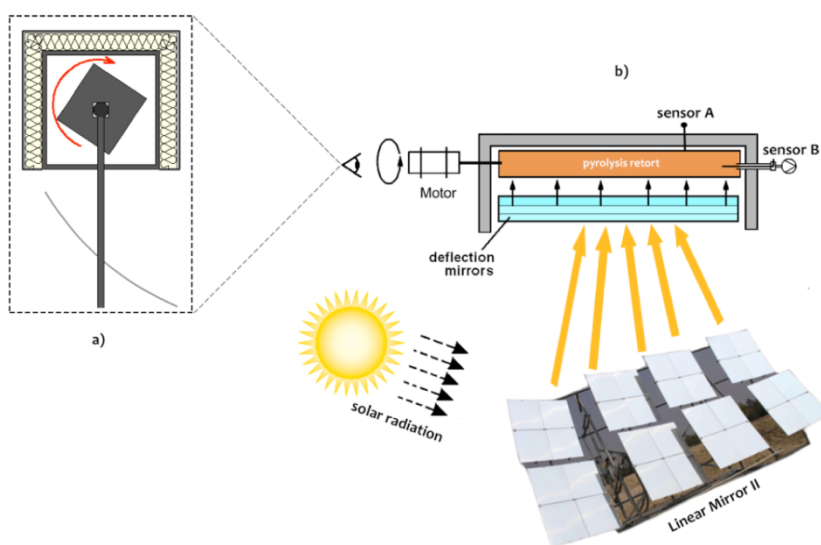


Figure 5.1: Scheme of the solar pyrolysis experimental setup

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<sup>5</sup> The quantity known as higher heating value (**HHV**) (or *gross energy* or *upper heating value* or *gross calorific value* (**GCV**) or *higher calorific value* (**HCV**)) is determined by bringing all the products of combustion back to the original pre-combustion temperature, and in particular condensing any vapor produced.

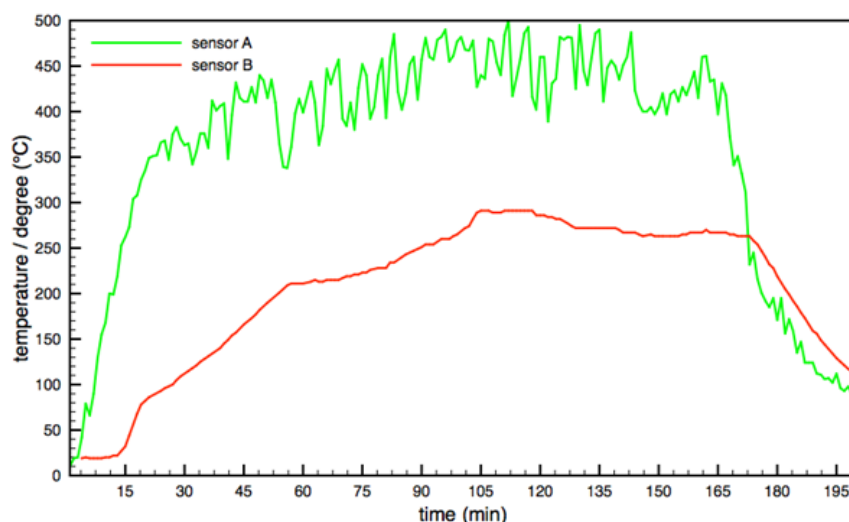


Figure 5.2: Temperature profiles measured by sensors A and B (°C).

### 5.2.1 Performance of the device

The pyrolysis retort was filled with 5.0 kg of straw, and exposed to the concentrated sunlight, and was rotating at a speed of two rotations per minute. At the end of the process, the material inserted in the pyrolysis setup was reduced from an initial mass of 5.0 kg to 1.7 kg (which corresponds to a yield of about 36%).

Since the pyrolysis process took 100 min of time, the device is able to process about 20 kg of straw in one day (8 hours), transforming it to 6.0 kg of solar carbon.

## 5.3 Chemical analysis of the solar carbon and straw

Chemical properties of straw and of the solar carbon produced were characterized through standard procedures, to compare the pyrolysed biomass with the conventional coal.

### **5.3.1 Biomass sample preparation and characterization of straw**

The feedstock used in this study was wheat straw provided by a local wheat farm located in Gorizia (Italy). The herbaceous biomass was ground and sieved to the particle size range 0.5–2.0 mm. The particles were dried at 105 °C for 8 hours before the experiment.

Thermogravimetric analyses of straw and charcoal were performed in a TGA 500TA instruments. TG analysis of the straw and of charcoal (solar carbon) was carried out in N<sub>2</sub> and subsequently in air at a flow rate of 100 cc/min. All the analyses are characterized by an isothermal step at 150 °C under N<sub>2</sub> flow to quantify the initial moisture of specimens [62].

Figure 4 summarizes the TGA results related to the decomposition of straw in N<sub>2</sub> and subsequently in air.

The first loss is associated to the amount of moisture in the straw, that is around 7 wt%. The decomposition of straw in N<sub>2</sub> increases rapidly from 170 °C to 500 °C registering the maximum rate at 325 °C. In this range, the weight loss is almost of 70%, then the process slows dramatically and at 900 °C the total mass has been reduced of the 80%. The 20% of mass left is constituted by a fraction of refractory carbon (~13 wt%) and by ash (~7 wt%). The formation of refractory carbon at the end of the process is probably due to the partial condensation of lignin and cellulose to form graphitic structures [62]. The TG profile obtained is consistent with the thermal properties of the main constituents of straw, which are the hemicellulose, cellulose and the lignin [63]. The decomposition and volatilization of these substances occur at increasing temperature, being the lignin the most fire-resistant component, followed by the cellulose and finally by the hemicellulose. This preliminary analysis indicates that an operating temperature of 500 °C should have led to an almost complete pyrolysis of the wheat-straw [63].

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### 5.3.2 Characterization of solar carbon

The higher heating value (HHV) of the wheat straw and of the solar carbon were measured using a bomb calorimeter IKA C200 instrument with the DIN 51900-1 standard [64]. The vessel was pressurized at 30 bar of oxygen. The uncertainty of the measurements is about 120 J/g. The high heating value (HHV) of solar charcoal ranges between 24.5 to 28.2 MJ/kg depending on the analyzed specimen, this variability could be due to a not homogeneous pyrolysis inside the retort, however the values measured are significant higher than that of straw 16.9 MJ/kg and close to the HHV of fossil fuel.

For the sake of comparison, several samples of the same wheat straw, used also in the pyrolysis setup described here, have been heated at different temperatures in controlled conditions, using an oven for tests with a maximum operating temperature of 1050 °C and isolation walls of high density ceramic fiber. The mass of the samples before and after heating, and therefore the residual mass in percentage have been measured, as shown in Table 5.1.

Raising the temperature, the residual mass percentage decreases as one would expect, and the higher heating value (HHV) increases. These values can be compared to the corresponding values obtained for the solar carbon in the pyrolysis experiment: this confirms that the temperature reached in the retort were between 350 and 500°C.

The chemical and physical properties of wheat straw and the solar charcoal are summarized in Table 2. The elemental analysis of straw and solar carbon was performed on a Vario EL Mod X (Vario Inc, USA).

Such analysis gives the weight percent of carbon, hydrogen, nitrogen, and sulfur in the samples simultaneously [65]. The oxygen content was estimated by mass difference, i.e. by subtracting from 100% the amount of C, H, N and ash [62].

Values measured are in agreement with those reported for straw-based biochars produced by conventional pyrolysis at 500 °C [62][65]. The hydrogen to carbon ratio is also consistent with that of other chars. However, the O/C

molar ratio is slightly higher, probably owing to a non-complete decomposition of lignin, the most thermal resistant constituent of straw [66]. Scanning electron microscopy (SEM) images were obtained with a EVO-40 XPP (Zeiss) microscope equipped with an energy-dispersive X-ray detector (EDX), at 5-10 KV.

SEM images of solar charcoal (Figure 5.4) show that the structure of feedstock is still visible. The material is characterized by oblong channels of 5-10  $\mu\text{m}$  of diameter and small pores (2-3  $\mu\text{m}$ ) distributed throughout the surface.

On the base of the above results and on the categorization proposed by Keiluweit, Nico, Johnson and Kleber [67], we classified the charcoal obtained via solar pyrolysis as a mixture of transition and amorphous chars, in which the structure of straw is partially preserved and in part altered by the heating process.

Temperature programmed oxidation (TPO) was carried out over 4 mg of solar carbon in a home-made equipment under 10 v% O<sub>2</sub> in He flow (500 cc/min) at a heating ramp of 10 °C/min up to 800 °C. The combustion products were monitored with a FT-IR multi gas analyzer (Multi-Gas 2030, MKS Instruments).

The combustion of the solar charcoal was investigated with a temperature programmed oxidation (TPO) experiment in airflow. Figure 6 shows that the combustion of this material occurs in the range of 200-500 °C, producing mainly CO<sub>2</sub>, and CO. The profile of combustion is complex with at least three components at 320, 400 and 450 °C. The component at lower temperature can be attributed to the combustion of volatile part of charcoal while the components at higher temperature are related to the combustion of non-volatile components (polyaromatics from lignin and refractory char formed during the process of pyrolysis)

TG analysis of solar charcoal in N<sub>2</sub> (Figure 5.6) shows that at the end of the process the charcoal still contains 30 wt% of volatiles while the fixed carbon is of the order of 60 wt%. Considering that at 500 °C the thermal pyrolysis of

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straw led to an almost complete decomposition of it (see Figure 5.3), we inferred that the temperature reached inside the pyrolyzer was on average lower than that measured at its outer walls. Such internal temperature was probably sufficiently high to decompose hemicellulose and cellulose, but only partially the lignin whose conversion to char requires temperature higher than 400 °C [68]. On the other hand, the range of the measured HHV values suggests that an incomplete pyrolysis can be related to a non-homogeneous temperature inside the retort, despite temperature of 500 °C can be reached. The result is indeed encouraging by keeping in mind that the system is a prototype and several improvements can be done to optimize the heat transfer from the outer walls to the inside of retort and homogenize the temperature of process. After this encouraging result, in the following chapter, several samples of different feedstocks have been prepared to be pyrolyzed by Linear Mirror II and a deeper characterization has been done.

Table 5.1: Results from heating samples of wheat straw at different temperatures, in terms of residual mass in percentage and higher heating value (HHV).

<b>Feedstock</b>	<b>Temperature (°C)</b>	<b>% residual mass</b>	<b>HHV (MJ/kg)</b>
<b>Wheat straw</b>	300±10	51.5±0.5	22.6±0.1
	400±10	39.6±0.4	27.5±0.1
	500±10	31.2±0.3	28.5±0.1



Table 5.2: Characterization of wheat straw and charcoal obtained through solar pyrolysis with the Linear Mirror II. a.- Average value estimated over three pyrolysis tests of measurements from different samples.

<b>Parameters (wt%)</b>	<b>Wheat straw</b>	<b>Solar carbon</b>
<b>Carbon</b>	46±1	70±1
<b>Hydrogen</b>	6.0±0.1	3.5±0.1
<b>Nitrogen</b>	0.3±0.1	0.8±0.1
<b>Oxygen</b>	41±1	15±1
<b>Sulfur</b>	0.3±0.1	0.4±0.1
<b>Ash</b>	7.0±1	10.5±1
<b>O/C (molar ratio)</b>	0.7	0.2
<b>H/C (molar ratio)</b>	1.6	0.6

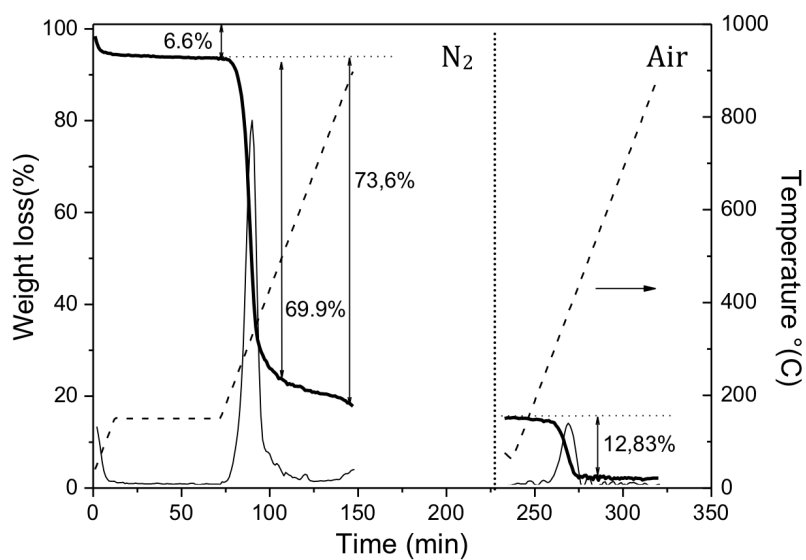


Figure 5.3: TG analysis of the wheat straw.

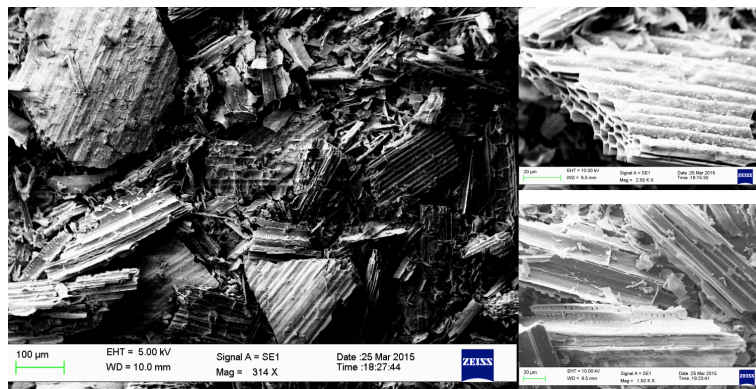


Figure 5.4: Micrographs of charcoal obtained from solar pyrolysis of wheat straw at 500 °C.

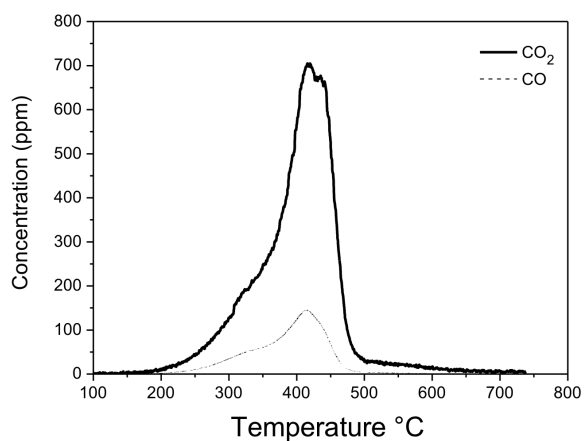


Figure 5.5: TPO profiles of the charcoal obtained via solar pyrolysis.

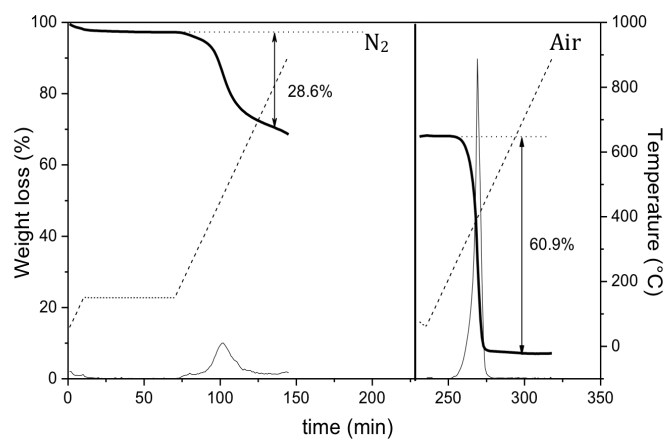


Figure 5.6: TG analysis of charcoal obtained via solar pyrolysis.

# Chapter 6

## Characterization of solar carbons

Giving the encouraging results obtained with the first pyrolyzation test, the research described in this thesis concentrates now in studying several local biomasses, performing their detailed characterization before and after pyrolyzation using the Linear Mirror II, to compare their properties and select the best ones to be used. To understand properties of solar carbons several more in-depth analysis have been carried out.

### 6.1 Samples preparation and pyrolyzation

The selected feedstock under study consists of organic residues derived from agricultural production systems: vine shoots, corncobs and wood pellet. They are provided by a local farm located near Udine (Italy). The sample preparation involves processes of grinding and sieving of samples to the particle size range 0.5–2.0 mm. Prior to the pyrolysis experiments, the particles were dried at 105 °C for 8 hours. Some of the raw feedstock (corn cob, wood pellets and vine shoots), are shown in Figure 6.1.



Figure 6.1: Few examples of the raw feedstock studied: a) corncob. b) wood pellets. c) vine shoots.

The prototype pyrolysis retort described in the previous chapter was filled with these different feedstocks and exposed to the concentrated sunlight. The retort as in the previous was rotating at a speed of two rotations per minute. Biomasses were introduced in the retort apparatus and pyrolyzed at temperature between 200 and 600°C. The temperature increase rate was measured to be 10°C min<sup>-1</sup>. When a temperature was reached between 100 and 127 °C, the water vapor was driven out until totally dried. The temperature was increased to the set-point, i.e. 200,300,400,500°C and was held for 2 h, as preliminary study showed that 2 h was the most appropriate time for carbonization. At the end of the process, the material inserted in the pyrolysis setup was reduced with respect to the initial mass. Since the pyrolysis process took 100 min of time, the device is able to process about 20 kg of biomass in one day (8 hours), transforming it to 6.0 kg of solar carbon.

## 6.2 Characterization of biomasses

Characterization studies are important to evaluate suitability of

feedstock for thermochemical conversion. Biomass sample and solar carbon were evaluated in relation to their devolatilization characteristics, through thermogravimetric analysis performed in TGA 500TA instruments [62]. TG analysis was carried out using N<sub>2</sub> carrier gas and subsequently air at a constant flow rate of 100cc/min. All the analyses are characterized by an isothermal step at 150°C in N<sub>2</sub> atmosphere to measure the initial moisture of specimens.

TG diagrams show weight loss with respect to temperature increase. Figure 6.2 summarizes the TGA results related to the decomposition of vine shoots in N<sub>2</sub> atmosphere and subsequently in air. Weight loss of around 9 wt% can be observed and it is related to the moisture content in the vine shoots. The decomposition of vine shoots under N<sub>2</sub> atmosphere began when the temperature reached 180°C and 77 wt% of the weight had been lost when the temperature of 900°C reached. The curve demonstrated three stages of weight lost which can be attributed to the decomposition of different constituents of vine shoots. The first stage occurred between 180°C and 355°C where 49 wt% of the weight was lost. The second stage began at 355°C and ended at 500 °C during which 62 wt% of the total weight had been lost. The last stage belongs to the temperature range of 500-900°C. The 23% of mass left is composed of refractory carbon (~14 wt%) and by ash (~9 wt%).

TGA results of corncobs decomposition in N<sub>2</sub> atmosphere are displayed in the Figure 6.3. Moisture content in the feedstock affects the weight loss of about 4 wt% observed in the TGA curve. The degradation of corncobs and volatile release started at the temperature of 250°C and ended at 900°C where total weight lost was 92wt%. The temperature increased rapidly to 500°C reaching the maximum degradation rate at 460°C. During the temperature range between 250 and 500°C the weight loss is almost of 80%, then the degradation process slows down radically to 800°C. The remained mass of 8% is consisted of refractory carbon (~1 wt%) and ash (~7 wt%).

Figure 6.4 shows TGA decomposition curve of wood pellets in N<sub>2</sub>

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atmosphere and air. Weight loss of around 6wt% occurs due to the moisture presence in the raw feedstock. The decomposition of wood pellets takes place in the temperature range between 215°C, which is an initial temperature, and 900°C which is the end temperature of pyrolysis process. The maximum temperature reached is 390°C and by the temperature of 500°C the total weight of 68wt% had been lost. During the last temperature range the total mass reduced was 84wt%. The 16wt% of mass left is composed of refractory carbon (~13 wt%) and ash (~3 wt%).

Thermogravimetric analysis indicated the thermal decomposition of lignocellulosic component and the formation of solar carbon at the end of the process. Biomass primarily consists of three constituents which are hemicelluloses, cellulose and lignin. These components pyrolyze at different rates and by different pathways. Diverse chemical structures determine different thermal stability. Cellulose and hemicellulose decompose over a narrow temperature range. Due to high molecular weight, lignin decomposes over a wider range of temperature, contributing for the formation of condensed aromatic carbon in char's structure [69].

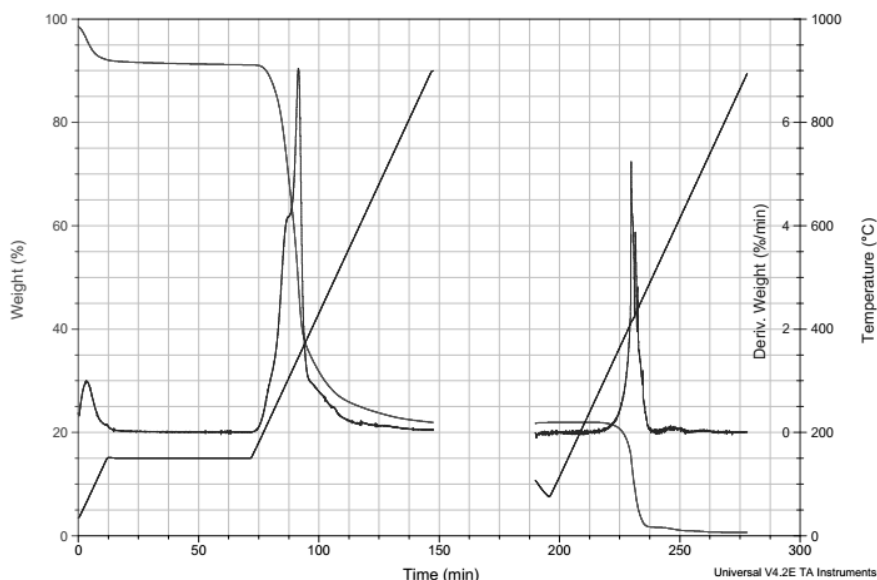


Figure 6.2: TG analysis of the vine shoots.

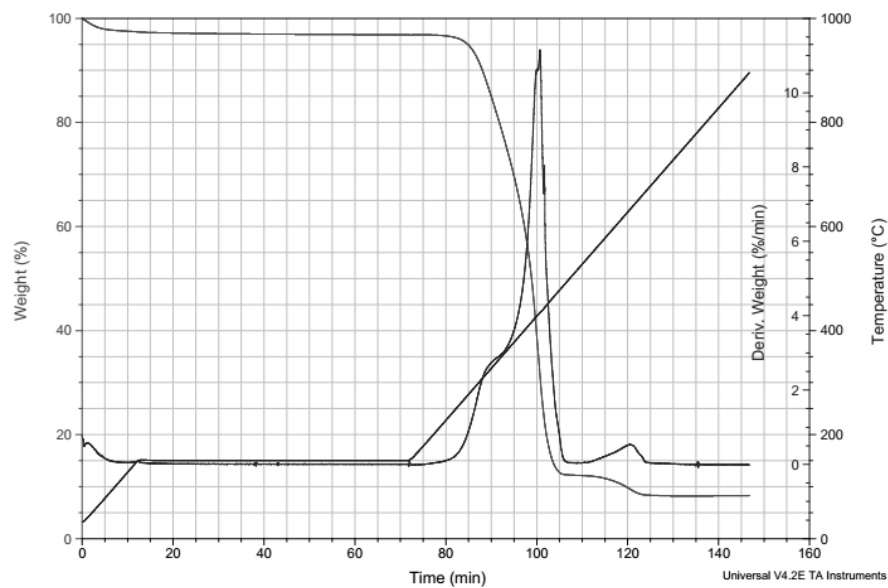


Figure 6.3: TG analysis of the corncobs.

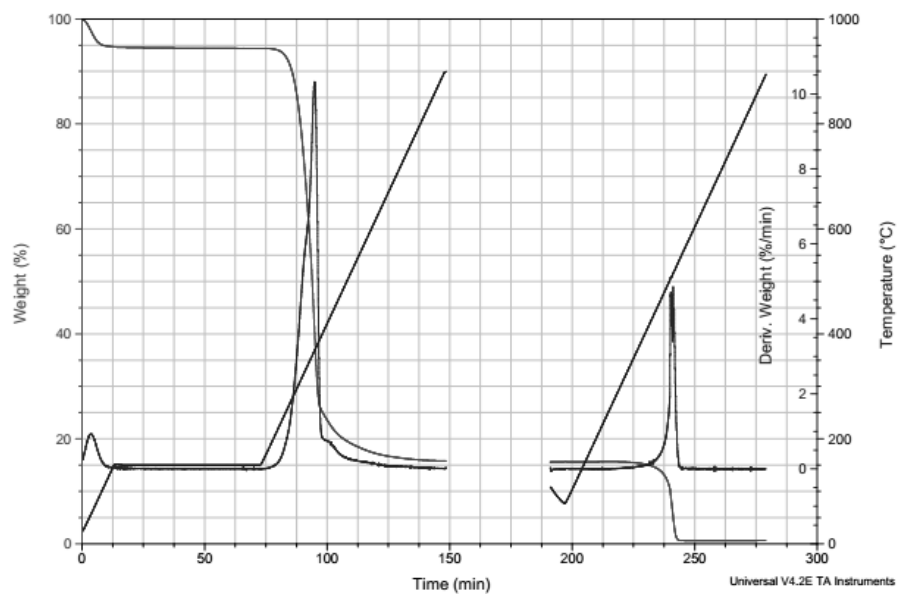


Figure 6.4: TG analysis of the wood pellets.

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## 6.3 Characterization of solar carbon

Measurement of the higher heating value (HHV) of the feedstock and of the solar carbon took place in a bomb calorimeter IKA C2000 instrument with the DIN 51900-1 standard [64]. The calorimeter operates under specified conditions for combustion processes to occur. The decomposition vessel is filled with a specific quantity of sample and after the sample has been ignited, the increase in temperature of the calorimeter system was measured. The calorific value of the sample is calculated from the weight of the sample, the heat capacity of the calorimeter system and the increase in temperature of the water within the measuring cell. The decomposition vessel is filled with pure oxygen (99.95%) in order to optimize the combustion process. The pressure of the oxygen atmosphere in the vessel was 30 bar. In addition of heat generated from the combustion of the sample, heat in the form of extraneous energy is also formed. Therefore, this effect needs to be considered in the calculation of heating value. The inaccuracy of the measurements is about 120 J/g.

Set of experiments was carried out with several samples of each feedstock in oven with a maximum operating temperature of 1050°C and isolation walls of high density ceramic fiber. The mass was measured before and after the heating and the values along are presented in the Table 6.1.

The higher heating value of solar carbon ranges between 24.5 and 28.2 MJ/kg considering the measurement of different samples in the calorimeter and non-homogeneous pyrolysis inside the retort. The values measured are significant higher than that of vine shoots (18.8 MJ/kg), corncobs (17.6 MJ/kg) and wood pellets (18 MJ/kg) and close to the HHV of fossil fuel. With temperature increase, the residual mass percentage decreases and the higher heating value (HHV) increases. These values are comparable to the corresponding values of the solar carbon in the pyrolysis experiment confirming that the temperature reached in the retort were between 350 and 500°C. The calculated residual mass (%) and HHV (MJ/kg) at three



temperatures are presented in

The elemental composition of feedstock and solar carbon was performed on a Vario EL Mod X (Vario Inc, USA) and it is summarized in the Table 6.3, Table 6.4 and Table 6.5.

The content of carbon, hydrogen, nitrogen, and sulfur (wt%) was directly determined in the samples, while oxygen content was calculated by subtraction from 100% the amount of C, H, N and ash. The oxygen content was estimated by mass difference, i.e. by subtracting from 100% the amount of C, H, N and ash [62]. The char elemental composition was used to calculate the H/C and O/C ratios.

With temperature increase, there was rapid growth of carbon content while the hydrogen and oxygen contents reduced sharply. The carbon content increase with temperature most likely originated from the carbonaceous structure graphitization at high temperatures. High pyrolysis temperature causes a higher degree of polymerization, leading to a more condensed carbon structure in the biochar. The higher the content of aromatic structures is, the greater the resistance of the biochar to microbial degradation [70]. Decrease in hydrogen and oxygen contents correspond to the cracking and cleavage of weaker bonds within char's structure, particularly at higher temperature [71]. Decrease in H/C and O/C ratios with increase in temperature and char became increasingly more carbonaceous in nature at a high temperature. The low ratios indicate increased aromaticity and a lower hydrophilic tendency. An increased aromatic character of biochars is related to dehydration reactions and elimination of O and H functional groups, as well as the creation of aromatic structures since charring is intensified. Ash contents increased with an increase in pyrolysis temperature. The elemental analysis of biochar at three temperatures (200,300, 400 and 500 °C) showed high ash content as temperature increased, probably due to large amount of inorganic compounds (K, P, Ca, and Mg) which accumulated after volatilization of C, O, and H compounds [70].

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### 6.3.1 pH measurement

Measurements of pH values for each feedstock at different temperatures are presented in the Table 6.6. The pH value was measured in 1:20 w/v ratio in either H<sub>2</sub>O or 1N KCl solution. The pH value in 1N KCl presents the potential pH, since high ionic KCl solution could release exchangeable protons of biomass into solution (Cheng&Lehmann, 2009) [72].

The water of the biochars is slightly acidic to alkaline and the pH values are higher than 6.0 units. Increase in pH has been observed with temperature increase and this can be explained by the effect of the temperature on the release of volatile matter. Volatiles are composed of acid functional groups and concentrate ash contents, consequently elevate the pH [73]. It is also believed that an increased temperature causes an enrichment of basic cations in the ashes, which may be related to alkaline species such as carbonates, oxides and hydroxides and a decrease in the concentration of acidic surface functional groups. However, pH values are comparable with values found in literature and increased with higher pyrolysis temperature [70].

### 6.3.2 SEM analysis

The shape and the size of the char particles, as well as porous surface structure, were characterized by Scanning electron microscopy (SEM). Scanning electron microscopy (SEM) images were obtained with a EVO-40 XPP (Zeiss) microscope equipped with an energy-dispersive X-ray detector (EDX), at 5-10 KV. The material is characterized by oblong channels of 5-10  $\mu\text{m}$  of diameter and small pores (2-3  $\mu\text{m}$ ) distributed throughout the surface. Based on the aforementioned results and the categorization proposed by Keiluweit, Nico, Johnson and Kleber [67], we classified the charcoal obtained via solar pyrolysis as a mixture of transition and amorphous chars, in which the structure of biomass is partially preserved and in part altered by the

heating process (Figure 6.5, Figure 6.6, Figure 6.7).

The surface area of biochar may strongly influence the reactivity and combustion behavior of the biochar. At higher temperature, the devolatilization is more severe making the biochar more porous. At the temperature of 400°C, it is expected that the biochar particles are thick walled and covered by tar agglomerates, while the biochar particles obtained at pyrolysis temperature of 600 °C create the hollow, highly porous and mostly spherical particles. The particles are very fragile and thin walled. The quick release of volatiles during pyrolysis produces significant internal overpressure and the coalescence a more open structure. In general, SEM porosity increases with a pyrolysis temperature increase. Pyrolysis temperature affects the size and shape of particle through a general increase in size and amount of voids and a decrease in cell wall thickness [74].

### **6.3.3 TPO analysis**

Temperature programmed oxidation (TPO) was carried out over 4 mg of solar carbon in a home-made equipment under 10 v% O<sub>2</sub> in He flow (500 cc/min) at a heating ramp of 10 °C/min up to 800 °C. The combustion products were monitored with a FT-IR multi gas analyzer (Multi-Gas 2030, MKS Instruments). The combustion of the solar charcoal was investigated with a temperature programmed oxidation (TPO) experiment in airflow. Figure 6.9 shows that the combustion of this material occurs in the range of 200-500 °C, producing mainly CO<sub>2</sub>, and CO. The profile of combustion is complex with at least three components at 320, 400 and 450 °C. The component at lower temperature can be attributed to the combustion of volatile part of charcoal while the components at higher temperature are related to the combustion of non-volatile components (polyaromatics from lignin and refractory char formed during the process of pyrolysis).

TG analysis of solar charcoal in N<sub>2</sub> atmosphere (Figure 6.9) shows that at the end of the process the charcoal still contains 30 wt% of volatiles while the fixed carbon is in the order of 60 wt%. Biomass decomposition

normally occurs during the temperature range of 200–400 °C, which is responsible for the main degradation of biomass. Decomposition of hemicellulose mainly occurs between 250 and 350 °C, followed by cellulose decomposition, which mostly takes place between 325 and 400 °C. Lignin, the most stable component, decomposes at higher temperature range of 300–550 °C [75]. The temperature of around 500 °C the thermal pyrolysis of biomass should be sufficiently high for complete decomposition of it. It could be inferred that the temperature reached inside the pyrolyzer was on average lower than that measured at its outer walls resulting in incomplete pyrolysis. This can be related to a non-homogeneous temperature profile inside the retort, despite temperature of 500 °C can be reached. However, the outcome of the tests is promising as the concept of solar pyrolysis is still at the research stage and some improvements can be done to optimize the heat transfer from the outer walls to the inside of retort and regulate the temperature of process.

Table 6.1: The initial and residual mass of vine shoots, corncobs and wood pellets in the pyrolysis experiments.

<b>Feedstock</b>	<b>Temperature (°C)</b>	<b>Initial mass (g)</b>	<b>Residual mass (g)</b>
<b>Vine shoots</b>	200±10	252.4	161.5
	300±10	255.2	83.4
	400±10	248.3	64.9
	500±10	251.6	56.0
<b>Corncoobs</b>	200±10	654.8	406.0
	300±10	632.3	236.1
	400±10	704.2	210.2
	500±10	614.1	138.0
<b>Wood pellets</b>	200±10	58.4	39.7
	300±10	56.2	22.1
	400±10	54.2	14.2
	500±10	58.6	15.7

Table 6.2: Results of residual mass in percentage and higher heating value (HHV) of each feedstock.

<b>Feedstock</b>	<b>Temperature (°C)</b>	<b>% residual mass</b>	<b>HHV (MJ/kg)</b>
<b>Vine shoots</b>	200±10	64±1	19.4±0.1
	300±10	33±1	24.9±0.1
	400±10	26±1	26.3±0.1
	500±10	23±1	27.9±0.1
<b>Corncobs</b>	200±10	62±1	18.8±0.1
	300±10	37±1	23.8±0.1
	400±10	30±1	26.9±0.1
	500±10	22±1	29.2±0.1
<b>Wood pellets</b>	200±10	68±1	18.2±0.1
	300±10	39±1	24.5±0.1
	400±10	26±1	27.0±0.1
	500±10	27±1	29.4±0.1

Table 6.3: Characterization of vine shoots at different temperature and solar carbon obtained through solar pyrolysis with Linear Mirror II.

<b>Parameters (wt%)</b>	<b>Vine shoot</b>				<b>Solar carbon</b>
	200°C	300°C	400°C	500°C	
<b>Carbon</b>	62±1	69±1	73±1	80±1	70±1
<b>Hydrogen</b>	5.2±0.1	4.7±0.1	3.6±0.1	2.9±0.1	3.5±0.1
<b>Nitrogen</b>	1.2±0.1	1.0±0.1	0.8±0.1	0.8±0.1	0.8±0.1
<b>Oxygen</b>	24±1	19±1	15±1	7.0±1	15±1
<b>Ash</b>	5.2±1	5.9±1	7.5±1	8.7±1	10.5±0.1
<b>O/C (molar ratio)</b>	0.3	0.2	0.2	0.1	0.2
<b>H/C (molar ratio)</b>	1.0	0.8	0.6	0.4	0.6

Table 6.4: Characterization of corncobs at different temperature and solar carbon obtained through solar pyrolysis with Linear Mirror II.

<b>Parameters (wt%)</b>	<b>Corncob</b>				<b>Solar carbon</b>
	200°C	300°C	400°C	500°C	
<b>Carbon</b>	55±1	61±1	68±1	74±1	70±1
<b>Hydrogen</b>	2.2±0.1	2.6±0.1	2.5±0.1	2.0±0.1	3.5±0.1
<b>Nitrogen</b>	0.8±0.1	0.9±0.1	0.8±0.1	0.8±0.1	0.8±0.1
<b>Oxygen</b>	35±1	32±1	25±1	17±1	15±1
<b>Ash</b>	3.9±1	4.1±1	4.2±1	6.6±1	10.5±0.1
<b>O/C (molar ratio)</b>	0.5	0.4	0.3	0.2	0.2
<b>H/C (molar ratio)</b>	0.5	0.5	0.4	0.3	0.6

Table 6.5: Characterization of corncobs at different temperature and solar carbon obtained through solar pyrolysis with Linear Mirror II.

<b>Parameters (wt%)</b>	<b>Wood pellet</b>				<b>Solar carbon</b>
	200°C	300°C	400°C	500°C	
<b>Carbon</b>	62±1	68±1	75±1	85±1	70±1
<b>Hydrogen</b>	4.2±0.1	4.3±0.1	3.8±0.1	3.4±0.1	3.5±0.1
<b>Nitrogen</b>	0.2±0.1	0.2±0.1	0.1±0.1	0.1±0.1	0.8±0.1
<b>Oxygen</b>	28±1	25±1	19±1	8±1	15±1
<b>Ash</b>	2.4±1	2.2±1	2.4±1	3.3±1	10.5±0.1
<b>O/C (molar ratio)</b>	0.3	0.3	0.2	0.1	0.2
<b>H/C (molar ratio)</b>	0.8	0.7	0.6	0.5	0.6

Table 6.6: pH measurement of feedstock at three different temperatures.

<b>Feedstock</b>	<b>Temperature (°C)</b>	<b>pH value</b>
<b>Vine shoots</b>	200	6.52
	300	6.79
	400	7.14
	500	9.34
<b>Corncoobs</b>	200	6.42
	300	6.62
	400	7.01
	500	9.56
<b>Wood pellets</b>	200	5.40
	300	5.85
	400	6.43
	500	7.23

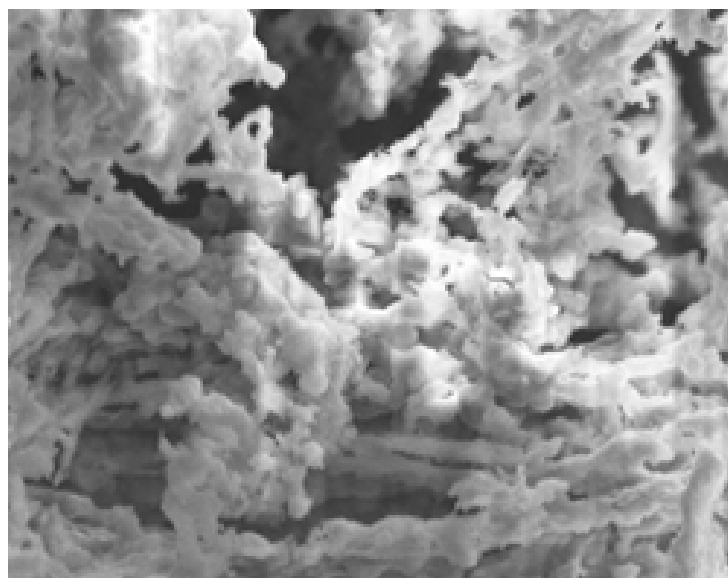


Figure 6.5: SEM photograph of vine shoots at pyrolysis temperature of 400°C.

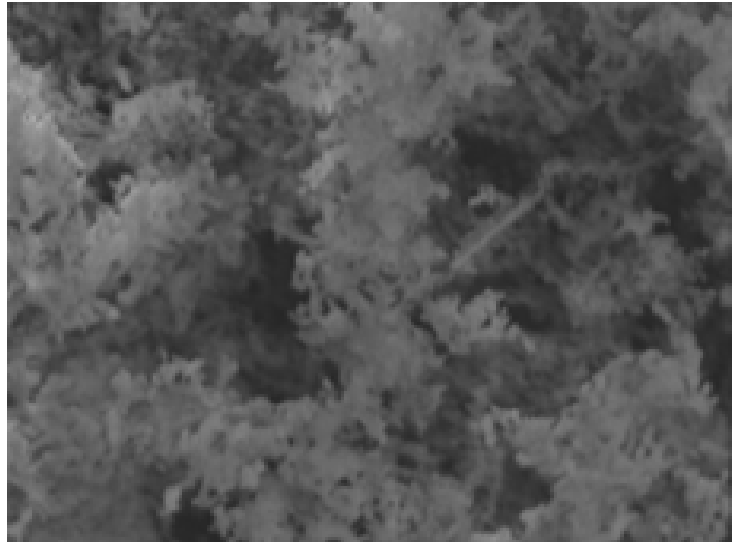


Figure 6.6: SEM photograph of the corncocks at pyrolysis temperature of 400°C.



Figure 6.7: SEM photograph of the wood pellets at pyrolysis temperature of 400°C.



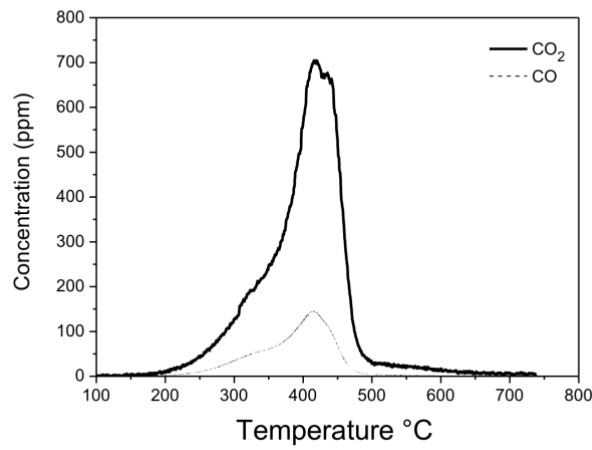


Figure 6.8: TPO profiles of the charcoal obtained via solar pyrolysis.

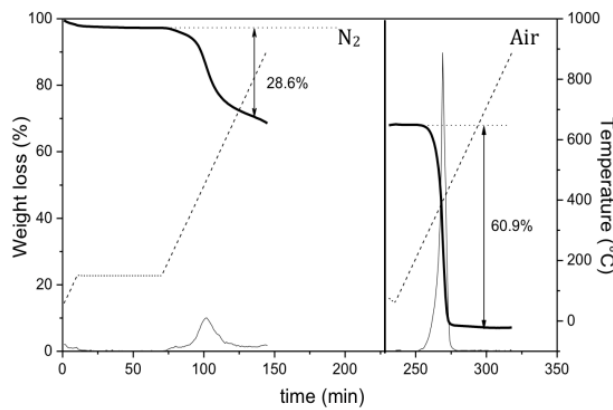


Figure 6.9: TG analysis of charcoal obtained via solar pyrolysis.

## 6.4 Further analysis

Measurements of other feedstocks at different temperatures are presented in the Table 6.7 and results of residual mass in percentage and higher heating value (HHV) of each feedstock are shown in Table 6.8. The full characterization of these feedstocks is currently under investigation.

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Table 6.7: The initial and residual mass of hay, tomato peat and wood pellets in the pyrolysis experiments.

<b>Feedstock</b>	<b>Temperature (°C)</b>	<b>Initial mass (g)</b>	<b>Residual mass (g)</b>
<b>Hay</b>	200	240.3	177.8
	300	265.4	92.9
	400	239.8	71.9
	500	241.7	41.1
<b>Tomato peat</b>	200	625.4	424.3
	300	622.5	242.8
	400	684.2	177.9
	500	624.4	156.1
<b>Branches</b>	200	745.2	536.5
	300	764.5	260.0
	400	740.6	214.8
	500	782.4	140.8

Table 6.8: Results of residual mass in percentage and higher heating value (HHV) of each feedstock.

<b>Feedstock</b>	<b>Temperature (°C)</b>	<b>% residual mass</b>	<b>HHV (MJ/kg)</b>
<b>Hay</b>	200±10	74±1	16.9±0.1
	300±10	35±1	19.7±0.1
	400±10	30±1	21.9±0.1
	500±10	17±1	23.0±0.1
<b>Tomato peat</b>	200±10	68±1	15.8±0.1
	300±10	39±1	18.2±0.1
	400±10	26±1	20.9±0.1
	500±10	25±1	22.8±0.1
<b>Branches</b>	200±10	72±1	16.8±0.1
	300±10	34±1	20.2±0.1
	400±10	29±1	23.8±0.1
	500±10	18±1	24.8±0.1

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# Chapter 7

## Conclusions and Outlook

The world's growing energy demand led to the continuous use of fossil fuel-based energy sources, which became challenging with respect to the reduction of fossil fuel reserves, greenhouse gas emissions and other environmental concerns, geopolitical and military disagreements, as well as the constant fuel price variations. These challenges can be addressed using renewable energy sources that are the best alternative to the fossil fuels. In this thesis, a new way of producing charcoal from biomasses has been investigated: vine shoots, corncobs and wood pellets are a plentiful waste material that can be exploited, also in the FVG region, as an energy source.

The innovative solar system Linear Mirror II, developed by Isomorph srl at the University of Udine, concentrates solar energy on a focal area of rectangular shape, which does not move its position with time and which is close to the ground. It has successfully been used in this thesis for pyrolysis of agricultural and forestry biomass, with a prototype setup which I contributed to realize, and the results of the test have been published. In this preliminary study, the Linear Mirror II was combined with a rotator kiln to transform certain amounts of biomass into charcoal in about two hours. Assuming eight lighted hours of operation per day, the conversion of 20 kg of vine shoots, corncobs and wood pellets per day is equivalent to 48, 47 and 50 kWh,

respectively [68].

A new protocol and method to identify agriculture feedstocks useful for solar pyrolysis has been designed. Vine shoots, corncobs and wood pellets are a plentiful waste material that can be exploited, mainly as an energy source. When vine shoots, corncobs and wood pellets were pyrolyzed in solar driven process, the quantity of biomass volatilized was 77, 92 and 84 wt%, respectively. Most of this energy is stored in the resulting carbon and in the pyrolysis gases, i.e. in products with a higher energy density than the initial biomass. These products can be stored for long period of time without losses.

The original purpose was to study the HHV of various pyrolyzed samples at different temperature to understand the correlation between pyrolyzation and temperature. We found that solar carbon heated to high temperatures has an energy content which is about as high as that of fossil coal.

However, since the determination of HHV is not enough to select a particular feedstock as a good feedstock for solar pyrolysis and to understand better the thermal decomposition of lignocellulosic component, a detailed thermogravimetric analysis of all the samples has been conducted.

The TG diagrams obtained show weight loss with respect to temperature increase and present a proof of the formation of a carbon (solar carbon) at the end of the process. The results triggered an even deeper analysis, in order to obtain a full chemical characterization. For this reason, a full elemental analysis of solar carbon at four temperatures (200, 300, 400 and 500 °C) has been carried out.

Results show that the carbon content increases with temperature most likely caused by the carbonaceous structure graphitization at high temperatures and by the fact that high pyrolysis temperature causes a higher degree of polymerization, leading to a more condensed carbon structure in the feedstock.

Since the surface area of this pyrolyzed feedstock may strongly influence the reactivity and combustion behavior of the carbon I carried out

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SEM, pH, ash and TPO analysis to verify that.

The results show that the SEM porosity increases as the pyrolysis temperature increases: pyrolysis temperature affects the size and shape of particle through a general increase in size and amount of voids and a decrease in cell wall thickness. At higher temperature, the volatilization is more severe making the solar carbon more porous.

This porous (and graphitic) structure and chemical composition suggest that solar carbon produced as activated carbon could be a very versatile material also for catalysis. Activated carbon also enhances soil fertility and allows a more sustainable use of some soils.

All in all, the properties studied in this thesis prove there is no fundamental difference between fossil coal and solar carbon in practical applications. These very good results encourage a further study of the graphitic properties of these solar carbons. This full characterization of solar pyrolysis products was not yet available in literature and is another element of originality of this thesis.

Pyrolytic processes completely solar-driven could become a promising method for producing solar fuels because of their potential for converting limitless amounts of solar energy into chemical energy. This substitution of traditional fossil fuels would not require additional complex technologies as the Linear Mirror II is a simple and scalable system. Optimization of the system will be the focus of further studies.

We also find, that distinct biomasses, which have quite different energy contents and in particular combustion qualities in their natural states, and which even may not combust at all (like green grass and hay), become increasingly similar to each other with increased heating temperature. This is a necessary pre-condition for the creation of industrial processes, based on these new materials.

Solar carbon is also a new way of storing solar energy for long periods of time, and without losses [48], contributing in the diffusion of solar energy at northern latitudes as FVG region.

## 7.1 Outlook

Using solar energy for heating biomass is not only ecological, but it has also advantages from an industrial point of view, since it is not dependent on the properties of this biomass. This allows potentially for an industrialization of this process, which has been performed only as a scientific experiment up to now. To actually perform this industrialization should be a high priority for future research.

Also, the applications of industrially produced solar carbon seems to be very promising. Besides the obvious use in combustion facilities (for instance in power plants), solar carbon should also be useful for producing gas in a gasifier, similar to how town gas has been produced some decades ago. Furthermore, it should be possible to use solar carbon as starting material for a Fischer-Tropsch process, or similar processes, in order to produce CO<sub>2</sub> neutral liquid fuels.

Many attempts have been made to convert biomass to liquid fuel in the past (for instance, the CHOREN project in Germany) [6], and these attempts have not been successful. The likely reason for the failure of these enterprises might be the fact, that it was tried to perform the transformation of biomass to liquid fuels in one single step, in "one machine". It clearly would be much easier, to make use of solar carbon, instead of green material. After having laid the scientific foundations for this new kind of solar industry, those and other industrial applications must be developed next. At the University of Udine our activities have helped to create a center dedicated to the renewables in the form of the school SIER (see Appendix A)- SIER would be the ideal means of maintaining the close contact between industrial development and scientific research which is needed for advancing this new field in a competitive way.

As a first step, one would need to study how to combust solar carbon or roasted biomass. For instance, the fragile constitution of solar straw may cause problems for combusting it in traditional furnaces. Up to now, there is

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no engineering knowledge and no experiments have been performed on this important issue.

Based on the research presented in this thesis, Italy could take a leadership in the reduction of CO<sub>2</sub>, based not exclusively on incentives (only in an initial phase these would be needed), but on new technologies.

And FVG could take a leadership position within Italy in this exciting and economically important field, with the University of Udine working in close connection to the agrarian and industrial sectors in the region.



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[77]"Thermocouples," [Online]. Available: <https://www.allaboutcircuits.com/textbook/direct-current/chpt-9/thermocouples/>.

[78]"Thermocouple amplifier," [Online]. Available: <https://www.adafruit.com/product/269>.

# **Appendix A**

## **SIER-Scuola di introduzione alle energie rinnovabili**

SIER is a one week basic training course named “Introductory school on renewable energy” organized by The University of Udine, University of Trieste and ICTP organize. The course is addressed primarily to participants selected among university students. Director and promoter of the school is Prof. Marina Cobal but I contributed since the very beginning in the preparation and running of the school.

### **A.1 Scope of the SIER**

This one week school aims to introduce students to the many aspects of renewable energies and of their development in response to today's climate and energy issues. Students will explore and discuss the technologies and their implications with industry experts operating in the region, learn about the various technologies involved in the development of renewable energies and their economic potential - both in urban and rural settings. The course should provide participants with a structured overview of the different sources of renewable energy: how they can be exploited and used for the production of energy in the form of electricity, heat and cold.

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## **A.2 SIER Training and topics**

The school is equipped with several laboratories to see up close some of the topics covered: pyrolysis plants, solar, photovoltaics, biomasses, stirling engines, etc. ...

The course foresees lectures on the main technical, regulatory and financial features given by qualified experts, academics and highly skilled technicians, matched with visit to laboratories and power plants.

The training is structured to favor the exchange of experiences among participants by means of their direct involvement through fruitful interaction in group study activities.

### **Principal topics:**

- Energy Policy
- Renewable energy
- Solar photovoltaics
- Solar thermal for heating
- Eolic and geothermic energy
- Bioenergy and biomasses
- Hydropower
- Grid integration of renewable energy sources
- Excursion - Visit to local systems of renewable energies

## **A.3 SIER in figures**

### **Participants:**

- I Edition 2015 26 participants
- II Edition 2016 19 participants



- II Edition 2017 18 participants

**Scientific Committee:**

- Prof.ssa Marina Cobal (Director - UniUd)
- Prof. Paolo Giannozzi (Vice Director - UniUd)
- Prof.ssa Marta Boaro (UniUd)
- Prof. Pietro Giannatasio (UniTs)
- Prof. Alessandro Massi Pavan (UniTs)
- Prof. Sandro Scandolo (ICTP)
- Prof. Andrea Vacchi (UniUd)
- Prof. Vanni Lughì (UniTs)

**Organizing Committee:**

- Prof. Marta Boaro (UniUd)
- Dr. Marco Citossi (UniUd)
- Prof. Marina Cobal (UniUd)
- Prof. Paolo Giannozzi (UniUd)
- Prof. Gilberto Giugliarelli (UniUd)
- Dr. Filippo Pascolo (UniUd)
- Prof. Piero Pinamonti (UniUd)
- Dr. Andrea Pizzariello (UniUd)

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# Appendix B

## BeagleBoneBlack source code and interfacing system

The Beagle Bone Black is a great improvement since it allows to go from microcontrollers (examples being: AVR, PIC, ARM Cortex M3, 8051, Propeller, and many more.) to microcomputers. A microcomputer has the FLASH, EEPROM, RAM etc. separated like any other classical computer like a desktop or laptop. Microcontrollers, differently, has these parts assembled on one chip [76].

The main processor core of a Beagle Bone Black runs at 700MHz and a chunk of 256M DDR RAM. It has a main storage which is permanently made on a micro-SD card. All this makes it a great machine able to run major programs like Linux, Python, a webserver, FTP clients, SSH, and many more.

The Beagle Bone Black also is comprised of built-in accessories. Examples are; onboard Ethernet with 10/100M connectivity, JTAG debugger that can be used for advanced hacking, mini USB port with TTL serial converter, power management IC that is responsible for keeping the board safe from unplugged adapter, USB host port used for connecting a hub/ Wi-Fi/etc. and tons of 0.1 inch spaced break outs.

Another major powerful ability of the Beagle Bone Black is that it is made up of I2C, SPI and GPIO at a hobbyist-friendly 3.3 V level instead of the 1.8V which is much more difficult to connect and it can also run more complex programs such as the webserver.

## **B.1 Thermocouple Amplifier breakout board**

Thermocouples are very high sensitive devices that require great thermocouple amplifier with a reference junction compensation [77]. The major purpose of a thermocouple amplifier in this set up is to act as a connection between the thermocouple and the Beagle Bone Black. Many thermocouple amplifiers are influenced by the ranges, properties, controller type, etc. examples of the thermocouple amplifiers include; MAX31855, MAX6675, MAX31856, MAX31850. MAX31855 (se Figure B.1) and MAX31855K are examples of an extensive range of properties [78]

### **Properties of MAX31855 and MAX31855K**

1. Easy connection/interfacing with any available microcontroller including the ones that lack an analog input.
2. The constituents of the breakout board are; the chip, level shifting circuitry and 3.3 V regulator containing 10uF bypass capacitor. All these parts are usually assembled and tested.
3. These thermocouple amplifiers have a 2 pin terminal block whose main purpose is to connect to the thermocouple. It also comes with a pin header that is just plugged into any breadboard.
4. These amplifiers can measure wide temperature ranges.

---

## MAX 31855 FRONT VIEW    MAX31855 BACK VIEW

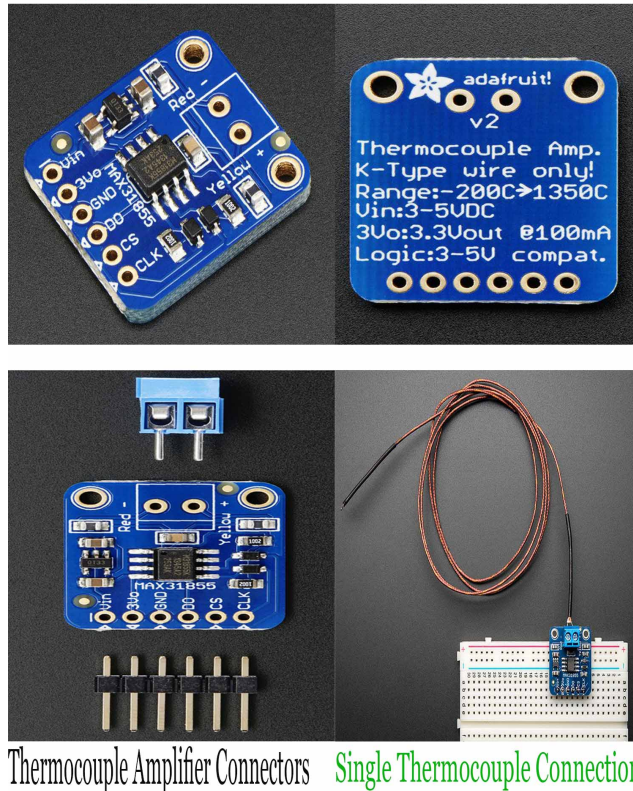


Figure B.1 Front and Back view of MAX31855 Amplifier.

## B.2 Beagle Bone Black interface with thermocouples.

The procedure steps which brought to interfacing the Beagle Bone Black to the thermocouples are listed in the following:

1. Installation of the Beagle Bone Black.  
The installation procedure was extracted from this link (<https://learn.adafruit.com/beaglebone-black-installing-operating-systems?view=all>) based on the operating system to be used.
2. Connecting the three devices, Beagle Bone Black and the two thermocouple amplifiers together required the use of Software SPI and the following procedure was followed (see Figure B.2).

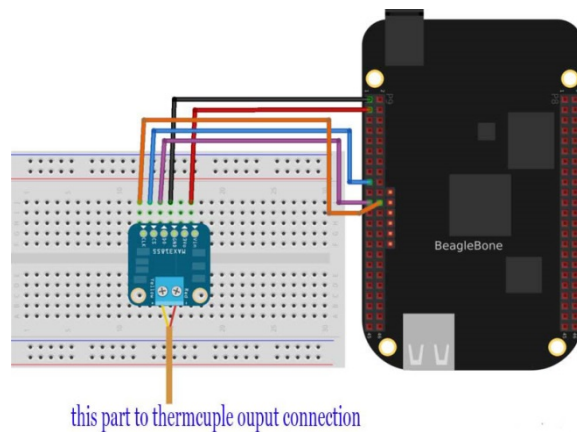


Figure B.2 Thermocouple output connection.

- Beagle Bone Black P9\_1 DGND was connected to MAX31855 GND.
- Beagle Bone Black P9\_3 3.3V was connected to MAX31855 Vin.
- Beagle Bone Black P9\_22 SPIo CLK was connected to MAX31855 CLK.
- Beagle Bone Black P9\_17 SPIo CS was connected to MAX31855 CS.
- Beagle Bone Black P9\_21 SPIo MISO was connected to MAX31855 DO.

In the procedure described above, the wiring done adopts a hardware SPI connection on the Beagle Bone Black and to be more specific, **/dev/spidev1.0**. A tree overlay was enabled in order to turn the SPI pins ability to function just before using the SPI device interface. This is achieved by configuration of the Beagle Bone Black to automatically load the tree overlay.

The file uEnv.txt, found on the drive 'boot', was edited after the Beagle Bone Black was interfaced to the computer via USB by adding:

**optargs=capemgr.enable\_partno=BB-SPIDEV0**

The files with the following name appear after the device was been reboot **/dev/spidev1.0** and **/dev/spidev1.1**

---

## B.3 Source code

Steps that were followed during the installation of MAX31855 Python library are: Through a wireless connection or use of Ethernet, the board was connected to the internet to successfully download dependencies.

**By execution of the codes below in blocks, the dependencies were installed.**

```
1. sudo apt-get update
2. sudo apt-get install build-essential python-dev python-pip python-smbus
   git
```

On a Beagle Bone Black the line of code below was executed to make sure the Adafruit\_BBIO library was installed:

```
1. sudo pip install Adafruit\_BBIO
```

The code below was used to configure the connection with the MAX31855 board:

```
1. # software or hardware SPI.
2.
3. # Software SPI configuration.
4. CLK = 25
5. CS = 24
6. DO = 18
7. sensor = MAX31855.MAX31855(CLK, CS, DO)
8.
9. # Hardware SPI configuration.
10. #SPI_PORT = 0
11. #SPI_DEVICE = 0
12. #sensor = MAX31855.MAX31855(spi=SPI.SpiDev(SPI_PORT,
    SPI_DEVICE, max_speed_hz=5000000))
13.
14. # BeagleBone Black software SPI configuration.
```

```

15. #CLK = 'P9_12'
16. #CS = 'P9_15'
17. #DO = 'P9_23'
18. #sensor = MAX31855.MAX31855(CLK, CS, DO)
19.
20. # BeagleBone Black hardware SPI configuration.
21. #SPI_PORT = 1
22. #SPI_DEVICE = 0
23. #sensor = MAX31855.MAX31855(spi=SPI.SpiDev(SPI_PORT,
    SPI_DEVICE, max_speed_hz=5000000))

```

At end of the previous configuration, the thermocouple and internal temperature displayed every second:

```

1. Press Ctrl-C to quit.
2. Thermocouple Temperature: 22.000°C / 71.600°F
3. Internal Temperature: 23.312°C / 73.963°F
4. Thermocouple Temperature: 22.250°C / 72.050°F
5. Internal Temperature: 23.375°C / 74.075°F
6. Thermocouple Temperature: 27.500°C / 81.500°F
7. Internal Temperature: 23.312°C / 73.963°F
8. ...

```

```

1. import Adafruit_MAX31855.MAX31855 as MAX31855

```

Importing the MAX31855 module with a Python import statement.

```

1. # Uncomment one of the blocks of code below to configure your BBB to
    use
2. # software or hardware SPI.
3.
4. # Software SPI configuration.
5. CLK = 25
6. CS = 24
7. DO = 18
8. sensor = MAX31855.MAX31855(CLK, CS, DO)
9.
10. # Hardware SPI configuration.
11. #SPI_PORT = 0

```

---

```

12. #SPI_DEVICE = 0
13. #sensor      =      MAX31855.MAX31855(spi=SPI.SpiDev(SPI_PORT,
    SPI_DEVICE, max_speed_hz=5000000))
14.
15. # BeagleBone Black software SPI configuration.
16. #CLK = 'P9_12'
17. #CS = 'P9_15'
18. #DO = 'P9_23'
19. #sensor = MAX31855.MAX31855(CLK, CS, DO)
20.
21. # BeagleBone Black hardware SPI configuration.
22. #SPI_PORT = 1
23. #SPI_DEVICE = 0
24. #sensor      =      MAX31855.MAX31855(spi=SPI.SpiDev(SPI_PORT,
    SPI_DEVICE, max_speed_hz=5000000))

```

Configuring the software SPI is done by either passing explicit CLK, DS, and DO digital GPIO pins, or by passing a SpiDev hardware SPI object to the MAX31855 class initializer.

```

1. # Loop printing measurements every second.
2. print 'Press Ctrl-C to quit.'
3. while True:
4.     temp = sensor.readTempC()
5.     internal = sensor.readInternalC()
6.     print      'Thermocouple      Temperature:      {0:0.3F}*C      /
    {1:0.3F}*F'.format(temp, c_to_f(temp))
7.     print      '                Internal  Temperature:  {0:0.3F}*C      /
    {1:0.3F}*F'.format(internal, c_to_f(internal))
8.     time.sleep(1.0)

```

Finally the example enters a loop where it reads temperature measurements and prints them out every second. Two of the most important things to be noted are the temperature measurements functions readInternalC() and readTempC(). the function readInternalC() reads the internal temperature to the MAX31855 chip while the function readTempC() reads the thermocouple probe temperature.



```

1 import Adafruit_BBIO.ADC as ADC
2 import time
3 import datetime
4 import Adafruit_MAX31855.MAX31855 as MAX31855
5
6 # BeagleBone Black software SPI configuration.
7 CLK = 'P9_12'
8 CS = 'P9_15'
9 DO = 'P9_23'
10 sensor = MAX31855.MAX31855(CLK, CS, DO)
11
12 sensor_pin = 'P9_40'
13 now = datetime.datetime.now()
14 dayexperiment = str(now.day)+str(now.month)+str(now.year)
15
16 myfilename = "myData"+dayexperiment+".dat"
17
18 index = 0
19 count = 1
20
21 timestep = 10
22
23 ADC.setup()
24
25 with open(myfilename,'w') as file:
26     file.write('#Index Time IR TK TKI')
27     while True:
28         reading = ADC.read(sensor_pin)
29         millivolts = 2.94*10*(reading)
30         tempIR_c = 10*(millivolts)
31         tempIR_f = (tempIR_c * 9/5) + 32
32         tempTK = sensor.readTempC()
33         tempTKinternal = sensor.readInternalC()
34
35         print ('lettura da IR')
36         print('C=%f' % (tempIR_c))
37
38         print 'Thermocouple Temperature: {0:0.3F}*C'.format(tempTK)
39         print 'Internal Temperature: {0:0.3F}*C'.format(tempTKinternal)
40     now = datetime.datetime.now()
41     file.write('\n'+str(index))
42     file.write(' '+str(now.hour)+' '+str(now.minute)+' '+str(now.second)+' '+str(tempIR_c)+' '+str(tempTK)+' '+str(tempTKinternal))
43
44     index +=1
45     time.sleep(timestep)

```

```

9. # Loop printing measurements every second.
10. print 'Press Ctrl-C to quit.'
11. while True:
12.     temp = sensor.readTempC()
13.     internal = sensor.readInternalC()
14.     print 'Thermocouple Temperature: {0:0.3F}*C /
15.     {1:0.3F}*F'.format(temp, c_to_f(temp))
16.     print 'Internal Temperature: {0:0.3F}*C /
17.     {1:0.3F}*F'.format(internal, c_to_f(internal))
18.     time.sleep(1.0)

```

---