Slow pyrolysis in a rotary kiln reactor: Optimization and experiment

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SLOW PYROLYSIS IN A ROTARY KILN REACTOR: OPTIMIZATION AND EXPERIMENTS

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A 30 credit units Master's thesis

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ABSTRACT

Biomass is the fourth largest source of energy worldwide after coal, oil and natural gas. Among the various technologies encompassing biomass energy conversion, some may be considered to have reached a level of technological development which allows use on an industrial scale while others require further testing to increase yields and reduce costs of energy conversion and management. The thermochemic conversion of biomass (pyrolysis, gasification, combustion) represents the most promising technique for energy production.

In this context fits the application of the process of slow pyrolysis of biomass in a rotary kiln reactor with an integrated gas burner of small size for a continuous production of syngas. The objectives of this work are:

- To run a micropyrolyser in a rotary kiln reactor which was out of use for several years
- To connect the micropyrolyser with a gas burner for determination of produced and exhaust gases
- To run the pyrolyser in a continuous way for continuous production of syngas.
- To determine biomass mass flow and mass and energy balance of the system
- To perform Proximate and Ultimate analyses of initial biomass and produced char and tar with a gas chromatographer to determine LHV of syngas

Two tests were performed during the course of this thesis work: A drying test of biomass and a pyrolysis test with a direct combustion of the produced syngas inside a gas burner. An analyzed sample of a gas mixture indicated a lower calorific value of 2,86 MJ/kg of the syngas due to the intake of a considerable amount of ambient air and unintentional leaks and loose-fitting seals. Theoretically, if an anaerobic environment could be achieved inside the micropyrolyser, the produced syngas would have the calorific value of 12,79 MJ/kg, a figure that can also be found in literature. To increase the calorific value of continuously produced gas in a micropyrolyser, the sealing system should be improved.

The work was conducted on a micropyrolyzer located in a pilot plant at the Department of Industrial Engineering, Faculty of Engineering at the University of Perugia, Italy.

SUMMARY

Utilization of biomass energy is, so far, limited to large-scale energy production, while small-scale production tends to be technically immature with high installation costs. The construction of facilities for small-size production with high efficiency based on mass production integrated with a gas microturbine or an internal combustion engine could, from this point of view, represent a possible way of biomass energy convertion.

Energy conversion on a small scale certainly has a smaller environmental impact because it can benefit from the local availability of biomass and decentralization of energy sources. With reduced energy losses along the distribution lines and *in situ* production of electricity, isolated communities could benefit from it.

In this context, a demonstration plant with a micro pyrolyser was constructed in the Pyrolysis Laboratory at the Department of Industrial Engineering, Engineering Faculty at the University of Perugia in Italy. During my experimental work the plant was equipped with a syngas safety electric valve and basically all seals around the reactor, hopper, screw conveyor, discharge section, de-ashing device and at the water scrubber were replaced, tested, optimised and put in order. The pyrolyser and the gas burner were connected separately and in continuous order. Due to safety reasons the gas burner was tested first by burning gas of known gas compositions (butan-propan) and afterwards with produced syngas. The direct combustion of continuously produced syngas from a micropyrolyser in a gas burner has proven the combustibility of the syngas. During a series of tests many issues were brought up and many solutions were conceived in order to achieve the ambitious goal.

The work was developed through the implementation of two tests: a drying test of biomass and a pyrolysis test with a continuous production of syngas and combustion of produced syngas in the gas burner.

During the first trial the thermal efficiency of the reactor was assessed and a series of improvements of the plant was carried out. The test was an opportunity to test the functionality and system management of the screw-coupled reactor, which ensured the continuous mass flow.

The second test, pyrolysis, is important and unique for the progress of research in this field. Effective combustibility of the produced gas in a continuous way from the micropyrolyser was successful and it presents a starting point for the optimization of the plant. The results show weaknesess on which future actions should be focused.

The syngas mixture sampled (caloric value of 2,86 MJ/kg - beech), which was diluted with ambient air, suggested an immediate reduction in the intake of the air blower. In parallel, a significant reduction of air infiltration inside the pyrolyser must be achieved to reach a calorific value of 12,79 MJ/kg. Security would also improve with reduced air infiltration and a warning for CO intoxication outside the safety box would be issued.

Due to the scope of this thesis, mass and energy balance of the system should be carried out, but because of a time shortage and late laboratorical analysis reporst from the Biomass Research Center, that was executed only partially.

ACKNOWLEDGEMENTS

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1   INTRODUCTION

The world population (6,75 billion people in 2008) has doubled in the past four decades, and in the past three, the world's energy consumption has more than doubled. In the future we can expect a distended consumption of energy on a global scale if the world's population reaches nearly 9 billion by the year 2040, which it will according to some projections [1].

The world economy requires enormous amounts of energy, most of which comes from fossil fuels (oil, natural gas, methane and coal).
In particular, it is envisaged that in the coming three decades, this type of fuel will cover 85% of the energy needs. However, in relation to this view, two important concerns emerge:

- Accessibility of resources and energy security with its price;
- Greenhouse gases emitted from the use of fossil fuels, changing the global climate system.

The energy sector is most responsible for the production of so-called "greenhouse gases" (GHG). Therefore, alternative energy sources need to be utilized to slow down the emission of these harmful gases. A series of parallel actions needs to be taken for improving energy efficiency in the relevant sectors of the economy:

- The increase in conversion efficiency;
- Protection and development of mechanisms for collection and removal of greenhouse gases;
- The promotion of sustainable forest management, afforestation and reforestation;
- The adoption of measures to limit and reduce greenhouse gas emissions in the transport sector;
- Limiting methane emissions through the recovery and use of gas in the area of waste management;
- Research, promotion, development and increased use of renewable energy technologies for capturing and isolating carbon dioxide and advanced technologies and innovative environment.

Renewable sources of energy in context of the threat of the global climate change are one of the best means to resolve the issue of future energy demand and protection of environment.

Renewable energy is generated from natural resources such as sunlight, wind, rain, tides and geothermal heat. Those sources are naturally replenished. Currently, various forms of financial incentives issued by the European Union, individual states or local authorities exist. Among the technologies for the conversion of renewable resources are hydro power, geothermal energy, wind and wave energy, photovoltaics and biomass.

Biomass such as forest residues and agricultural crops can, under certain conditions, provide a viable renewable source for electricity generation and heat. It can supply local communities close to production areas or offer products (biodiesel, biogas) that can replace some of the current fuels used for heating and transportation.

Particularly interesting in this context are energy crops, which are intended to provide biomass to produce electricity or heat. The modern techniques of cultivation (Short Rotation

Forestry) have maximized the yield per hectare by using fertilizers, pesticides and genetically modified tree species. The species used in energy production should have the important agronomic values of high growth rates and increased biological and climate resistance. Currently, electricity production from biomass is achieved through the technology of thermal incinerators and energy recovery from the flue gas of steam cycles. Higher efficiencies can be achieved through technologies such as gasification and pyrolysis. These technologies have not yet reached the industrial level of technological development needed for the production of synthetic gas of medium to low heat calorific value, which can used in internal combustion engines and gas turbines. An interesting perspective is that the use of syngas from biomass, given the optimal performance with minimal environmental impact, is based on the use of micro gas power in the range of 30-500 kW.

A micropyrolyzer, as a pilot plant, was built (at the Department of Industrial Engineering at the University of Perugia, Italy) to reach a high degree of confidence against rotary kiln reactors in the field of small power in the range of 30-100kW. The main operating parameters of the process, such as yield, composition and energy content of products, size and initial moisture content of biomass, pyrolysis temperature, heating rate and residence time were investigated in order to determine the optimal process conditions.

The purpose of this thesis work is to conduct a study on the working parameters which influence the process of pyrolysis. Various implementations and interventions were studied and tested in order to optimize the configuration of the micropyrolyzer and to obtain optimal test results in terms of the energy content of the products.

The objective of this work is the experimental implementation of the pyrolysis process in a continuous production of syngas, with the final combustion in a gas burner, and a characterization and analysis of the end products.

Chapter 2 of this work shows the world energy outlook according to future scenarios, and a quick renewable resources review.

Chapter 3 is concerned, specifically, with the production of energy from biomass and other energy conversion technologies with a description of different processes and their resulting products.

Chapter 4 describes in detail the pyrolysis process with the use of biomass products and the main process parameters that affect the complex reactions. The most common slow pyrolysis reactor – the rotary kiln reactor- is also described

The beginning of chapter 5 is devoted to a detailed description of the components of the laboratory micropyrolyzer. The second part of the chapter deals with the problems encountered at the beginning of this work and with the interventions carried out to guarantee optimization at the end of the test pyrolysis to obtain results that are as satisfactory as possible.

In Chapter 6 the experimental work of two types of tests conducted in the laboratory is described. The drying test was intended to verify the performance of the rotary kiln in producing heat transfer, in the test phase of drying, through the resolution of the thermal energy efficiency of the reactor.

The second test pyrolysis was intended to succeed in carrying out this process and to analyze the products obtained in order to understand the composition and energy content with particular attention to pyrogas (syngas from pyrolysis) and its calorific value. For determination of LHV, a burner was attached to complete the reaction.

This thesis deals with the slow pyrolysis of biomass, a phenomenon inherent in the thermal conversion of wood. Slow pyrolysis of biomass in a rotary kiln reactor has the potential for energy (electricity) production in remote areas or as a transportational LHV biogas fuel. In order to achieve a continuous production of combustible syngas in a mycropyrolyzer, several technical improvements of the power plant were carried out prior to the experiment.

2   WORLD ENERGY OVERVIEW

The energy market is crucial for the economies of developed and developing countries. The world's total energy consumption has increased twofold during the last 30 years, reaching over 11 000 Mtoe[1] in 2006. [2].

The countries' energy demand, supply, production, usage and the energy market are among the elements that characterize the economy of each country. They are, in fact, of strategic importance to business and affect mobility and overall quality of life.

The energy market is also very complex and is strongly influenced, even at the local level, by the international political climate.

Energy policy has three main functions: to ensure the security and continuity of energy supply, the economy and environmental compatibility.

These three pillars, which sometimes contradict each other, are the criteria which direct the energy sector in the short run and in the long run.

From an environmental point of view the issue of energy policy is related to the pollution of the environment, changing the biodiversity of ecosystems, and losing natural habitats as a result of anthropogenic added greenhouse gas emissions, which manifest themselves in global climate change.

Between 2000 and 2030 it is expected that the demand for primary energy in the world will grow by 60%, reaching an equivalent of 16.5 billion tonnes of oil (Figure 1).

Two-thirds of the increased world energy demands will stem from the economic growth of developing countries.

Energy sources usually consist of fossil fuels, renewable energies and nuclear power. Figure 1 shows the breakdown of the world's energy supply according to energy sources from 1971 to 2004, together with the expected distribution until 2030. The world energy need is expected to increase in all energy sources by 2030, due to the increased energy consumption in developing countries.

2.1   Fossil fuels

Fossil fuels are defined by the European Environment Agency as "coal, natural gas and petroleum products, such as oil, formed from the decayed bodies of animals and plants that died millions of years ago" [3].

• Oil:

Oil is and will remain the main energy source in the world for the coming decades. Its consumption will increase further, primarily due to transportation needs, where its consumption is unrivalled. The world crude oil production of 85.54 million bbl/day (in 2007) [4] will increase until it reaches the maximum rate of global petroleum extraction, known as Peak oil production. After that the rate of oil production will experience terminal decline.

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[1] *Million tonnes of oil equivalent*

Different forecasts estimate that the peak will begin by 2020 or later, while some assume that the peak has already passed.
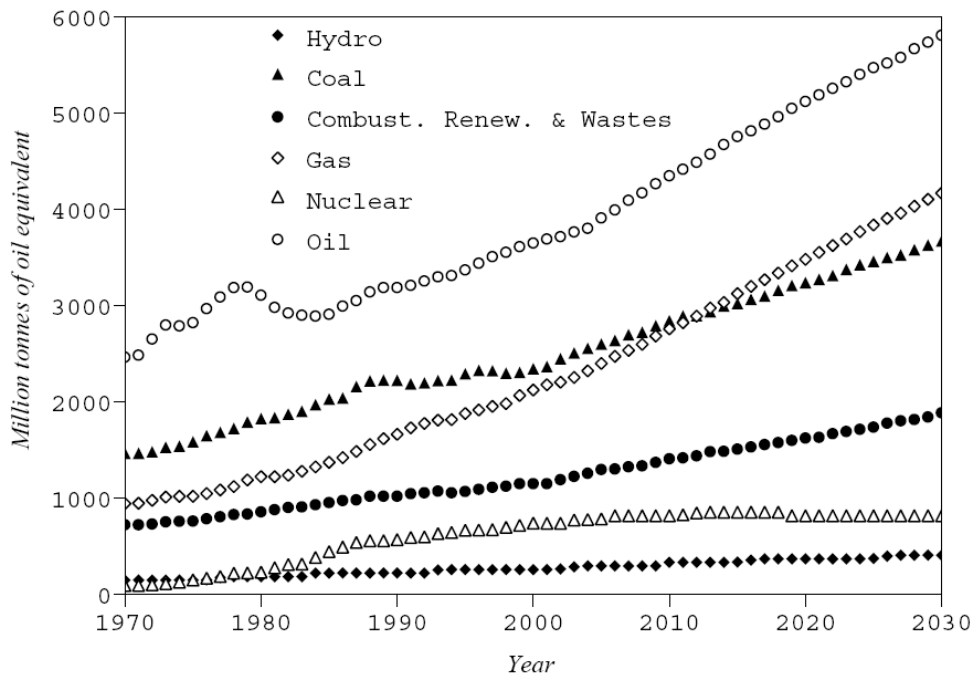
Figure 1. World energy supply by energy source. Adapted from IEA, 2006 [5]

• Coal:

Coal is mainly used for heat and power generation, with a share of 40% of the world's total electricity production. Coal is the most abundant fossil fuel. According to the International Energy Agency (2006) the proven reserves of coal are around 909 billion tonnes, which could sustain the current production rate for 155 years. That would results in competitive and stable prices compared to gas and oil [6].

• Natural gas:

Natural gas is coal's main competitor for heat and power production, especially in developed countries where environmental regulations are more stringent. It is a cleaner fuel which requires less treatment to meet low-emission regulations and has lower capital costs. A natural gas power plant produces half the CO_2 of a coal-fired plant, which is an important benefit for countries having ratified the Kyoto Protocol.

2.2   Nuclear power

Nuclear power contributes 16% to world electricity generation. Nuclear power is CO_2 neutral, with the respect to greenhouse gases. Uranium is a fairly common element in the Earth's crust and is about 35 times more common than silver. By using various techniques uranium is enriched to contain a higher concentration of isotope U-235. That fuel is used in common light water reactors. With the use of fast breeder reactors that use uranium-238 (99.3% of all natural uranium) the estimated reserves will be available for at least 1000 years.

Nuclear power's reputation was tarnished by the Chernobyl disaster in 1986. Reprocessing can potentially recover up to 95% of the remaining uranium and plutonium in spent nuclear fuel, putting it into new mixed oxide fuel. Economically, the costs of construction, operation and decommissioning make nuclear power less attractive with the current liberalization of the electricity markets. There are no longer electricity monopolies which can secure a long-term return on the heavy investment required to build nuclear power plants. Electricity providers seek shorter returns, which favor technologies, such as natural gas, with lower capital costs.

2.3   Renewable energy

The International Energy Agency includes in the term "renewable energy" the following energy sources: combustible renewables and wastes (CRW), hydropower, wind, solar, geothermal and ocean energy [4].

Combustible renewables and wastes are in turn defined as: solid biomass, biogas, liquid biofuels and municipal wastes.

- Combustible renewables and wastes:

CRW constitute the main part of today's renewable energy with a share of 11% of the world's energy supply. They are made up mainly of wood and charcoal used by poor populations for cooking and heating. It should be noted that for those populations, solid biomass is far from being the clean green energy used in developed countries. The World Health Organisation estimates that 1.5 million deaths per year are caused by indoor air pollution from cooking with solid biomass [5].

During the last few years, liquid biofuels have risen in popularity to supplement the use of fossil fuels in transportation. Brazil (from sugar cane) and United States (from maize) extensively use bioethanol to replace gasoline. In Europe, biodiesel (transesterification from vegetable oils) is used as a blend to common diesel. The European Union has an objective to substitute 20% of the traditional fuels in road transport with biofuels before 2020.

- Hydropower:

Hydropower is the second largest renewable energy source, with a share of 2% of the world's total energy supply. It accounts for 16% of global electricity production. Hydropower has the particularity to be the only large scale means to store electricity through the collection of water into large reservoirs for later re-conversion into electricity. Hydropower growth is limited as the most viable sites are generally already in use.

- Wind, solar, geothermal and ocean energy sources:

These alternative energy sources are still negligible in terms of energy production compared to classical energy sources. They represent less than 0.5% of the world's total energy supply and are not depicted in Figure 1. However, there is a real market for them, especially in developed countries. Wind power production has notably quadrupled worldwide since 1995 and in some countries has become a significant part of electricity generation, as in Denmark, where it accounts for 23% of national energy production. Wind power can also be designed as an independent off grid system.

3 ENERGY-RELATED ISSUES

3.1 Global warming

During the 20th century, the average global surface temperature on Earth has increased by 0,6 ± 0,2°C. There is a general agreement in the scientific community that "most of the observed warming over the last 50 years is likely to have been due to the increase in greenhouse gas concentrations " [7, 8].

Greenhouse gases are H_2O, CO_2, CH_4, N_2O and halocarbons. CO_2 is the main source of concern as it contributes to half of the greenhouse effect originating from human activities. CO_2 emissions come from the combustion of fossil fuels, which are essential for modern countries as they represent 85% of the world primary energy consumption. Hence it is extremely difficult to significantly reduce CO_2 emissions without affecting the development of nations.

Models differ concerning the consequences of the global warming. Nevertheless, major upheavals for humans, animals and plants are expected to change in local weather patterns and the geography of shorelines.

An international agreement on the reduction of greenhouse gas emission, the Kyoto Protocol [8], was signed in December 1997, and came into force in February 2005. The Kyoto Protocol divides countries into developed and developing nations. The developed nations which have ratified the protocol should cut their CO_2 emissions by 5.2% from their 1990 levels over between 2008 and 2012. The developing nations are not bound to reduce their emissions. The Protocol promotes the trade of CO_2 emission credits, which decreases the costs of emission reduction for countries heavily dependent on fossil fuels. In 2005, the trading scheme of the European Union included 12 000 heavy industrial and heat and power facilities.

The Kyoto Protocol incites developed countries to invest in new technologies for energy conversion, such as the development of renewable energy and zero-emission technologies (ZET) with CO_2 capture and storage.

3.2 Energy dependence

Energy is vital for all modern societies. The recent dispute between Ukraine and Russia about natural gas, when Russia cut off gas exports to Ukraine during the winter of 2008/2009 as well as in winter 2006, is a vivid example of the importance of energy supply diversification.

Therefore, governments are trying to diversify their energy bases. Conversion technologies have been developed to gain more fuel independence. Here are some examples:

- Gasification of coal/wood/wastes to produce syngas (mixture of CO/H_2).
- Fischer-Tropsch process to produce liquid biofuels from syngas.
- Fermentation of biomass to produce bioethanol as gasoline replacement.

Meanwhile, there is a trend of making multi-fuel driven thermal conversion devices, such as coal/wood co-combustion power plants and bioethanol/gasoline driven car engines. Crude oil prices have been relatively stable after the two energy crises (1973, 1979) but started to

increase in 1999 and 2008, due to OPEC[2] oil restrictions and geopolitical instability in the Middle East. The prices are expected to increase further with the growing demand in China and India. High oil prices burden the balance of trade for countries without local oil reserves and constitute another incitement to develop alternative energy.

3.3 Wood

3.3.1 Renewal of interest in wood in developed countries

Wood as an energy source is the focus of a renewed interest in developed countries. In the European Union, wood energy shares grew from 3% to 3.2% of the total energy consumption in 2003 [9].

Wood cannot totally replace fossil fuels. However, it may be a partial answer to the problems of CO_2 emissions and oil dependency. Wood is a CO_2-neutral fuel, provided trees are grown as much as they are burned, and wood is available in almost all countries.

Furthermore, harvesting, transforming and converting wood into thermal energy requires manpower. The development of the wood energy industry benefits local employment and contributes to sustaining social and economic activity in rural and forested areas.

3.3.2 Wood compared to coal

Table 1 presents a comparison between the physical properties of wood and its fossil counterpart, coal.

Table 1. Typical properties of wood and coal [10]

	Wood	Coal
Density (dry fuel) (kg/m^3)	~ 570	$\sim 1\,500$
HHV^a (kJ/g)	19.4-22.3	23-34
Volatiles (wt % of dry fuel)	81-87	16.0-35.0
Friability	Low	High
Particle size	$\sim 3\,mm$	$\sim 100\,\mu m$
Ash (wt % of dry fuel)	0.2-1.35	6.0-23.3
C (wt % of dry fuel)	49-52	65-85
H (wt % of dry fuel)	5.4-7.0	3.1-5.6
O (wt % of dry fuel)	40-44	3.4-13.8
N (wt % of dry fuel)	0.00-0.35	0.9-1.6
S (wt % of dry fuel)	0.00-0.07	0.4-4.3

^{a} Higher Heating Value

Wood is a cleaner fuel compared to coal. It has low sulphur content. There is usually no need for De-SO$_x$[3] treatment of the flue-gas in wood combustion [11]. The fuel-bound nitrogen is typically 1% in coal and the combustion temperature is also lower due to a lower HHV, which

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[2] Organisation of the Petroleum Exporting Countries

[3] denitrification

reduces the fuel and thermal NO_x formation. However, a De-NO_x installation might still be necessary.

The product of HHV and density gives the energy density. Calculations from data in Table 1 give an energy density for coal 3 to 5 times greater than for wood.

Hence, for wood to be cost competitive, it is important to limit fuel transportation and storage needs. As a result, wood power plants are usually considered in forested areas. The volatile content in wood is much higher than in coal, typically 4 times. It is an important parameter in the design of combustion chambers as it is necessary to cope with the large release of combustible gas. Therefore wood combustion chambers are larger than coal combustion chambers. This is further amplified by the fibrous nature of wood which makes it hard to mill it into very small pieces. Larger particles need longer residential time to be totally combusted. As heat transfer and combustion intensity (ratio of energy output to chamber size) decrease when the size of a combustion chamber increases, fluidised beds are often preferred for wood power plants, as opposed to coal, for which pulverised combustion is the prevalent technology. Fluidised beds also feature good heat transfer from the fuel to the walls, and are tolerant to large particles and high moisture contents. For wood wastes and woody fuels with large irregular geometry moving grates are most commonly used.

Coal power plants produce up to 1 000 MW, wood plants are usually of small-to-medium size, from small domestic burners - stoves to ~ 45MW facilities. Because of the low combustion intensity of the wood and the costly transport of bulky material, wood is limited to local harvesting range. Typical facilities that use wood systems are schools, colleges, hospitals, public buildings, hotels and motels, commercial buildings, greenhouses, large-scale agricultural operations and manufacturing plants [12].

3.3.3 Thermal conversion of wood

When considering wood as fuel, the final goal is to convert the wood-contained chemical energy into heat, either for direct heating purposes or for later conversion into electricity or mechanical work. Maximum wood chemical energy is retrieved by combustion. It is the complete oxidation of wood by oxygen into carbon dioxide and water:

$$Wood + O_2 \rightarrow H_2O + CO_2 + NO_2 + SO_2$$
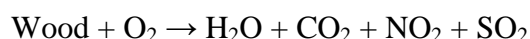
However, other thermal processes may be applied to wood prior to combustion in order to transform it into a different fuel.

One of these processes is pyrolysis. Pyrolysis is thermal devolatilization of an organic material under an inert atmosphere [13]. Pyrolysis products are char[4] and volatiles:

$$Wood \xrightarrow[\text{T>350}]{\text{inert atmosphere}} Char + Volatiles$$
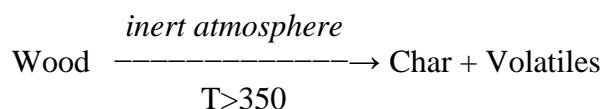
Slow pyrolysis is commonly used to produce charcoal, a fuel for cooking and heating. Charcoal is popular in developing countries as it burns without either smoke or flame. Charcoal is also used in the metallurgical industry as a high-grade reducing agent for the conversion of silica into silicon [14]. Charcoal production is a long (~ 4–12h) and inefficient process: only a third of the initial wood chemical energy is conserved in the charcoal. Therefore slow pyrolysis is economically limited to particular applications.

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[4] Wood char is commonly called charcoal and coal char, coke.

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On the contrary, fast - or flash - pyrolysis, is a more efficient process (~ 60% energy yield [15]) as most of the wood energy is kept in the final product. Flash pyrolysis turns wood into pyrolytic oils. It was the focus of intense research during the last two decades as pyrolytic oils were thought to be a replacement for petroleum oil in some applications. In flash pyrolysis, wood undergoes very fast heating (>1000°C/s) at relatively low temperature (~ 500°C) with a residential time, for the volatiles, of less than 2 seconds [16, 17]. The liquid oil that is formed is acetic with pH lower than 2.5. Oil has variable viscosity and, in the presence of char particles, requires special treatment or equipment before any use. The costs of these treatments are currently an obstacle to commercial use of flash pyrolysis.

Another method for thermal conversion of wood is gasification. It converts wood into a combustible gas mixture. A general gasification process consists of:

- Rapid pyrolysis of a wood particle:

$$Wood \rightarrow Char + Volatiles$$

- Combustion of volatiles and char:

$$Char + Volatiles + O_2 \rightarrow CO_2 + H_2O$$
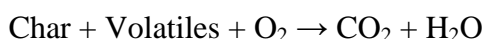
The quantity of fed oxygen is lower than that which is required to combust all the wood. Therefore, part of the volatiles and char remain unburned.

- Some of the water and carbon dioxide resulting from the combustion are reduced to hydrogen and carbon monoxide by reacting with the remaining char and volatiles:

$$Char + Volatiles + CO_2 + H_2O \rightarrow CO + H_2$$

- The composition of the mixture of CO_2, H_2O, CO and H_2 is fixed by a water-gas shift reaction:

$$CO + H_2O \rightarrow CO_2 + H_2$$
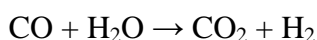
which is close to equilibrium at temperatures above 800°C.

The description above is only schematic. Depending on the design of the gasifier, the reactions may take place in the same location, as in a fluidised bed gasifier for example, or occur in different stages, as in gasifiers with separate beds and indirect heating. Air or oxygen mixed with water may be used as a gasification agent. Air gasification produces a gas mixture with a lower heating value due to the presence of nitrogen.

Air gasification is a candidate process for cogeneration and for converting wood into gas before co-combustion with pulverised coal. Oxygen-blown gasification is studied for producing syngas for chemical use (methanol production, Fischer-Tropsch process) [18].

Gasification is not limited to wood: coal gasification with oxygen followed by a water-gas shift is currently being utilized to produce a stream of carbon dioxide and hydrogen. Carbon dioxide is then separated from hydrogen and stored. The process should result in a clean fuel - hydrogen without any release of CO_2 into the atmosphere.

3.3.4 Thermal conversion of wood through pyrolysis

Complex phenomena take place during combustion and gasification, including:

- Turbulent reacting flows
- Heat, momentum and mass transfer
- Chemical reactions
- Interactions between different phases
- Pyrolysis

The fact that pyrolysis is present in combustion and gasification, which are the processes occurring in oxidising atmospheres, might be surprising at first. However, the wood particle[5] is indeed isolated from the oxidising atmosphere: a particle submitted to the high temperatures of combustion or gasification (T>800°C) quickly starts to decompose into volatiles and char. The outgoing volatiles keep oxygen from entering the charring particle. Hence wood undergoes rapid heating under an inert atmosphere, i.e. pyrolysis conditions. When devolatilisation is over, oxygen diffuses toward the particle centre and heterogenous combustion of the remaining char takes place.

Therefore, any attempt to understand wood combustion or gasification first requires a good understanding and description of wood pyrolysis.

Pyrolysis itself is a complex phenomenon, not well understood, which involves heat transfer, drying, flows of liquids and gases, surface recession and a large number of chemical reactions. A set of non-linear algebraic partial differential equations is needed to describe pyrolysis in detail; the solution of these equations requires substantial computational efforts [10].

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[5] In this context, a particle refers to a log, a pellet, a chip, etc.

4 PYROLYSIS

4.1 Description of the process

Thermochemical conversion of biomass (pyrolysis, gasification, combustion) represents the most promising technique for energy production (Figure 2 and Figure 3). Pyrolysis is the process of thermochemical decomposition of organic materials that occurs at temperatures between 400 and 800°C in complete absence of an oxidizing agent, or with a very small amount of oxygen that will not cause gasification (in the latter case, the process can be described as partial gasification). If the temperature is below 400°C, pyrolysis is defined as carbonization where charcoal, fuel gas and liquid fuels (heavy and light oils) are produced. When the temperature reaches 1000°C there is a complete gasification of biomass.
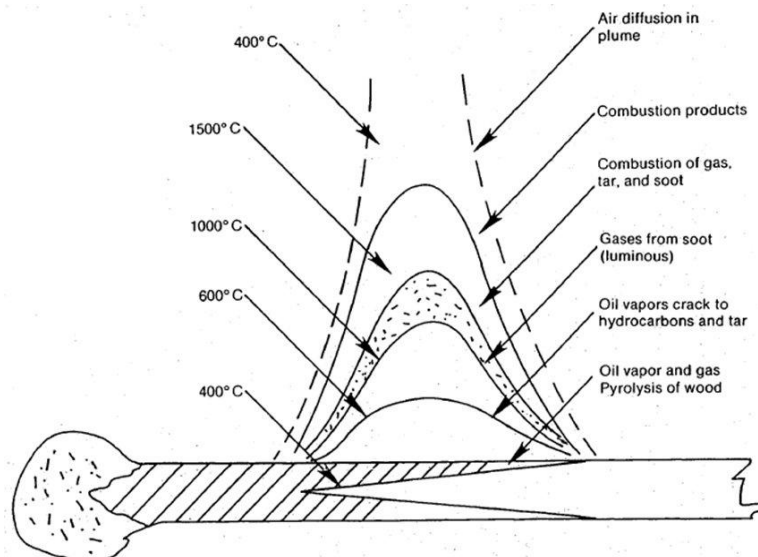
Figure 2. Pyrolysis, gasification, and combustion in the flaming match [19]
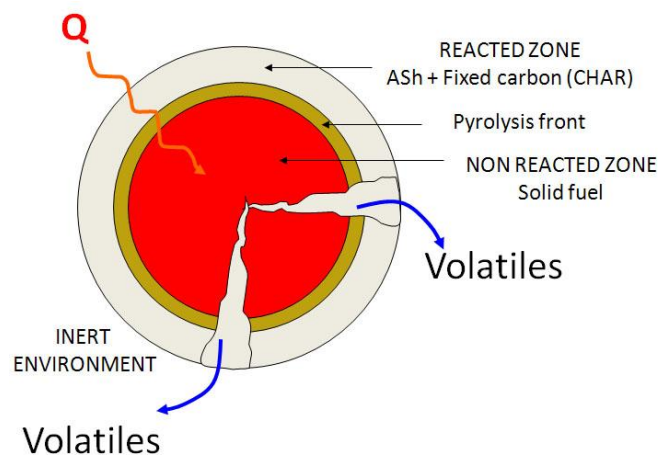
Figure 3. Schematic reaction zones of wood pyrolysis [19]

Through pyrolysis the material is transformed into liquid and gas fractions with low to medium calorific value (SYNGAS, consisting of CO, H_2, CH_4 and other low molecular weight hydrocarbons). The liquid fraction contains water and organic compounds at low to medium molecular weight (TAR) and a solid carbonaceous portion (CHAR).

Pyrolysis offers a great opportunity from an environmental point of view since it allows the use of a wide variety of materials (wood, waste, tires, plastic) which produce low emissions of nitrogen oxides and sulphur in comparison with the current technologies that are used in the process of incineration. Moreover, while they provide energy recovery of 40%, the values reach up to 70% through pyrolysis [20].

Generally, the products of the pyrolysis reaction can be classified into three main groups:

• **Syngas:** composed primarily of hydrogen, carbon oxides (CO, CO_2) and gaseous hydrocarbons such as methane, with a calorific value of around 13-15 MJ/Nm^3.

• **Tar:** the liquid produced by pyrolysis is a condensable organic (bio-oil) characterized by a complex chemical composition: carboxylic acids, aldehydes, alcohols, water vapour and tar. The oily liquid portion consists of two phases: an aqueous phase containing a wide variety of organic compounds containing oxygen with a low molecular weight and a non-aqueous phase containing insoluble organic compounds (especially aromatic) with a high molecular weight.

• **Char:** the product is a solid carbon residue with a low content of ash and a relatively high PCI (30 MJ/kg), with a density of about 150-300 kg/m^3. Char can be used as a fuel to power the pyrolysis process or for drying the biomass before putting it into the reactor. Char is more stable and complex for handling and does not degrade biologically.

The degradation of biomass into these three products is a complex process accompanied by the formation of more than one hundred intermediates. The scheme of reactions known as the kinetic mechanism of Broido-Shafizadeh is shown in Figure 4.
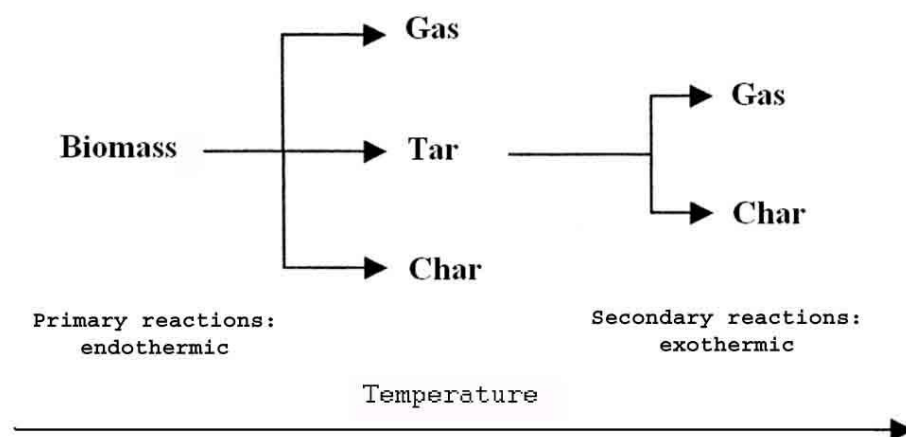
Figure 4. Schematic kinetic reaction pyrolysis [21]

In the first stage, the heat supplied to the biomass triggers primary reactions, breaking the long chain of the organic polymer matrix. The depolymerisation occurs at lower temperatures and produces a fraction of volatiles (primary gas and tar) and a solid fraction (primary char). In the second stage, tar, primary at higher temperatures, changes to a secondary exothermic

reaction (char particles) and transforms into gas with a lower molecular weight through the cracking process.

The pyrolysis process can be divided into four phases depending on the reached temperature and final products:

• Values for temperatures below 200°C form only non-combustible gases, especially water vapour, small concentrations of CO_2, acetic acid and formic acid. At this stage, the vaporization absorbs much of the heat to the process of thermal degradation, so it is necessary that the water content of the biomass is below a certain percentage (< 50-60% by mass) so that the process evolves according to pyrolysis.

• Between 200 and 280°C devolatilisation begins, the components of the biomass react with each other to form CO and some intermediate compounds such as alcohol and acid. At this stage, the reactions are endothermic and the products are almost non-flammable.

• From 280 to 500°C exothermic reactions begin the second stage, causing a rise in the temperature, leading to the formation of combustible gases (CO, CH_4 and H_2) and highly flammable liquids in the form of tar.

• More than 500°C: the initial biomass is almost totally degraded and the reactions of the second stage are prevalent; the yield of tar, after reaching a maximum value, decreases significantly, transforming into gas (syngas), and to a lesser degree char, which continues to serve as a catalyst for secondary reactions.

Depending on the temperature, different products can be obtained. Normally, an increase of the temperature leads to an increase in the final production of gas at the expense of solid product. Studies [22] show that for almost all types of biomass, the maximum liquid yields are obtained between 475 - 525°C if the residence time of the volatile components is between 0.2 – 0,6 seconds. Moreover, as the pyrolysis temperature increases, not only does the amount of syngas increase, but it also changes its chemical composition, increasing the proportion of hydrogen and carbon monoxide, while that of methane decreases, so the gas has a lower calorific value.

4.2 Use of pyrolysis products

The products of the pyrolysis process can have different performance or usage, according to their specific chemical and physical characteristics (Figure 5. and Figure 6.).

Tar can be used directly as a fuel or can be transformed chemically (up-grading). In the first case it is used in industry (for heating a baking furnace for cement and lime, high efficiency) or in the processes of pyrolysis due to high energy content of some components such as methanol. In the latter case, the tar produced by pyrolysis can be used directly in combustion although it rarely reaches the standards required for fuels.
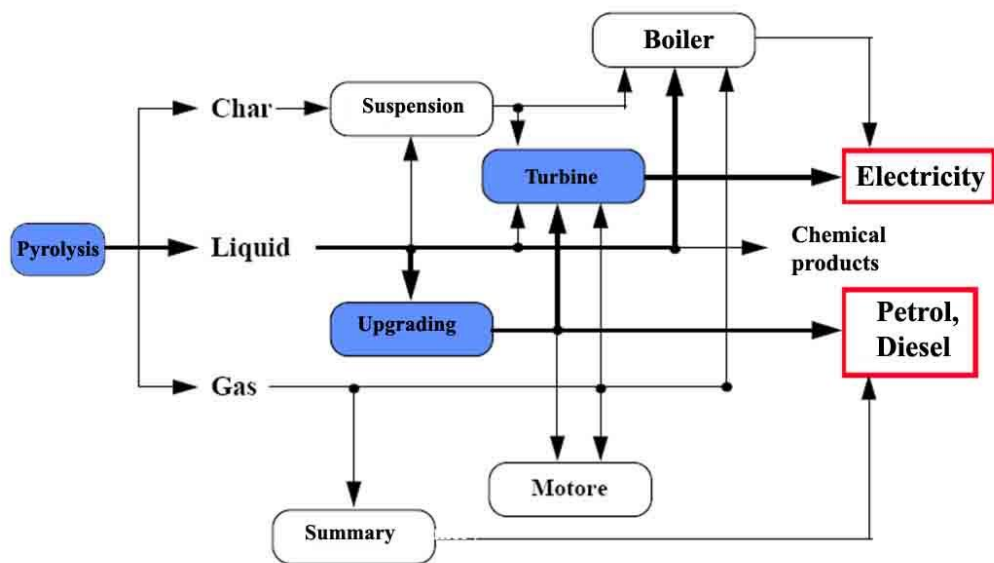
Figure 5. Use of pyrolysis products, lines indicate currently favoured options in research on energy[23]
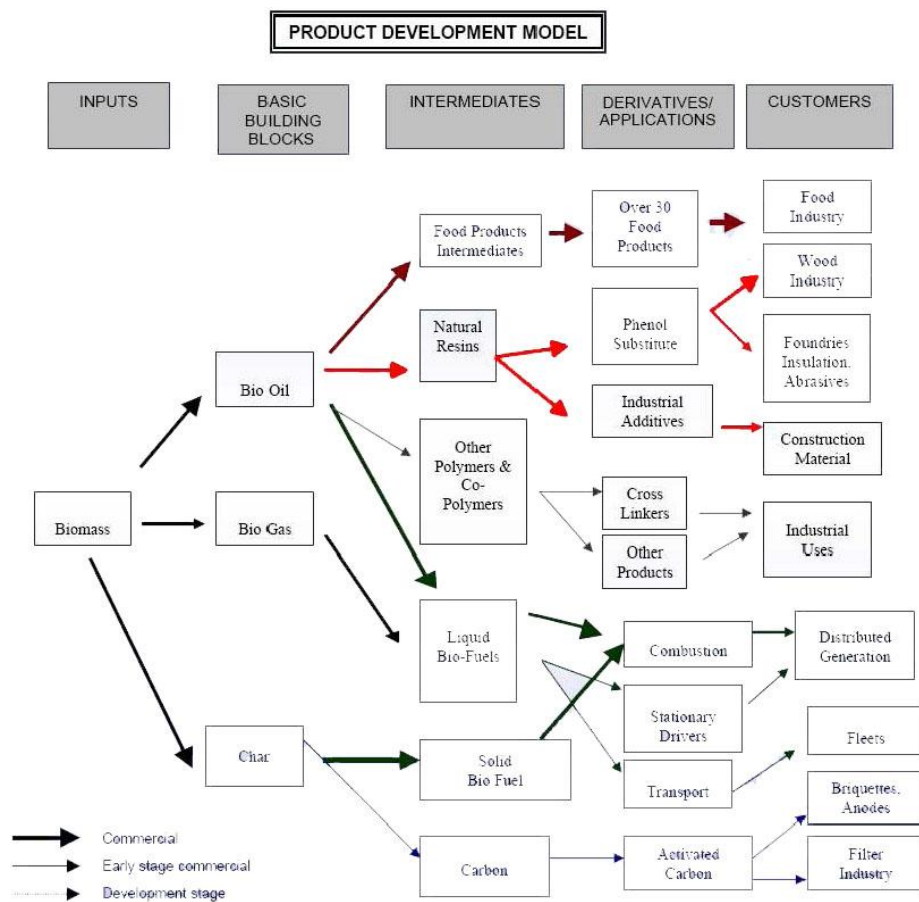
Figure 6. Pyrolysis product development model [24]

The development of new and economic applications for bio-oils as fuels involves technology aimed at reducing the viscosity, corrosivity and increased volatility of the products. These aims can be achieved largely through the elimination of oxygen. The presence of oxygen makes the excess tar less dense and less rich in energy content. The removal of oxygen can be achieved through high pressure hydrogenation in the presence of catalysts (cobalt, molybdenum), or through dehydrogenation with zeolite minerals.

Hydrogen can be produced by steam reformation. This involves the formation of reactive vapours that can be converted into hydrogen, carbon monoxide and carbon dioxide using a catalytic steam environment. These systems have many advantages over the traditional technology for the gasification of biomass. The bio-oil products can be transported more easily and possibly with reduced costs.

The solid part (char) can be used as a fuel in the form of briquettes. After further treatment it can be used for the preparation of active carbon for its absorptive capacity due to the porous surface. Active carbon is used as a catalyst in many applications, as well as in the process of purification and recovery of solvents.

The generated gas (syngas or pyrogas) has a medium to low calorific value but may contain enough energy to power a pyrolysis plant or a micro-turbine.

For the use in a pyrolysis plant, gas does not need cleaning since the small particles contribute to an increase in the capacity of heating. In addition, the combustion of gas requires simple technical support and presents a pollution problem, containing small quantities of sulphur oxides. The use of syngas in a turbine requires a removal of particles to avoid any damage to moving mechanical parts. This solution has more potential since the use of syngas in a turbine allows the adoption of a combined cycle for the production of electricity.

4.3   Influence of process parameters on products of pyrolysis

Although the three fractions (solid, liquid, gas) are always present as a result of the pyrolysis process, the increase of yield to one of them in relation to others is possible by selecting the appropriate pyrolysis technology and process conditions.

The main parameters that affect the mechanism of reaction are:

- the final temperature of the reaction
- the heating-rate
- the residence time of the material
- the size and shape of biomass to be treated
- the presence of catalysts
- pressure
- moisture
- the chemical composition of biomass

4.3.1   Effect of temperature on final products of pyrolysis

In general, an increase of temperature leads to an increase of gas fraction in the final products. Decomposition of biomass at a higher temperature is the result of secondary exothermic reactions. The liquid fraction increases until it reaches a maximum value of 35% of total products at around 500°C and then decreases with increasing temperature. The secondary exothermic reactions (cracking) at higher temperatures increase the proportion of gas at the

expense of liquid. Consequently, the initial analysis suggests that in order to obtain a greater yield of tar than other products, the temperature should be between 500 and 550°C to prevent the completion of the secondary reactions. In parallel, the gas production is characterized by a trend opposite to that of tar. The yield of gas decreases until 500°C is reached and then increases significantly at higher temperatures due to the development of cracking reactions, involving the liquid phase.

The depolymerisation of tar takes place at high temperatures, at which there is also an increase in the energy content of the gas produced. The lower calorific value increases, reaching a maximum of 15 MJ/Nm^3 at 750°C, then decreases at higher temperatures (as shown in the Figure below).
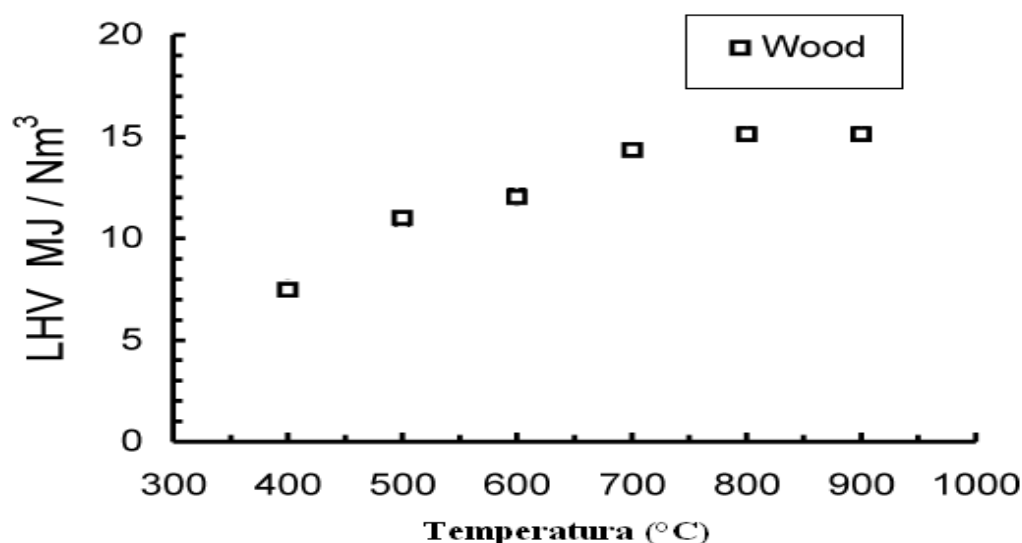
Figure 7. Lower calorific gas as a function of temperature. The results refer to experimental pyrolysis performed at a heating rate of 30°C/min [25]

The composition of the gas fraction (

Table 2) varies significantly with temperature, in particular the concentration of CH_4 is the highest between 600°C and 700°C, concentrations of CO and H_2 are rising while CO_2 decreases uniformly with the temperature. The high temperature favours the formation of H_2 at the expense of heavy hydrocarbons that are dehydrogenated from cracking. The evolution of concentrations of carbon monoxide and carbon dioxide is linked to the gasification of carbon ($C + CO_2 = 2CO$) which increases in intensity with the increasing temperature causing a higher concentration of CO.

Table 2. Composition of the gas phase as a function of temperature [25]

Compound	400°C % Vol.	500°C % Vol.	600°C % Vol.	700°C % Vol.	800°C % Vol.	900°C % Vol.
CO	34.2	39.7	42.5	44.3	50.2	53.5
CO_2	51.9	36.6	23.0	16.7	9.1	5.0

H$_2$	1.3	7.6	10.8	15.5	20.8	25.3
CH$_4$	9.3	12.8	16.5	16.1	14.2	12.1

As for gas including solids, energy content increases with temperature. The calorific value is changed from 28 MJ/kg at 250°C to 32 MJ/kg at the temperature of 900°C. This is explained by the fact that the energy value is directly proportional to the fixed content of carbon that is growing with the increasing temperature of pyrolysis.

In experimental studies [26], low-temperature pyrolysis of municipal household wastes in a fixed bed reactor was performed to show the influence of the final pyrolysis temperature on the product yield.
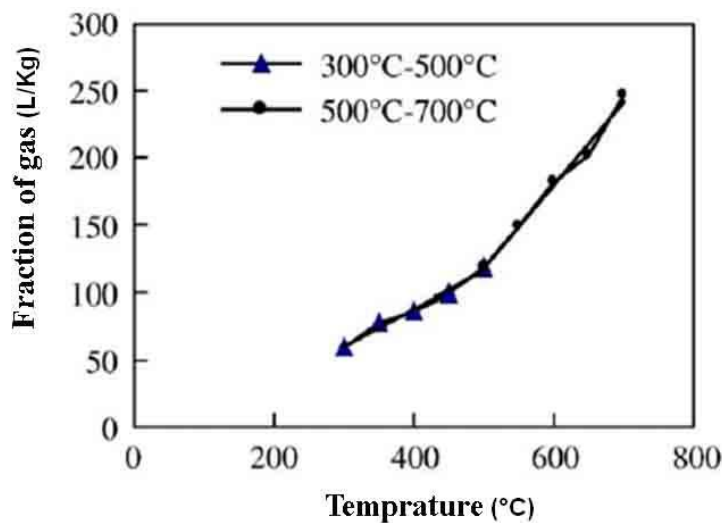
Figure 8. Variation of the fraction gas produced as a function of temperature (26).

The final temperature of pyrolysis is a factor in the production of gas. The yield of the product is directly proportional to the temperature at the whole range considered (300 to 700°C). Below 500°C gas production is at 52.37 L/kg, but at higher temperatures slope change and the gas fraction increases significantly, reaching 135 L/kg which is about two and a half times more. The reason for this phenomenon is that at the temperature of 500°C decomposition of tar in non-condensable gases starts.

4.3.2 Effect of particle size on final products of biomass pyrolysis

The influence of the particle size on the final performance is linked to the heat transfer between the heated reactor wall and the biomass inside the reactor. The larger particles warm more slowly than smaller particles. The average temperature of the particles is lower and less volatile compounds are extracted.

Experiments [27] show how the particle size with diameter of particle between 0.425 mm and 1.8 mm when keeping the temperature at a constant 550°C varies . The particle size around a central value of particle diameter between 0.85 mm and 1.25 mm is believed to give the maximum relative yields of gases and liquids and a minimum of solids.
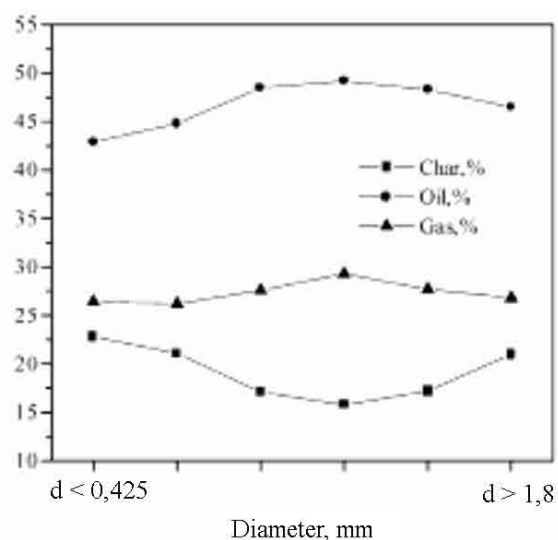
Figure 9.   Yields of slow pyrolysis depending on the size of the particles[27]
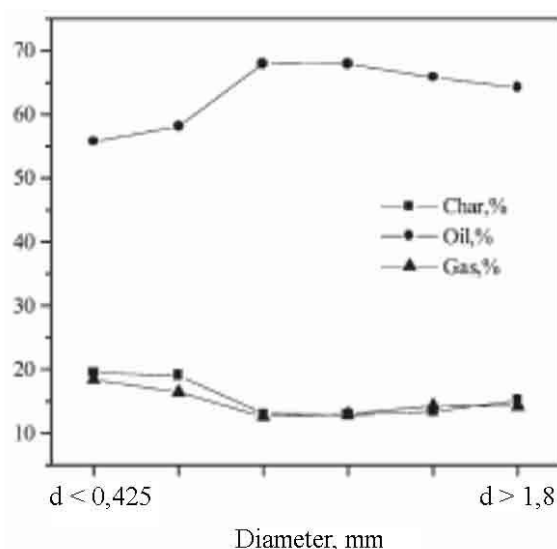
Figure 10.   Yields of fast pyrolysis as a function of the particle size[27]

Fast pyrolysis is influenced by the particle size while maintaining a constant temperature (equal to 550°C) and heating rate.

Studies on fast pyrolysis [28] have shown that there is a relationship between the composition of the gas produced and the particle size of the material that is fed to the reactor. Reducing the size of the particles from 0.9-2.0 mm to 0.2-0.3 mm, the gas produced increases in its concentration of hydrogen (3-22 mol%) and methane, but decreases in the concentration of carbon dioxide.
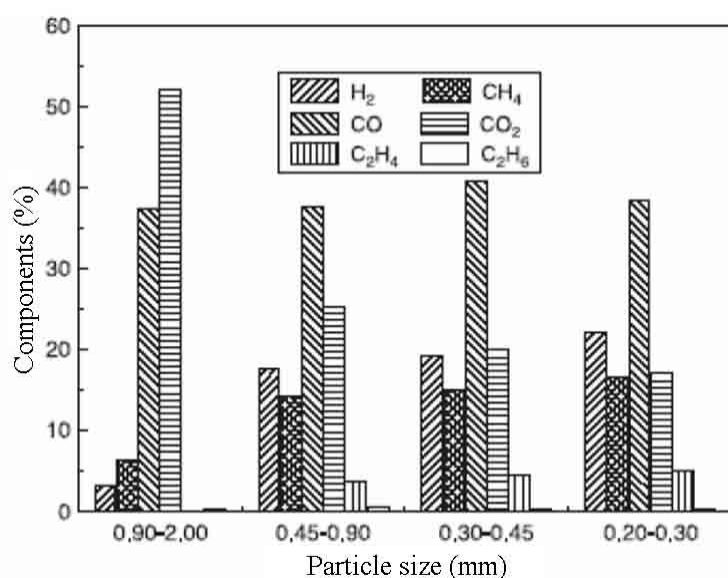
Figure 11.   Effect of particle size on the composition of the gas produced[28]

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4.3.3 Effect of moisture on final products of pyrolysis

The initial reactions of pyrolysis include a depolymerisation and dehydration. The biomass moisture content has an important role as the heat of vaporization significantly affects the amount of fuel needed. The moisture should not exceed 20% - 40%, otherwise a pre-drying treatment is needed. That can be conducted by leaving natural biomass for a period of time at a room temperature or by a furnace at a temperature around 100°C to prevent possible ignition of the material. The water content in biomass influences the reactions of pyrolysis and thus the yields of products. The liquid fraction consists of two phases: an aqueous phase containing organic molecules with a low molecular weight and a non-aqueous phase containing soluble organic molecules with a high molecular weight.

The presence of water will significantly influence the yield and physical properties of the liquid fraction. For higher water content (60.5%) there is a higher yield of the liquid product, especially for temperatures from 670°K to 700°K.

Qualitative observations indicate that pyrolysis of materials with a lower concentration of solid fraction in biomass increases the water content which favours the reactions of char gasification, causing the decline of the solid fraction which increases the gas yield.

That is important for the design of systems based on different process conditions of pyrolysis, especially in the sizing of components designed for transport and storage of the products.
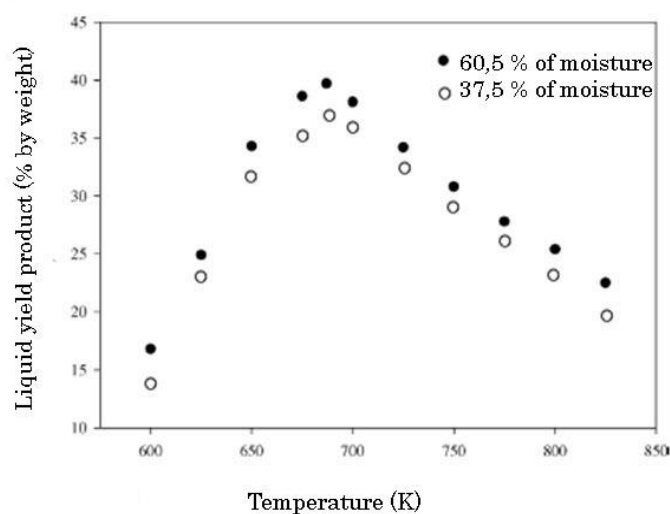
Figure 12.   Liquid yield (water and tar) in relation to the pyrolysis temperature for different water contents[25]

4.3.4 Effect of composition of biomass on final products of pyrolysis

The biomass used most in pyrolysis is characterized by agro-forestry residues and waste from the industrial processing of wood. These materials consist primarily of three components: hemicellulose, cellulose and lignin which interact with each other during thermal degradation (Figure 14 and Figure 13).

Figure 13   General composition of lignocellulosic biomass feedstock [19]

Figure 14. Average content of wood fuel [36]

Pyrolysis of cellulose is evolving in two different phases. The first is a molecular dehydration that leads to the formation of water, CO and CO_2; this process is endothermic and occurs at temperatures below 300°C. In the second phase, at temperatures above 300°C, cellulose is depolymerised and forms levoglucosamina, a more stable compound that gives high yields of char. Hemicellulose begins to decompose at the temperature of 250°C and at 500°C it has completely degraded to tar, (water and CO_2) and other hydrocarbons. Lignin is the most stable among the components of wood and does not present an intermediate compound as cellulose. Lignin, however, suffers a slight thermal decomposition at very low temperatures and then totally decomposes at temperatures above 500°C, releasing CO and H_2.

Experimental results [29] are obtained through thermogravimetric analysis (TGA) at a heating rate between 2 and 25°C/min on biomass. The TGA analysis results compared to the results from a kinetic model indicate a qualitative relationship between the thermal decomposition of the original biomass and degradation of hemicellulose, cellulose and lignin.

The yield of products during thermal degradation varies depending on the composition of biomass selected. From the experimental studies [30] conducted in a micro-pyrolysis unit using isolated components of biomass (only cellulose and lignin), a mixture of cellulose and lignin in different proportions (results shown in Table 3) were obtained.

Table 3. Yield of products (% of weight) of the individual components [30]

Components	Char (%)	Tar (%)	Gas (%)
Cellulose	11.1	46.8	43.0
Lignin	41.7	26.8	30.5

Table 4. Yield of products (% of weight) samples of synthetic biomass with different ratios of cellulose and lignin (C: L) [30]

C:L	Char (%)	Tar (%)	Gas (%)
3:1	18.1	40.5	41.3
1:1	29.8	33.1	37.0
1:3	36.1	31.5	32.8

Thermal degradation of cellulose produces minimal yield of char and maximum yield of tar and gas while thermal degradation of lignin alone produces a high yield of char and less of gas and tar.

The yields of products depend directly on the initial composition of the mixture. The rise of the cellulose content will decrease the char yield but increase the tar and gas yield. Consequently, cellulose is primarily responsible for the formation of the volatile fraction of the products while lignin mainly contributes to the formation of the solid fraction.

The effect of temperature on the yield of products has characteristics specific to different compositions of biomass. Trials [27] performed in a fluidised bed reactor with a constant heating rate (10°C/s), using two types of biomass, one consisting mainly of lignin (51.43% of weight) and the other consisting mainly of cellulose and hemicellulose (present up to 62.21% of weight), led to the results shown in Figure 15. The temperature change from 500°C to 700°C in biomass with more cellulose and hemicellulose results in an increase of gas yield (70% -80% by weight) when liquid and solid fraction decreases. At higher temperatures (700°C to 800°C) the yields change a little or remain constant.
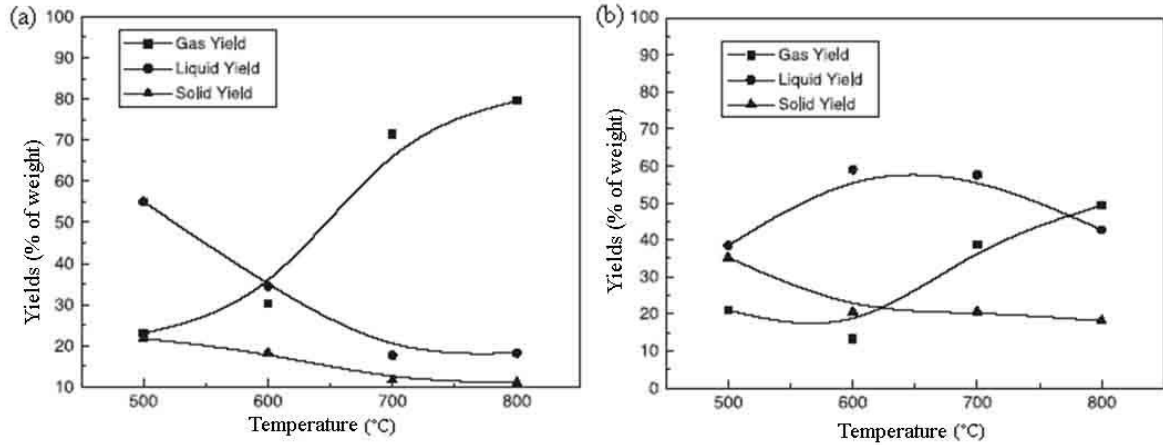
Figure 15. Effects of temperature on the final products in fast pyrolysis of biomass rich in cellulose (a) and lignin (b)[27]

The influence of the composition of the gas produced from biomass is also interesting. At higher temperatures the gas composition is favourable for the formation of gas with a higher concentration of hydrogen (from 2 to 25%) and this effect is more relevant in the case of biomass with high cellulose content (Figure 16).
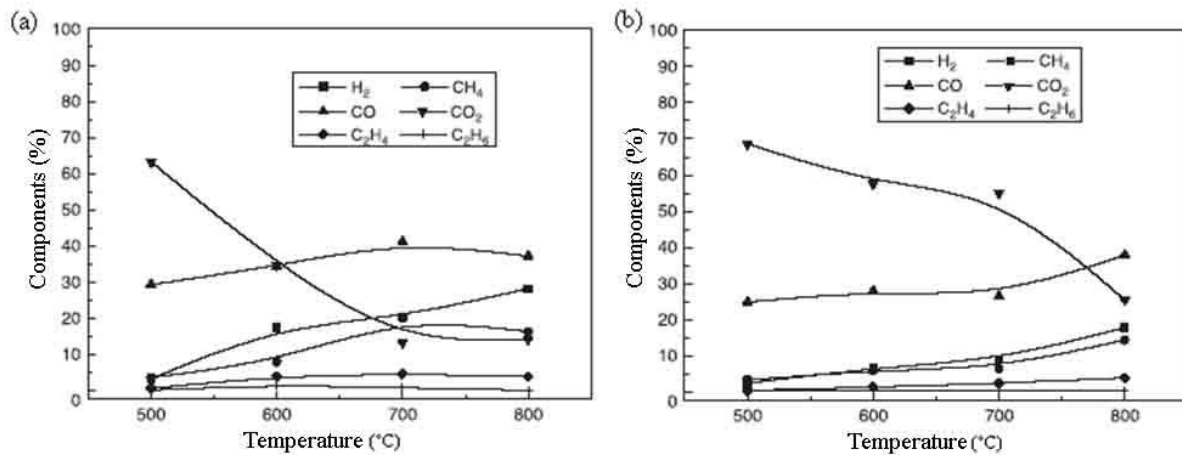
Figure 16. Effects of temperature on the composition of gas produced in fast pyrolysis of biomass rich in cellulose (a) and lignin (b)[31]

4.4　Types of pyrolysis

According to the parameters of the process and products, different types of pyrolysis can be distinguished. Based on the criteria (reaction temperature, heating rate, residence time), pyrolysis is classified, leading to the formation of different yield products.

Table 5. Formation of different products from various types of pyrolysis [19]

Mode	Conditions	Liquid	Char	Gas
Fast pyrolysis	moderate temperature, short residence time particularly vapour	75%	12%	13%
Carbonisation	low temperature, very long residence time	30%	35%	35%
Gasification	high temperature, long residence times	5%	10%	85%

4.4.1　Carbonisation

Carbonisation is a process for the conversion of an organic substance into carbon or a carbon-containing residue through pyrolysis by removing water and volatile substances from plant material. The reactions occur at temperatures between 400 to 500°C over a relatively long time (days) and lead to the production of charcoal with a percentage of carbon equivalent to about 75% and a calorific value of 6000-7000 kcal/kg. The production of gas is equal to 15 ÷ 20% of the dry components. Liquids can represent up to 30% of the total share and are made up of alcohol, acetic acid and acetone. Charcoal can be used as a fuel or as a raw material for the production of industrial chemicals such as activated carbon.

4.4.2　Slow pyrolysis

Slow pyrolysis occurs at temperatures exceeding 400°C and high residence time (4-8 minutes). With the heating rate of 1-5°C/sec, the reactions occur in balance. Under these conditions the gaseous phase of the products will be high because of the complete secondary reactions.

The final char yields are decreased by increasing the process temperature from 400°C to 700°C. The liquid products reach a maximum value at around 550°C and decrease at the temperature of 700 °C.

The decrease in char yield at higher temperatures is related to the increase of volatiles from tar. That is subjected to the secondary reactions, which means less production of liquid and more gas.

4.4.3　Fast pyrolysis

This type of pyrolysis occurs at temperatures between 500 - 950°C, with the heating rate of about 100-300°C/sec and a very short time of residence (1-5 seconds) to reduce the formation of intermediate products and increase the yield of tar. Tar product can reach up to 70% -80% of the weight of dry biomass if we can keep the temperature around 500 °C in order to limit the reaction of steam cracking, facilitating condensation and the subsequent formation of liquid.

When residence time is too short (<1 s), the result is an incomplete depolymerisation of biomass and a less homogeneous liquid product which contributes to the instability of bio-oil. In addition to a high heating rate it is necessary to cool down pyrolysis vapours very rapidly in order to obtain a more stable product.

In order to heat up biomass very rapidly, smaller homogenous particles must be used, often pre-treated with mechanical grinders.

The technologies related to this type of pyrolysis are receiving much attention because the liquid fuel that is produced is more dense and easier to handle.

4.4.4 Flash pyrolysis

Flash pyrolysis is a type of pyrolysis characterized by a high heating rate (> 1000 °C/s), short residence times (0.1-1 seconds) of solid and volatile components and a different temperature range depending on the wanted product. For temperatures between 450°C and 750°C, up to 80% of the weight of liquid fraction is achieved, while for temperatures above 750°C (flash pyrolysis at high temperature) gas production can reach 80% of the weight of the products and at the same time, given the high speed of reaction, it has less tar and the calorific value of gas increases by 5-10%.

Below is a tabular summary of the different types of pyrolysis described in this paragraph according to the parameters of the process and products (*Table 6.*).

Table 6. Types of pyrolysis in relation to operating processes and products with greater yield [19]

Pyrolysis type	Residence time	Temperature (°C)	Heating rate	Products
Carbonisation	days	400-500	very slow	char
Slow	4-8 minutes	400-700	*1-5°C/s*	gas
Fast	1-5 seconds	500-950	*100-300°C/s*	tar
Flash-liquid	<1 s	450-750	> 1000°C/s	tar
Flash-gas	<1 s	>750	> 1000°C/s	gas

4.5 Pyrolysis reactor types

Technologies of energy conversion through pyrolysis are still being researched, although there are several examples of industrial plants for the treatment and disposal of waste involved with this process. New types of reactors have been developed for the production of specific products of pyrolysis, each with different characteristics, depending on the plant, to maximize the quantity and quality of the product, paying attention to cost reduction and environmental impact.

A pyrolysis plant is generally divided into the following sections:

• A section for the supply and storage of biomass. In this section there are systems for the preparation of biomass such as shredders (blade, rotating, mills) for size-reduction of particles and dryers for decreasing the moisture content inside biomass. The supply of biomass is usually provided by cranes or similar equipped baskets which download biomass in special hoppers followed by a section of screw conveyors that prevent flame and air infiltration;

• A section for heat treatment. At this stage the transfer of heat to biomass is carried out in special reactors. There are various configurations of reactors according to the specific operating conditions of the pyrolysis product. The most commonly used, because of the flexibility of the fuel and well known technology is a rotary kiln reactor, but fluidised bed reactors are also used. The rotary kiln reactor will be explained later in detail.

• A section for the treatment of products. Here the gas is cooled (quenching) and washed with water. Then it passes through a system of dust removal (cyclones, electrostatic filters, a sleeve) and acids (washing soda). The line continues with a primary filter to remove hydrogen sulphide and at the end to reduce organic carbon compounds of complex molecules in these elements. To prevent condensation, the temperature of gas is lowered to about 5°C below dew point. Char is extracted through a cyclone with ashes. The efficiency of separation in a cyclone depends on the amount of char recovered, especially if the produced char is used as a fuel in the process. The condensation of liquids has been the biggest problem for a long time because of the nature of the product which is mainly in the form of aerosol vapour. In the cooling process, for example, the contact with cooling liquid is carefully controlled by temperature to prevent it from blocking the process of condensation. Electrostatic precipitation is considered very effective in recovering aerosols.

The equipment used in the process can be generally grouped into the following types depending on the type of pyrolysis.

In the case of slow pyrolysis, the equipment used includes:

• A fluidised bed reactor;
• Rotary kiln reactors.

The equipment for fast pyrolysis and flash pyrolysis includes:

• A fluidised bed reactor;
• A rotating cone reactor;
• An ablative pyrolysis reactor;
• A pyrolysis reactor vacuum.

According to the scope of this thesis, only a rotary kiln reactor will be described in detail.

4.5.1 Rotary kiln reactor

Rotary kiln reactors (Fig. 36) are used primarily for the disposal of waste from industrial sources, and only recently for the conversion of biomass energy.

A rotary kiln is basically a cylinder made from sheet steel, usually with a little inclination (usually 1 - 10°) to promote the advancement of biomass, covered internally with refractory material to protect the metal casing from high temperatures. Where biomass is loaded, specially prepared dampers prevent the entry and exit of gas during feeding. On the downstream side of the reactor is a combustion chamber for gas products.

The heat exchange is faster when biomass is directly in contact with the heated wall of a kiln. The efficiency of the contact can be increased by the introduction of internal elements such as horizontal and vertical sledge which carries the material up and then drops it.

The residence time required for the energy conversion is related to the size of a reactor (volume and length) and the type of the used biomass.

The heat exchange inside a reactor is quite complex and there are many studies regarding this issue. Depending on different types of motion, rotation speeds, degrees of filling, types of used material and sizes of particles optimization must be carried out [32].

Rotary kiln furnaces are used for very slow pyrolysis because of a high degree of mixing that allows the efficient exchange of heat and a considerable flexibility regarding the size and type of used material.
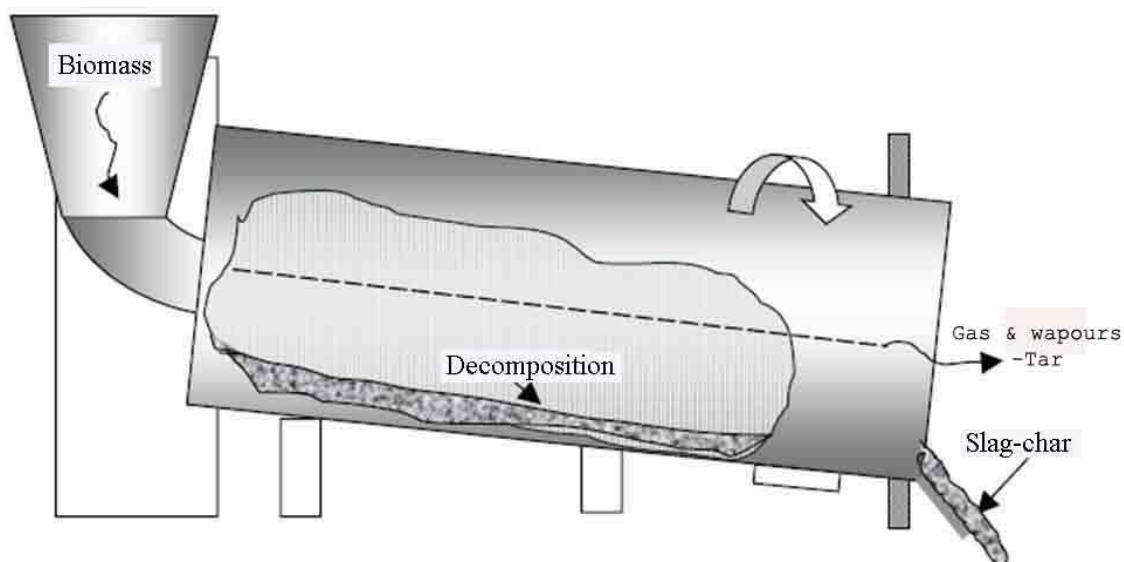
Figure 17   A scheme of a rotary kiln reactor [33]

5 LABORATORY OF SLOW PYROLYSIS PLANT

5.1 Layout of laboratory

The laboratory for pyrolysis at the Department of Industrial Engineering at the University of Perugia, Italy designed and developed a slow pyrolysis rotary kiln demonstration plant to support and provide the basic knowledge for the future development of IPRP (Integrated Pyrolysis Regenerated Plant). The demonstration plant provides a higher degree of confidence in using rotary kiln reactors in the field of small power range of 30-100kW and in terms of yield, composition and energy content of products. Depending on the particle size and nature of biomass, the pyrolysis temperature and the residence time of the biomass inside a reactor must be taken under consideration for the optimisation of the process.

The project specifications must be sufficiently flexible to take into account:

• The experimental demonstration plant has the dimensions of 2500 x 1500 mm and is placed inside a laboratory;
• the variety of feed material (biomass, waste plastic, tires) and its particle size (it can vary up to a maximum linear dimension of not more than 3 cm);
• the change in the range of temperatures between 400 and 700°C, to reach the optimal ratio between the amount of syngas and its calorific value;
• the residence time in a reactor;
• the ability to continuously vary the angle of inclination of a rotary kiln;
• the changing rotation speed of a screw conveyor for feeding a reactor;
• the possibility to transport the unit to use it, if necessary, with an internal combustion engine outside a laboratory;
• the need to constantly monitor temperature, flow rate and calorific value of the syngas product (a need for a combustion chamber and a data acquisition system). The purpose of this unit is, in fact, to derive data of mass and energy balance for different types of materials in terms of the yield of products and their energy content with particular attention to syngas.

The schematic figure of the pyrolysis laboratory with all its operational sections is shown in Figure 18. and presented in Table 7.

A variable amount of biomass is continuously loaded in a hopper and then carried out by a rotating screw conveyor inside a cylinder or the reactor system powered by an electric motor connected by chain. The rotation speed of the screw conveyor can be adjusted from $0 - 1$ rpm (rotation per minute) according to the need of biomass inside the reactor. A second electric motor is used to power and rotate the rotary kiln reactor at the constant speed of 3 rpm. The two ceramic shells wrapped around the cylinders are electrical resistors, providing the necessary heat for endothermic reactions of pyrolysis.

The end products of pyrolysis in the exhaust part of the reactor are separated according to their physical state. Char (solid) is transported through a post in the lower section of the exhaust and is collected in a special storage container. Volatile components (tar + syngas) converge, crossing the upper end of the discharge section where ash and dust are separated according to their size. Subsequently, gas is pumped out through a blower, passing through a consecutive system of filters. Syngas is cooled down in a water scrubber and washed (showered) in a bubbler. Here syngas is separated from tar (heavy and light) and water. Before the syngas reaches the compressor, the system of filters and separators prevents any damage being caused to the intake system due to the presence of drops of water or residual

tars in syngas. Clean and cold syngas is safely burned in the combustion chamber. The exhaust gas from the combustion chamber is conveyed to the chimney. The entire system and data collection is provided by a remote PC with a capture card that allows us to monitor the process outside the box containing the plant and thereby ensuring the ability to work in conditions of absolute security.

Table 7. List of laboratory demonstration pyrolysis plant components [33]

N°	Component	N°	Component
1	Hopper	27	Pressure security regulator
2	Screw conveyor	28	Gas compressor
3	Screw conveyor water cooling circuit	29	Inverter control engine for compressor
4	Electric cooling pump for screw conveyor	30	Pressure security regulator
5	Cooling nozzles circuit of screw conveyor	31	Flow-meter
6	Motor speed reducer	32	Gas flow signal
7	Engine gear of the screw conveyor	33	Safety valves
8	Transmission chain	34	Safety valves
9	Rotary kiln reactor	35	Pressure gas regulator
10	Electrical heaters from ceramic shells	36	Burner
11	Power switch for electrical heater	37	Outlet pipeline safety valve
12	Thermoregulator of electric heater	38	Pilot (methane)
13	Discharge section of char	39	P.I.D. Thermoregulator
14	Char discharged	40	Pressure air regulator
15	Storage for char	41	Blower valve to syngas burner
16	Thermocouple	42	Pressure regulation for the air directed to the burner
17	De-ashing device	43	Flange calibrated measuring air flow
18	Scrubber for cleaning gas and condensation of tars	44	Air flow signal
19	Secondary tank for light tar storage	45	Fan control
20	Tars stockage	46	Computer - PC
21	Cooling radiator	47	I / O interface
22	Electric pump for water cooling circuit of scrubber	48	DAQ equipment
23	Radiator of cooling water for cooling circuit of water Scrubber	49	Temperature measure
24	Filters to remove water in syngas coming from Scrubber	50	Serial Interface
25	Electric pump for water recirculation loop of Scrubber	51	Presetting for safety valve pyrolysed
26	Filter and demister	52	Motor for the screw conveyor
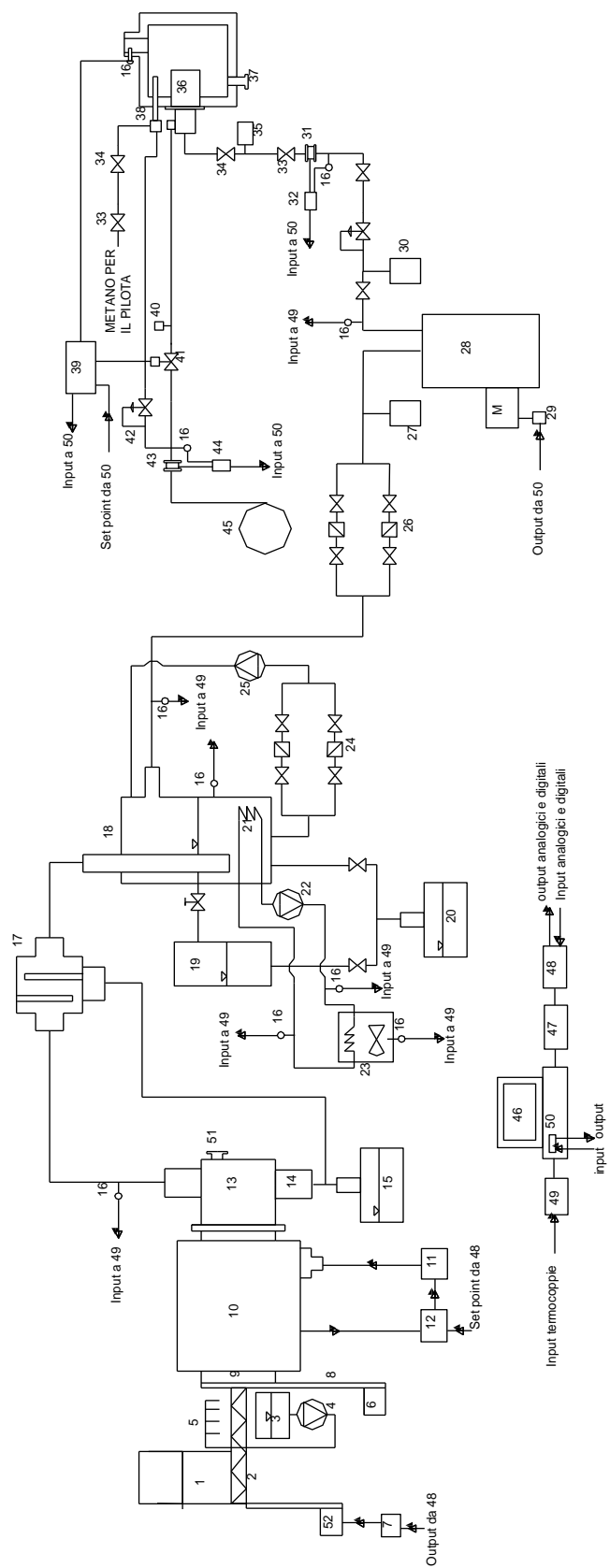
Figure 18   A scheme of the pyrolysis laboratory [33]

5.1.1 Security box

In order to ensure the safety of the personnel the plant is isolated. The whole plant is set inside a closed rectangular security box (215x530 cm) with the task of preventing harmful gases (CO, CH$_4$, H$_2$) from spreading into the "work environment", to isolate the noise made by the plant and to isolate any potential fires which could start up during the pyrolysis process.

Inside the security box a ventilation system was installed to enable sufficient air exchange (Figure 19) with a fan (Figure 20) of the maximum capacity of 7500 m^3/h which expels gas to the external environment and creates a vacuum inside that allows the return of fresh air through a separate ventilation grid.

For the detection of any toxic gases (CO) and flammable gases (CH$_4$, H$_2$), this unit is equipped with an external detecting box and connected to two sensors for measuring gas concentrations (Figure 21). In case a dangerous concentration of toxic or flammable gases is detected, an audible alarm goes off and warns the personnel to use safety precautions (use the ventilation system, a gas mask and fire extinguisher).

Figure 19.   Ventilation system
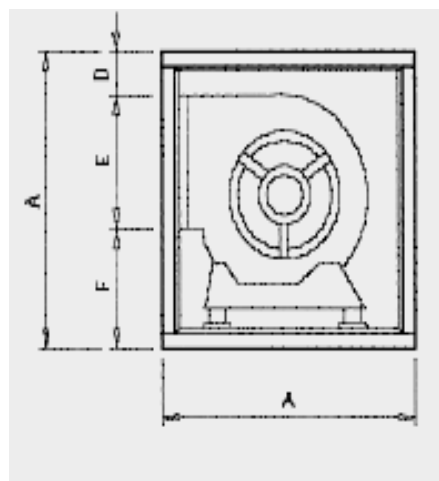
Figure 20.   *F*an intake system

Figure 21.   *External gas detecting box and panel unit for gas detection*

5.1.2 Skid support

The need to have the possibility to transport the paralyser outside of the laboratory led to the realization of skid support and a mobile frame which is equipped with wheels for easier transportation. It consists of two parts: one fixed and one mobile. The bottom frame is fixed and is connected by two hinges to the second, mobile part. The second frame caries a welded support section of the cylinder containing the screw conveyor, the rotary kiln and the discharge section. The presence of the two hinges allows us to vary the angle of the reactor up to 6° from the horizon so that it can act as an additional parameter. Rotation speed control of the screw conveyor can adjust a residence time of biomass inside the rotary kiln reactor in order to achieve an optimal progress of the various products formed during pyrolysis process.
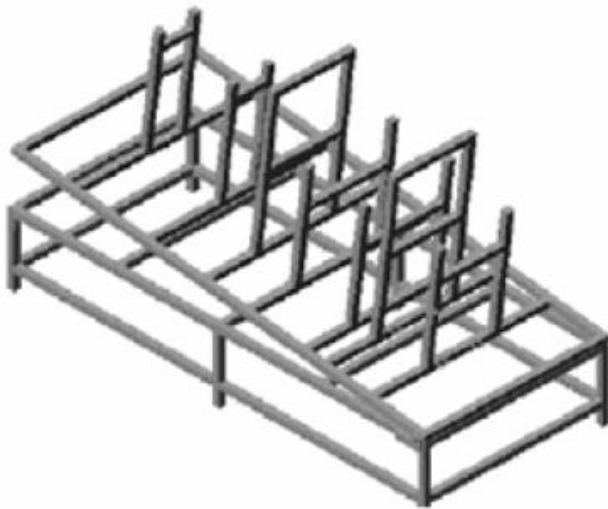
Figure 22.   Mobile skid support

Because of high temperatures and the large diameter of the cylinder of the rotary kiln, special rotating discs were constructed.
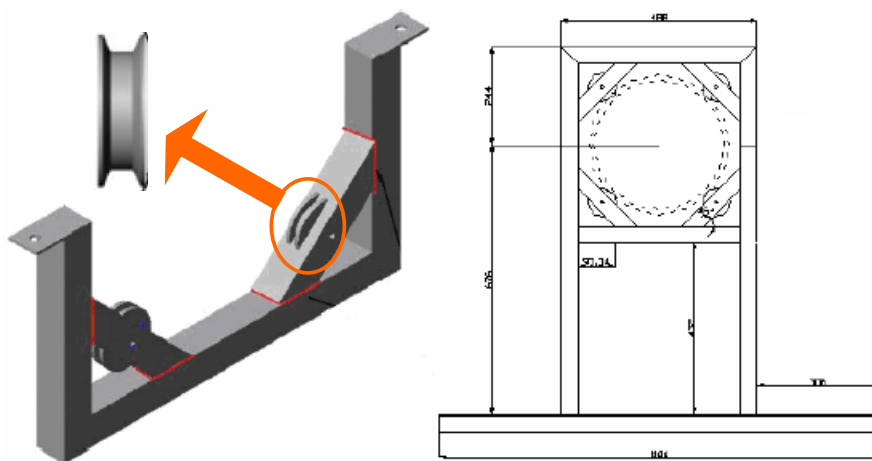
Figure 23.   Support section of the rotary kiln reactor

5.1.3 Power supply system

The power system consists of a hopper with a volume of 128 dm^3. The hopper is sealed on the top to prevent air from entering and thus to avoid burning in the reactor. In order to be able to work continuously it has a double shutter system (Figure 24) which consists of a sliding plate that divides the room into two volumes of 64 dm^3. That allows the hopper to operate continuously without the danger of air entering into the reactor.
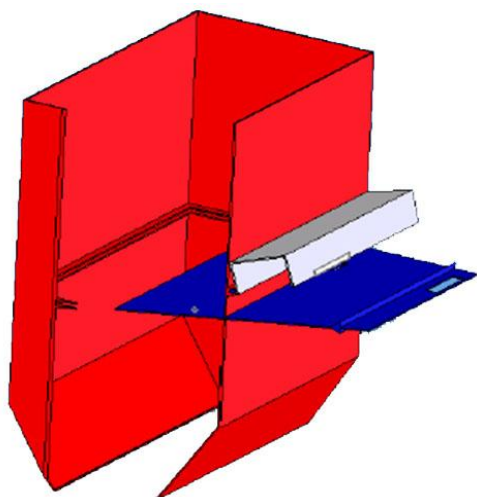
Figure 24. Double shutter operation system of hopper

The biomass transport system consists of a screw conveyor adapted to operate continuously and with materials of different sizes and compositions. The canal is a tube containing stainless steel with an external diameter 168 mm, thickness of 2 mm, length of 100 cm and shaped in such a way that allows the hopper to be fitted to the top part of the tube. That allows for the use of various biomasses with the maximum size of 30 mm to avoid the need for the reduction of biomass.
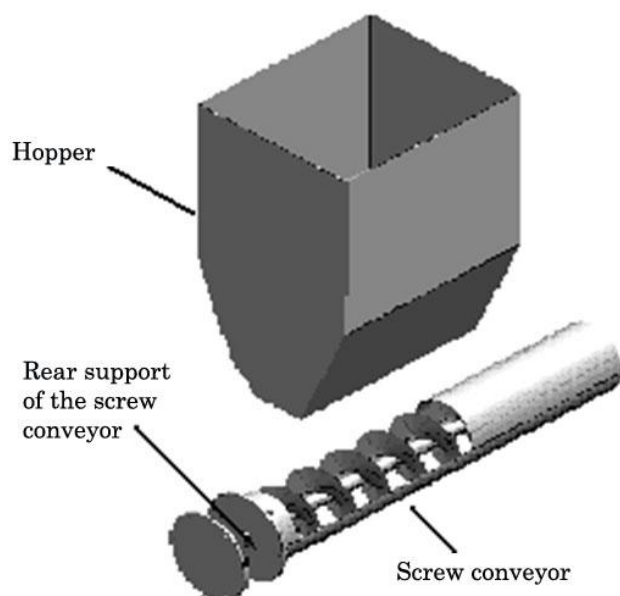
Figure 25.   Coupling screw conveyor - hopper

5.1.4 Rotary kiln reactor

The rotary kiln reactor offers the possibility to work with different types of material, ensures a better mixing of biomass inside the reactor, better residence times and high heat exchanges in favour of pyrolysis reactions.
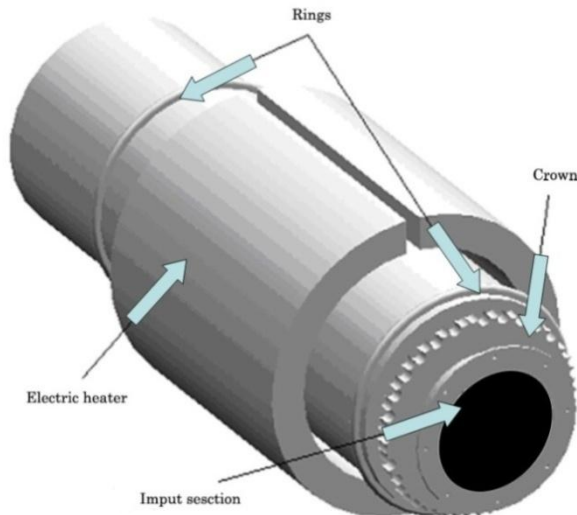
Figure 26.   Front view of rotary kiln reactor

This technology was designed to maximize the yield of syngas which is then supplied to a gas burner (microturbine, internal combustion engine).

The outer diameter of the reactor is 325 mm, a measure of compromise between the size of the fuel and those diameters that are commercially available for heating. The thickness is 3 mm. The length of the reactor is 1000 mm in order to reduce the clutter and, simultaneously, to ensure an adequate residence time for the biomass it will contain.

The reactor is made of stainless steel. On the inner wall of the rotating cylinder four lugs were welded throughout the whole dimension of the reactor (Figure 27). Their function is to achieve continuous mixing of the material and to increase the contact time between the material and the hot surface of the rector.
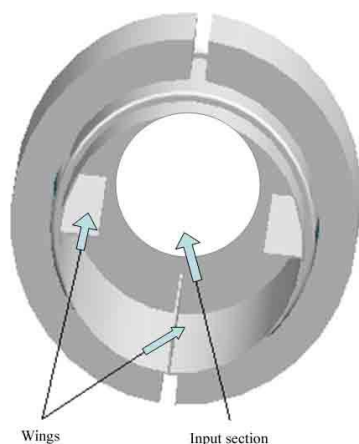
Figure 27.   Rear view of rotary kiln reactor

The rotary kiln is connected to the valley with a coaxial cylinder where the separation of char (char and tar) and syngas takes place. The upstream part of the reactor is partially enclosed by a thick disc.

5.1.5 Heating system

The heating system consists of two ceramic shells wrapped around cylinders. These are electrical resistors which provide the necessary heat for endothermic reactions of pyrolysis. The shells are wrapped around the rotary kiln leaving hollow air of about 15 mm on the radius around it as required by the manufacturer's specifications. These elements are made of ceramics in such a way that they limit the leakage of heat to the outside. Additional insulation of thermal wool was added along the surface to decrease heat losses.

Table 8. Construction characteristics of electrical shells [34]

Inner diameter	356 mm (14'')
Outer diameter	457 mm (18'')
Length	457 mm (18'')
Nominal power (W)	4200 (each)
Voltage (V)	240
Current (A)	35
Power density (W/cm^2)	1,6
Maximum operating temperature (°C)	1204

The components of the electrical connections are coated with special insulation to ensure their thermal and electrical non-conduction. The control and temperature regulation occurs through a thermoregulator Watlow 935 A which consists of a digital display, a temperature sensor (thermocouple) and two outputs. The thermolregulator is used to input the values of temperature set by the remote unit (PC).

Figure 28.   *Thermoregulator Watlow 935 A*

5.1.6 Exhaust part of reactor

Pyrolysis products (char, tar, syngas) created in the reactor are separated at the discharge section of the reactor. The exhaust system is fixed and anchored to the frame while the cylinder of the reactor is mobile. At the bottom section the discharge of char occurs naturally through a stainless steel container placed below the exhaust part itself. The exhaust part of the discharge section for char is sealed with a double shutter system to prevent intake of air while char is released into a closed stainless container. The sealing system between the separate parts of the plant is vital for pyrolysis. If the ambient air (oxygen) enters the pyrolyser, which is heated above 400°C, it can cause combustion and loss of energy in the form of gas.
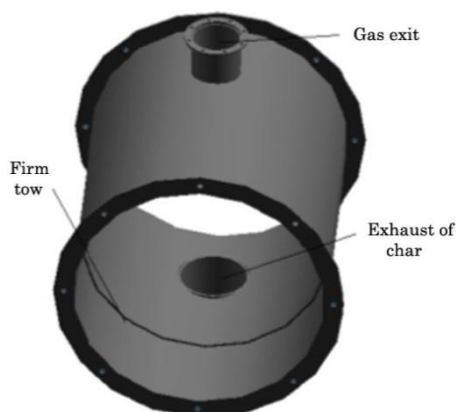
Figure 29.   Exhaust section of reactor

The gaseous products are extracted from the compressor located downstream from the plant and injected through a tube placed at the top of the discharge. The syngas with proper composition is led to the gas burner, which measures the LHV of gas. If gas does not contain a sufficient heating value it is automatically discharged into the atmosphere through the discharge tube.

On the surface of the electric heater, a water scrubber, and inside the reactor, thermocouples are installed to monitor trends of temperature during the pyrolysis process.

5.1.7 Gas washing section

From the reactor, the exhaust gas passes through a tube placed above the cylinder to the first section of the syngas cleaning – essentially a de-ashing device- for removing dust and heavier particles.
This element consists of a rectangular calm chamber which is made of steel and closed by a top plate. Gas, going inside the box, impacts the wall; ashes that are deposited on the bottom of the dust container drop.
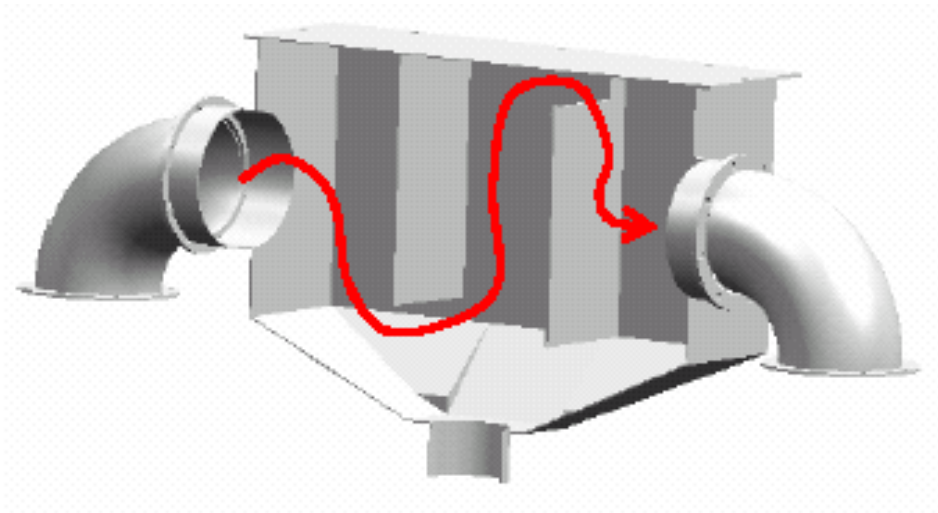
Figure 30.   De-ashing device and path of smoke within[33]

Dust is collected through a flange of wet scrubbers designed to cool the gas, which enters at around 500°C, down to a temperature output of about 50°C. Gas flows through the same condensation in which water vapour and tars are present.

Construction characteristics of water scrubber

This system consists of a vertical cylinder that is placed where a series of three different stages of washing occurs. First, gas passes through a calm chamber. The depression created downstream from the intake system gurgles throughout the cooling and condenses the water vapour and tars. Later, gas passes through three sieve plates, offering a large surface area for contact between gas and water from the spray cap which is placed on the cylinder.
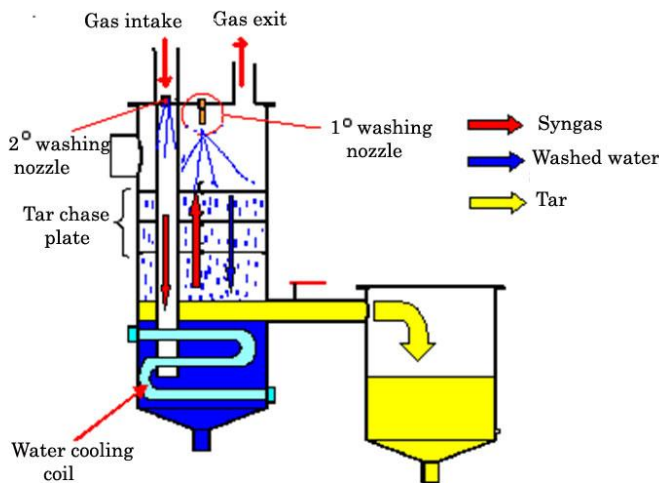
Figure 31.   Configuration section of washing bubbler-scrubber [33]

In the water scrubber, gas is "washed" with water sprayed from the nozzle placed below the lid of the cylinder and is fed by a pump, the scope of which is 1.5 m^3/h.
Rinse water is cooled by a cooling circuit that uses a car radiator which is immersed in water and placed at the bottom of the scrubber. The second spray nozzle, which provides cleaner gas, is placed inside the entrance of the pipe in the gas scrubber, so the gas is pre-cooled

(quenching). In order to maintain the water level in the scrubber, a secondary cylinder is added and connected to the first one. After opening a tap, excess water due to condensation of the gas and light tar, as such, remains afloat. Heavy tar is deposited on the bottom of the cylinder and is removed at the end of the process. Clean gas leaves the system through a tube attached at the top of the outer wall of the cylinder and is later drawn from the compressor.
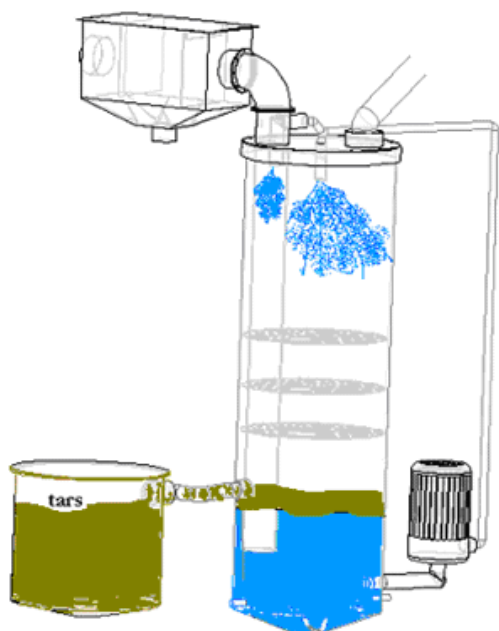
Figure 32.   3D configuration section of washing bubbler-scrubber [33]

5.1.8 Required systems

The proper development of anaerobic pyrolysis reactions requires a lack of air (oxygen) inside the reactor. Therefore it is necessary to prevent the escape of syngas rich products (CO, H_2, CH_4 and other hydrocarbon gases). To avoid such incidents bound systems, such as special sealings, were installed between the rotary kiln and the discharge section and between the rotary kiln and the feeding system.
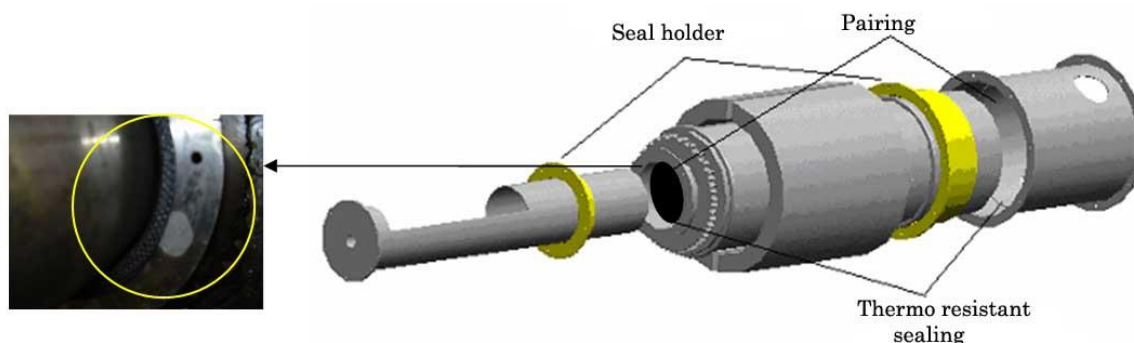
Figure 33.   Rotary kiln joint parts [33]

Due to the process temperature (700°C) it is not possible to use simple lubricated seals. In order to allow relative motion between the materials involved, without excessive power dissipation by friction, and to provide adequate resistance to high temperatures (500 - 700°C) and to an acidic environment, special seals were used. Glass fibre and pure graphite (99.9%) fibre, in which the particles of graphite are firmly locked between fibres, act as a lubricant and as a blocking agent to prevent losses. The seals are made of graphite yarn with minimum purity of 99%, which are treated with a corrosion inhibitor and pure graphite powder, suitable for temperatures of 250-450°C and aggressive environments. The low coefficient of friction makes it possible to rotate with minimal effort.

These elements are housed in special rooms, one upstream and one downstream, in order to seal the reactor and all sub-parts and prevent air from getting access. The use of sufficient amount of graphite sealing not only stops air infiltration, but also decreases the friction between the rotating reactor and the fixed screw conveyor tube which could lead to a serious overload of the electrical motor.
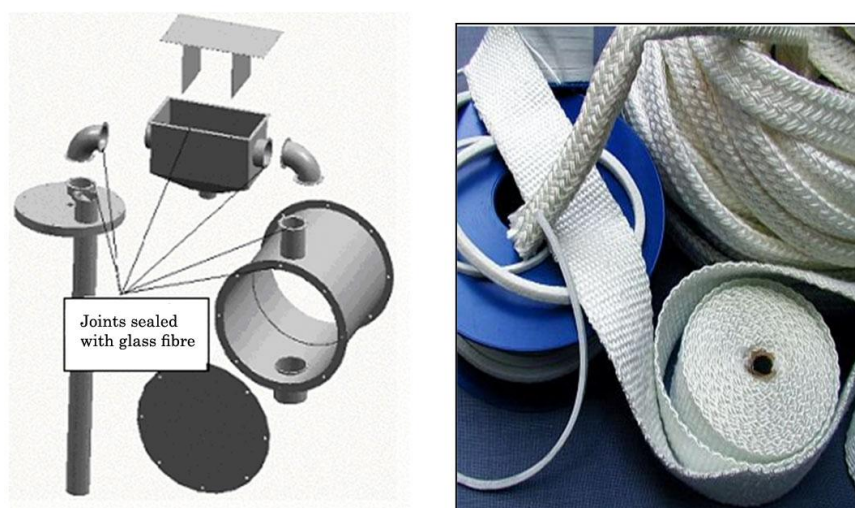
Figure 34.   Flanged joints and related fittings, glass fibre

5.2   Pyrolysis gas line

The experimental nature of the demonstration micro pyrolyser aims to achieve a high degree of confidence with respect to slow pyrolysis in micropyrolyser, to explore the limits of the system and study various end products of pyrolysis. A step further will be a continual production of syngas sent directly to the gas burner to determine the calorific value and scope in terms of operating parameters. This could lead to the use of syngas in an internal combustion engine.

5.2.1 Layout of pyrolysis gas line

The body of the burner is placed in the bottom of a rectangular box, close to a window and a passage of evacuation smoke pipe.
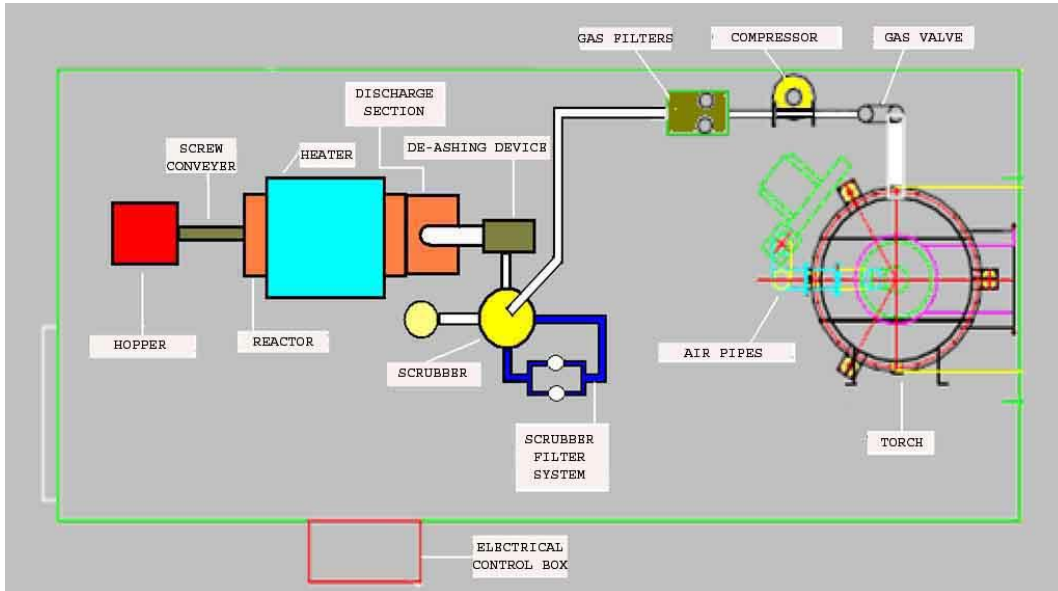
Figure 35.   Layout of the gas line [33]

5.2.2 Compressor suction

This element has the task of creating a slight vacuum inside the reactor so as to facilitate the gas flow to the burner down the pressure drop it encounters along the way, starting with dust passing through the wet wash section until it reaches the condensational splitter. The pressure drop should be between 35 – 100mbar. The compressor has a constant volumetric flow. Inside the compressor two safety pressure valves are inserted whose goal is to stop the compressor engine automatically when the compressor sucks vacuum beyond the settings. In these circumstances the safety valve opens automatically and gas is relisted.

Figure 36.   Compressor filters

The compressor is characterized by side channel blowers which provide higher pressure than normal centrifugal fans. The machine increases the pressure (in the case of blowing) or depression (in the case of suction) of fluid.

5.2.3 Gas burner

The body of the combustion chamber (Figure 37) is internally coated with a refractory material in order to observe the flame.

The gas burner (mod. 24XNM of Esapyronicss), installed on the ramp gas, is a burner with medium speed and nozzle mix type whose characteristics allow the construction to work in a stable flame. The management of the plant-burner XNM's excess air is carried out by maintaining a constant volume of gas fuel through the modulating valve set on the leading fuel and with a constant supply of air. The burner's pilot is always on to ensure the ignition of the gas-air mixture where the composition is within the limits of the flame. The burner's pilot uses natural gas at the pressure of 50 mbar and with the capacity of about 2000 kcal/h. The driver is in fact a burner with an independent programmer and electrode ignition and detection of its flame. The burner works with excess air provided by a centrifugal fan with medium pressure. A PC thermoregulator through the thermocouple regulates the valve for the exhaust gas so that the temperature inside the chamber remains constant.

Figure 37.   Pyrolysis torch and gas burner 24XNM Esapyronics

In case of blockage or creation of overpressure inside the pyrolyser, a second line drawn through a safety valve was provided. It goes directly to the discharge section of the pyrolyser, so that the combustion chamber remains in operation by means of the combustion fan.

The burner control is entrusted to a special programmer (model Esapyronics EsaEstro), shown in *Figure 38*, which automatically performs different stages of the operation: the opening of the valves for the gas process which occurs only after the ignition of the flame control and after the flame control automatically locks the main burner. The flame of the main burner can also be ignited by a low percentage of combustible material present in gas and does not block the burner. The same system also runs the flame control.
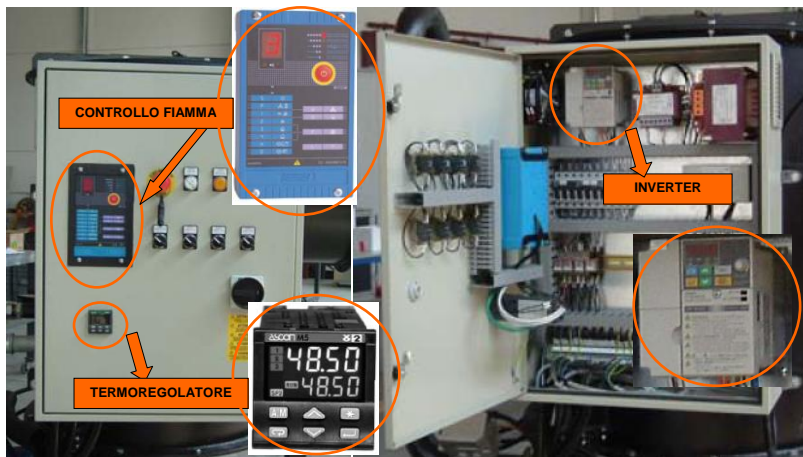
Figure 38. *Cabinet, closed and open (left, right)[33]*

Inside the cabinet, there is also a thermoregulator (Ascona M5) that, through a signal from the thermocouple located at the exhaust, acts directly on the servo valve mounted on the throttle to change the scope of the oxidizing air. The operation is based on the comparison between the temperature measured and the temperature determined as the set point or value. The operating mode is as follows:

• if the temperature of smoke is more than the set point, the thermoregulator will partially open the valve in order to dilute smoke with air, bringing the combustion even further away from the stechiometric conditions;
• if the temperature of the flue gas is below the set point, the thermoregulator will partially close the valve to bring the burning under conditions close to stechiometric.

The control of the compressor engine is made by an inverter (model 3GMV Omron), also present in the cabinet, which, on changing the frequency of the power, allows variation in the number of turns of the compressor and therefore the flow of gas extracted from the pyrolyser. The inverter can be operated both on the machine, using the potentiometer on the front, or remotely via digital signals or serial communications from the PC.

5.3   Measurement system

The system of control and monitoring of the inherent values of the pyrolysis process is outside the box, in which the entire plant is confined, to ensure safe working conditions for operators of the laboratory.

The system has the following aims:

• Management of the equipment necessary for the operation of the facility;
• Obtaining data for the purpose of producing energy.

The electrical signal output from each instrument housed inside the box (thermocouples for measuring temperature, flanges calibrated to measure the flow) and those needed to run the system for vehicle and heating are managed through an external computer system. Specific data acquisition and special software allow the control of the test through the development of the acquired signals and display of real-time results.

5.3.1 Software for management, control and acquisition of data

The program for monitoring the temperature of pyrolysis, for the regulation of the heating system and engine as well as for the management of the serial communication used in the pyrolysis gas line is carried out under LabVIEW 8.0.

This software allows the user to perform the instantaneous representation of the signals acquired and is specially designed for products from the National Instruments hardware, such as the purchasing card. At the same time it is suitable for the management of other communication devices, like the serial ports on the remote computer.

LabVIEW presents a real control panel projected onto the screen and comes with power on / off, LED lights, analog and digital indicators, 2D and 3D graphics which can be managed through input devices such as a computer mouse and keyboard.

The front panel for controlling the laboratory micro pyrolyser is illustrated in Figure 35. The control panel is divided into three separate blocks (orange, blue, green). The orange is for the acquisition of temperature and power supplied to the shells, the green is devoted to regulating the engine and the setting of the temperature of the heater and for final discharge of char.
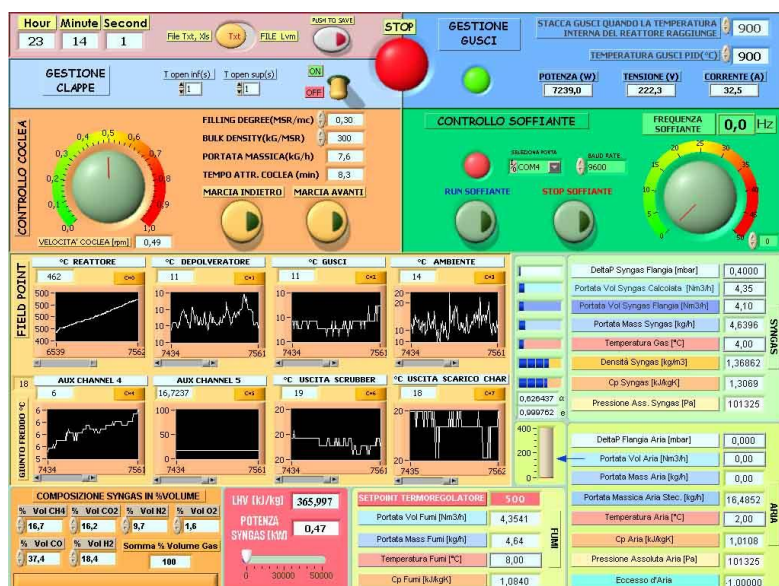
Figure 39.   Front panel for acquisition and data management

The measurement of the temperature is performed through a subroutine feature of the instrument of acquisition (Field Point): The temperatures of the individual channels are saved to a text file divided into separate columns.

The software for the management of the pyrolysis gas line also provides the calculation of the net calorific value of pyrolysis gas.

In particular, the program performs the following steps:

• Questions the gas line via serial and interpretation string read;
• Calculates efflux and compressibility of coefficients;
• Flow determination;
• Calculates specific heat of gas and smoke at constant pressure; determines lower calorific value of gas.

6 EXPERIMENTS

The tests that were performed during the course of this thesis work were:

- A drying test of biomass
- A pyrolysis test with a direct combustion of the produced syngas inside a gas burner

The drying test is a series of tests, all of drying, to determine the efficiency of energy exchange between the shells and the electrically heated reactor. Its aim is to determine the value of the return to the variation of the supplied material and operating conditions, in particular the temperature of the process. The temperature control is based on the actual temperature inside the reactor.

This made it possible to provide enough power to maintain the internal temperature of about 100°C without worrying about the value of the temperature between the electrical shells. The used materials were wood chips from two different kinds of wood (Norway spruce and beech). The second test, pyrolysis with a direct combustion of the produced syngas inside a gas burner, was a step forward in the progress of the previous years. Aimed at optimizing the reactor, it represents a starting point for a series of tests to determine the yields of pyrolysis products of varying parameters. The ultimate goal is to produce a continuous flow of syngas from the pyrolyser, enough to fuel an engine to produce electricity.

6.1 Drying test of biomass

6.1.1 Experimental methodology of drying test

Preparation of biomass

In order to achieve a representative comparison from the literature, two tree species from central Europe were chosen for a detailed analysis. From the coniferous, Norway Spruce (*Picea abies* (L.) Karst.) was used and from the deciduous - European Beech (*Fagus silvatica* L.) was used.

The natural range of the European Beech extends from southern Sweden to central Italy and east to the northwestern part of Turkey. The European Beech commonly fulfils the natural climax forest in Central Europe and is a very popular ornamental tree in parks and large gardens in Europe, as well as North America and New Zealand. Since the early nineteenth century there have been a large number of ornamental cultivars of the European Beech made by horticultural selection. The wood of the European Beech is used in the manufacture of numerous objects and implements. Its fine and short grain makes it an easy wood to work with, easy to soak, dye (except its heartwood), varnish and glue. It has an excellent finish and is resistant to compression and splitting. Milling is sometimes difficult due to cracking and it is stiff when flexed.

The trees were cut down and the bark was peeled off only the spruce logs before chipping. The spruce bark contains just a small fraction of volatiles but a significant amount of ash.

In particular, the chips used in the drying test and later in pyrolysis were brought from the northern part of Slovenia – Koroska (Carintia) as representatives of coniferous and deciduous trees.

Figure 40.   Wood chips of Norway spruce (without the bark), size 10-20mm

The drying test was conducted on 15/12/2008. It began at 15:00 with the supply of electricity to the system and had a duration of 2 hours and 1 minutes.

The rotation speed of the screw was set at 0.5 rpm, fueling the engine with a drag of alternating current frequency of 25 Hz and the reactor, as previously described, was set at 3 rpm.

The optimal conditions for the thermal evaporation, to avoid any signs of pyrolysis, gasification or combustion of biomass, were achieved through the internal control mechanism of the reactor using the thermocouple so that when it recorded a temperature of 100°C, the temperature set point, inside the drum, the shells would cease to provide power. Once these conditions were met the chips were fed into the hopper. For the entire duration of the drying test all crucial parameters (internal reactor temperature, power, speed of rotation of the screw conveyor, est.) were monitored and recorded through the control panel made by the management software - Labview.

The first chips came out of the char discharge section about nine minutes after being introduced into the hopper. The dried biomass was collected in the container placed on the electronic balance under the discharge section.

The constant conditions of the biomass mass flow input and output, in a 2 minute window, were reached 30 minutes after the beginning of the test.

After reaching the stable conditions of the mass flow, the test was terminated. From the dry biomass a sample of biomass, done by the Quarter Sampling Method, was taken for a thermogravimetrical analysis (TGA). A detailed analysis took place at the Biomass Research Centre of the Faculty of Engineering, University of Perugia, Italy.

6.1.2 Quarter Sampling Method

In order to prepare a representative sample of the biomass, several norms (prCENT/TS 14778; Methods for sampling, Methods for preparing sampling plans and sampling certificates, Methods for sample preparation) were used. They all refer to sampling the solid material. This is necessary because the characterization of bio-energy solid requires the support of unified methodologies for physical, mechanical and chemical sampling, as presented in [35]
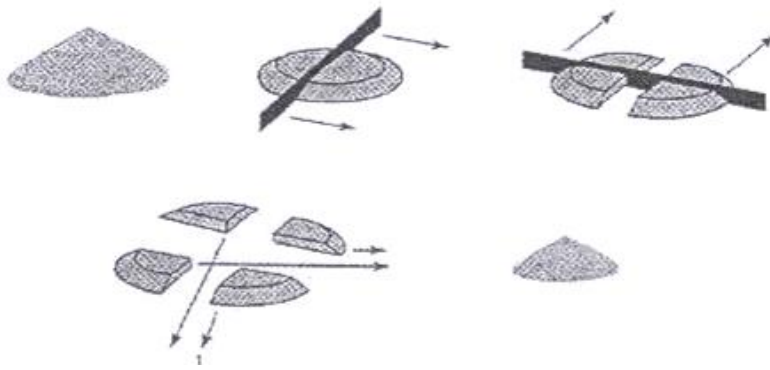
Figure 41. Quarter Sampling Method for sapling the biomass [35]

6.1.3 Analysis of drying test results

The report of the energy balance on the system that consists of a reactor, electrical heating shells and wood chips is expressed in terms of energy production and consumption during the constant mass flow conditions. An analytical expression can directly obtain the value of the parameter in terms of efficiency [η]:

$$E_i \cdot \eta = [(1 - \% U_{in}) \cdot m_{in} \cdot Cp_s \cdot (T_{out} - T_{in})] + [(\% U_{in} - U_{out}) \cdot m_{in} \cdot Cp_{H2O} \cdot (T_{out} - T_{in})]$$

$$+ [\% U_{ev} \cdot m_{in} \cdot \Delta H_{vap}] + [m_{air} \cdot Cp_{air} \cdot \Delta T_{air}]$$

The terms of the equation:

•   The energy absorbed by the dried chips during the transition in the reactor from the room temperature until the temperature of evaporation of the water;
•   The energy absorbed by the water not evaporated to warm up to the same temperature;
•   The energy consumption for the process of evaporation of the water contained in the chips;

For determination of the rate of return η, the following methods of calculation were used:

• E_i = energy supplied to the electrical heating shells.
To calculate the energy which was used as the active power for the entire duration of the constant phase of the drying process. In the time of the constant mass flow, conditions of that value can be easily converted into energy by multiplying the average power for the time of the test in seconds.

• U_{in} = initial moisture, U_{ev} = percentage of the evaporated water.
Once the stable mass flow conditions were reached, both the temperature and the mass flow rate were collected at regular intervals of two minutes. The thermogravimetrical analysis (TGA) of the samples showed the physical characteristics, especially the moisture content, inside the sampled biomass.

This analysis was followed by the European CEN / TS 14774 and CEN / TS 14775 standards on the assessment of the moisture, ash content and calorific value of the treated sample. The TGA was obviously made on a sample of the "original" chips in order to determine the water content before the test drying.

The TGA results were as follow:

Table 9. Test results of thermogravimetrical analysis (TGA) of Norway Spruce (Picea abies (L.) Karst.) and European Beech (Fagus silvatica L.) before and after drying test.

Norway spruce – wood chips, TGA	As received (%)	After the drying test (%)
moisture	30,42	6,92
volatiles (db)	94,29	90,12
ash (db)	0,94	0,38
fixed carbon (db)	4,77	9,49

The analysed spruce contains similar values of volatiles and fixed carbon as per the data found in literature (Table 10).

Table 10. Fuel compositions and heating value, proximate and ultimate analysis of spruce from literature [36]

Sample	Proximate Analysis			Ultimate Analysis						HHV (MJ/kg)
	VM (wt%)	Fix-C (wt%)	Ash (wt%)	C (wt%)	H (wt%)	O[a] (wt%)	N (wt%)	S (wt%)	Cl (wt%)	
Cellulosic fraction:										
Newspaper	88.5	10.5	1.0	52.1	5.9	41.86	0.11	0.03	n.a.	19.3
Cardboard	84.7	6.9	8.4	48.6	6.2	44.96	0.11	0.13	n.a.	16.9
Recycled paper	73.6	6.2	20.2[b] 22.4[c]	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	13.6
Glossy paper	67.3	4.7	28.0[b] 42.7[c]	45.6	4.8	49.41	0.14	0.05	n.a.	10.4
Spruce	89.6	10.2	0.2	47.4	6.3	46.2	0.07	n.a.	n.a.	19.3

• C_{pc} = specific heat of the dry chips.
Not available in literature. The specific heat of the dry chips at constant pressure could be taken from the report of Kofupanes [37] refering to the specific heat at constant pressure at the temperature of the wood chips output (100.39 ° C):

$$Cp = 1112 + 4,85 \cdot (T - 273)$$

The value sought was equal to 1598.9 J/kg K.

• C_{pH2O} = specific heat of water.
This value is available in literature and is equal to 4186 J/kgK.

• ΔH_{vap} = latent heat of water vaporization:
This figure is found in literature and is equal to 2257550 J /kg.

• min = mass of chips in the reactor.

In order to calculate the average mass flow of the wood chips through the reactor, biomass was weighted at the discharge section in two minutes interval. In the equation of energy balance the minimum mass input is connected to the evaporated moisture from biomass.

$$m_{in} = \frac{m_f}{1 - \%U_{ev}}$$

• T_{us} = temperature of the chips in the reactor.

The temperature output of the chips was determined as the average values of the time corresponding to the state of the evidence collected by the thermocouple located inside the reactor. The value was equivalent to 100.39°C.

• T_{in} = temperature of the chips at the entrance to the hopper.

The value of the temperature of the chips inserted in the reactor was obtained by calculating the average of the values recorded by the thermocouple properly positioned inside the security box of the pyrolyser.

• m_{air} = mass flow of air.

The determination of the mass flow of air was carried out according to UNI-10531 (Industrial Fans-Test methods and conditions of acceptance), which defines the methodology for the use of diaphragms and the pressure differences. According to this rule the mass flow was defined as m_{air} sectional average time of the mass of fluid through the cross-section of the pipeline in a time interval. To determine this figure the method of effusion for diaphragms in line was used as:

$$m_{air} = \alpha \cdot \varepsilon \cdot \frac{\pi \cdot d^2}{4} \cdot \sqrt{2 \cdot \rho \cdot \Delta P}$$

where:

• α is the coefficient of the flowmeter in line, in this case, it was assumed as the symbol for the value of 0.739499.

• ε is the coefficient of influence of compressibility and the value is 0.996164.

• d is the internal diameter of the diaphragm equal to 0.01685 m;

• ρ is the density of the fluid upstream of the diaphragm, in this case the value of air density in question was 1.2928 Kg/m³.

• ΔP is the pressure differential measured between the upstream and downstream of the diaphragm. This value was determined by using a plate and found to be equal to 38 mbar.

The result was as follows: m_{air} = 45.43823 kg/h.

• C_{PAR} = specific heat of air;
The figure is present in the rature and is equal to 1010 J/kg K.

• ΔT_{air}.
The temperature difference between air leaving the reactor and air inlet. Reference values were the temperature inside the reactor and the temperature of the safty box. The following value was obtained: 74.96°C.

All values obtained are reported in Table 11 and presented as the energy balance. The different stages of the process in terms of contributions of both energy consumption (chips, air, water and process vaporization), with energy provided (electrical heating ceramic shells) are visible. The summary of the energy balance is presented in Table 12.

Table 11. Parameters of the energy balance

Parameters	Values	Units
Energy supplied to the shells	10,32	MJ
Initial moisture	30,42	%
Final moisture	23,82	%
Evaporated moisture	6,6	%
Specific heat of biomass	280	J/kg K
Final temperature of biomass	103,51	K
Latent heat of vaporization of water	2257550	J/kg
Mass flow rate entering (biomass)	32,46	kg/h
Mass flow rate outgoing (biomass)	30,32	kg/h
Starting temperature of biomass	14,38	K
Mass flow rate of air	9,33	kg/h
Specific heat of air	1010	J/kg K
Temperature inside reactor	97,36	K
Environment temperature	14,38	K
Specific heat of water	4186	J/kg K

Table 12. Summary of energy balance

Energetic Terms	Values	Units
Energy absorbed by biomass	583852	J
Energy absorbed by water (not evaporated)	799407	J
Energy absorbed by water (evaporated)	4836861	J
Energy absorbed by air (in the reactor)	782226	J
Thermal efficiency of the reactor	**0,68**	

The thermal efficiency of the reactor is 68%. Lower humidity of the analyzed biomass caused a lower rate of return of the drying test compared to other tests that were conducted previously. A more effective insulation of the reactor and improved heat transfer inside the reactor can lead to higher thermal efficiency of the reactor.

6.2 Pyrolysis test with direct combustion of produced syngas inside gas burner

6.2.1 Methodology of experimental pyrolysis test

The successful pyrolysis tests were carried out on 16th and 27th of February 2009 with the aim to achieve the following objectives:

- to verify the combustibility of the produced gas;
- to achieve the continual production of syngas in the micropyrolyser
- to burn the produced gas inside the gas burner
- to analyse the products resulting from the pyrolysis process - char, tar and syngas;
- to search for specific improvements that could be made for the pilot plant to optimize the performance of the process according to the results obtained.

Biomass used

The same biomass was used for the pyrolysis after being dried as described in the drying test. To prepare the samples for the detailed analysis the Quarter sampling method was performed.

The biomass was chipped with a professional heavy duty chipping machine to reach homogeneous particle size, since the laboratorical shredder TRITO 25/66 did not give a sufficiently homogeneous quality of the produced particles.

Figure 42. Quarter sampling method – selection of representative part of biomass for analysis, according to the [38]

6.2.2 Test layout

In order to run a successful pyrolysis test with a direct combustion of the produced syngas inside the gas burner, numerous modifications and optimisations were carried out. That included changing all the sealings on the reactor, on the screw conveyor, on the discharge section of char, on the de-ashing device, on the water scrubber, on the compressor, on the hopper, on the water inlet and outlet and a complete isolation of the plant. A safety test was carried out on the gas burner and the pyrolyser with all the joining parts to ensure the complete safety of the equipment and the personnel. Before running any test a visual safety inspection of the plant was performed according to the standard procedure from the safety check list.

The thermocouples were installed to measure the temperatures of the water scrubber, de-ashing device, the electrical heating shells, the ambient temperature of the safety box and to measure the temperature inside the reactor. To be able to acquire the internal temperature of the reactor, an industrial long thermocouple was installed to reach the zone inside the reactor characterized by higher temperatures.

Figure 43.   Thermocouple for measuring temperature inside reactor

The thermocouple located at the water scrubber allowed us to continuously detect the temperature of gas.

Under tight control, the temperature inside the safety box was on average around 15°C, the temperature inside the reactor was at a maximum of 500°C and the temperature measured on the outer wall of the reactor remained at around 715°C.

Outside the laboratory a smoke analyzer was connected to the exhaust gas pipe coming from the plant for thedetection and continuous monitoring of the chemical composition of syngas.

Figure 44. Gas analyser Land Lancom III.

Figure 45.   Connection   of   analyzer   to external piping

For a detailed analysis of the syngas produced by the pyrolysis process a sample of gas was taken. A condenser filled with ice was used for removing the water and tar residue from syngas.

Figure 46.   Condenser   for   removing water and tar residue before sampling gas

Figure 47.   Gas   sampling   bag   with syngas

6.2.3 Description of operational test

The experimental test began on 16th February 2009 at 14:20 with the process of heating up the reactor using the electrical heating shells. By 19:21, when the test officially started and biomass was put inside the hopper, the internal reactor temperature reached 450°C. The test lasted for two hours. The speed of rotation of the screw conveyor was set to 0.65rpm. The rotary kiln had a constant rotation of 3rpm. During the test, 20,2 kg of the biomass was put inside the hopper, but 0,7 kg was not carried away by the screw conveyor. The compressor was set, through an inverter, at a frequency of 25 Hz. During the test the frequency was

increased to 40 Hz to increase the air flow and consequently to decrease the concentration of the pyrolysis gas to avoid gas leakage. After the test additional sealings were added or changed.

The water scrubber was loaded with 18,7 liters of clean water (≈18,7 kg), but at the end of the test 24,07 kg of the mixture of water, heavy and light tar was released in the special container. During the test three different gas samples for a detailed composition analysis were taken by the gas chromatograph.

The analysis results with the mass and energy balance will be discussed and commented upon in detail in the paragraphs to follow.

6.2.4 Results and analysis

The outcome of the test was positively pyrolitic: biomass, through the process of thermal degradation, was decomposed to three expected by-products, tar, char and syngas, as shown in the following figure.

Figure 48   . Pyrolysis test products char, light and heavy tar, test 16/01/2009

Figure 49.   Pyrolysis syngas

The combustibility of the produced gas was constantly checked during the test. The result was a blue flame.

During the whole process of pyrolysis temperature date were recorded. Temperature was measured in several places by thermocouples. The thermocouple from Figure 41was used to measure the temperature inside the reactor. The temperature inside the empty reactor was 463°C when biomass was introduced to the hopper. After that the temperature decreased constantly, since energy is needed to heat up the biomass, to evaporate the water from the biomass and thermal degradation of the biomass in inert atmosphere. After each loading of the biomass(3 times), the temperature inside the reactor decreased, as shown in Figure 49.
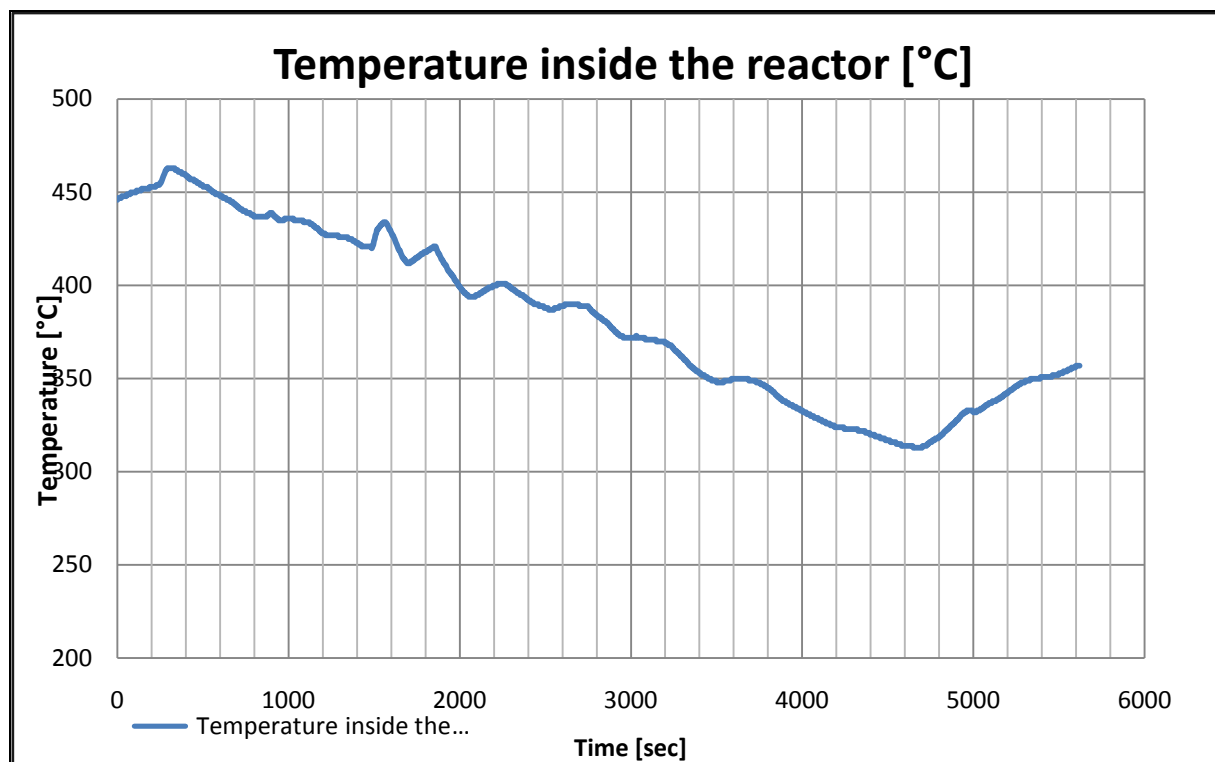
Figure 50. Temperature inside the reactor through the pyrolysis process

The temperature inside the reactor started to increase after all the biomass was pyrolysed and the energy from electric heaters was used to increase the reactor temperature. At that time the test was terminated.

With constant measurement of the temperature of exhaust gases coming from the gas burner, the combustion of the produced syngas was recorded. The combustion of syngas was expressed in the increased temperature of the exhaust gases, shown in Figure 50. Combustion is an exothermic reaction. Combustion of syngas inside the gas burner was also confirmed through the thermoregulator at the electric cabinet with an expressed numerical value -3, as shown in Figure 52. The combustibility of the syngas is reflected in the blue flame (Figure 53.). The direct combustion of the produced syngas took place inside a gas burner for 3 minutes continuously.
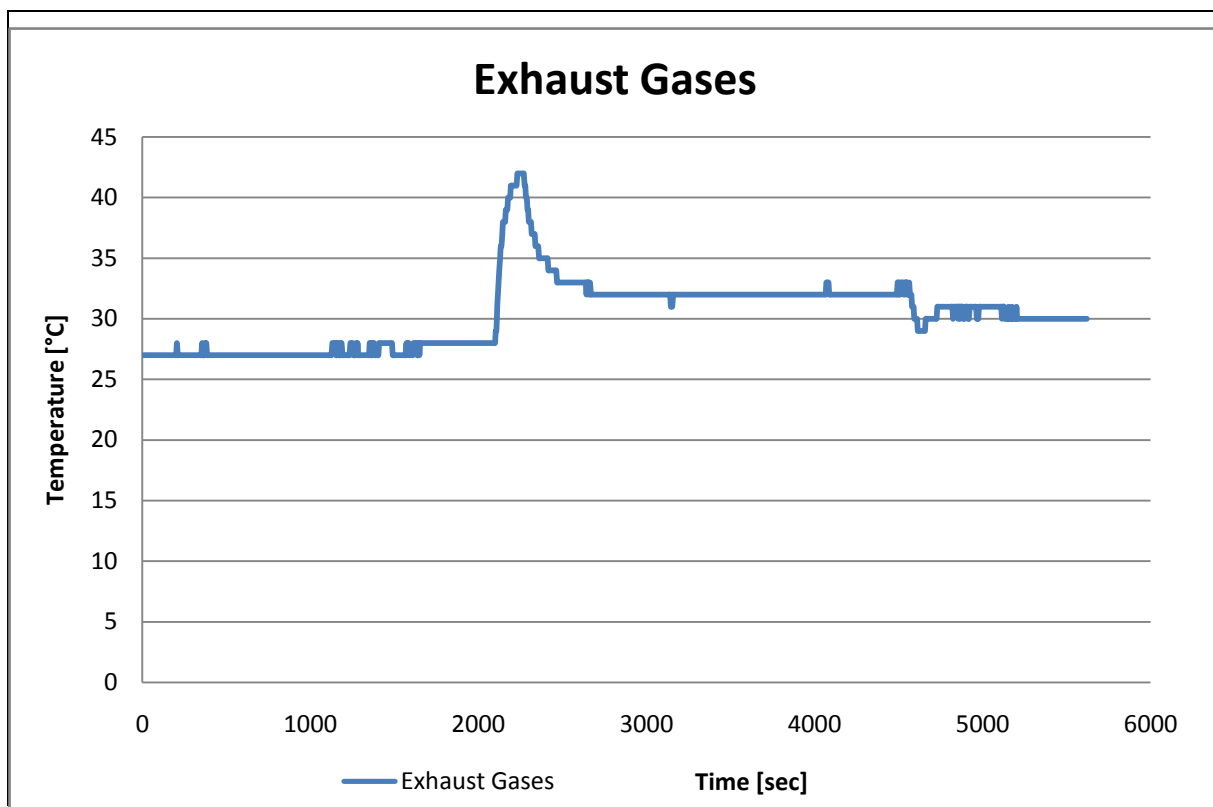
Figure 51 Temperature of the exhaust gases during combustion of the syngas inside the gas burner

A comparison of the temperature inside the reactor and the temperature of exhaust gases on the same graph (Figure 51). The temperature inside the reactor was divided by of 10 only for easier comparison on the temperature scale.
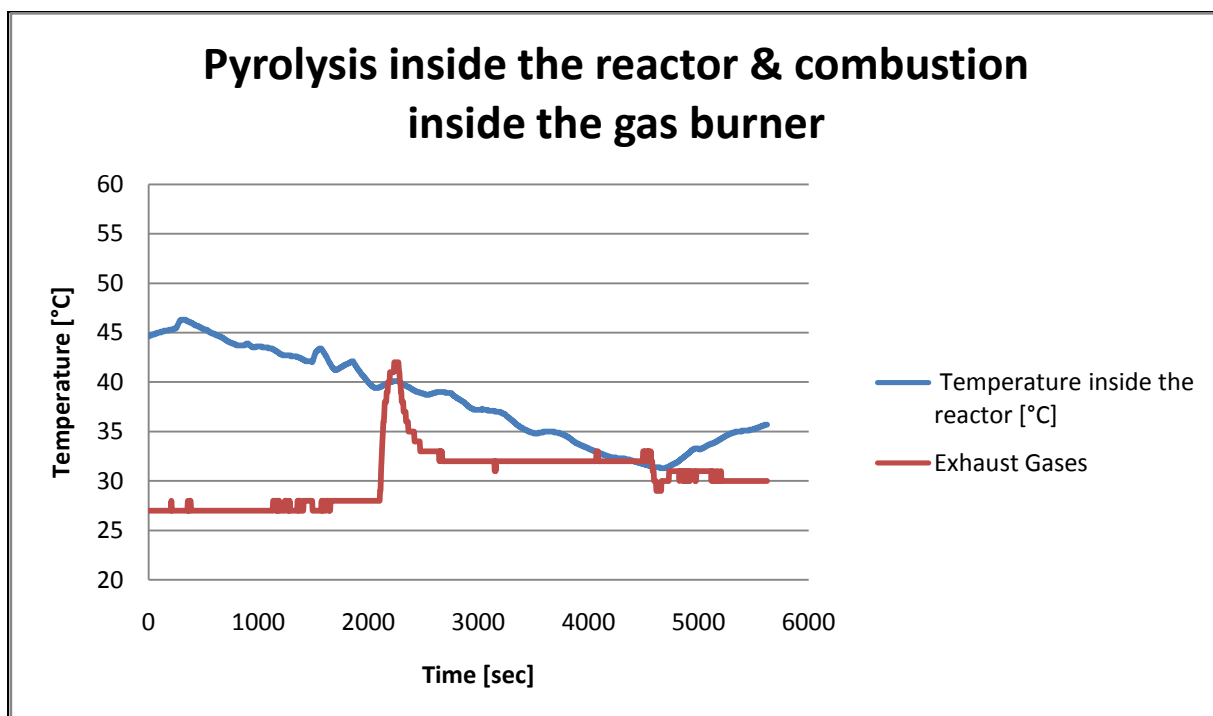
Figure 52. Pyrolysis inside the reactor & combustion inside the gas burner

Figure 53. Combustion inside the gas burner confirmed in the thermoregulator at the electric cabinet, flame control indicates number →3.

Figure 54. Pyrolysis syngas burning

With additional improving of the micropyroliser the test executed on 27th January 2009 confirmed the duration of continuous combustion for 9 minutes.

To obtain not only qualitative and quantitative results but also the products of pyrolysis, a detailed analysis was conducted on a sample of the initial biomass.

THERMOGRAVIMETRICAL ANALYSIS (Proximate analysis)

The sample was heated to 105°C and held at that temperature for a sufficient time to remove the contents of water, and then the temperature was raised to high levels in order to extract the volatiles. Finally the combusted material was taken out to get the ashes and the difference was quantified as a fixed carbon.

The thermogravimetrical analysis (TGA) was conducted from a sample of the initial wood chip biomass and char using the method CEN / TS 14774-14775. The corresponding temperatures were 105°C for moisture, 951°C for volatiles and 550°C for ash. The mass percentage of volatile, ash and fixed carbon are presented on a dry basis (db). TGA was done in the Biomass Research Centre of the Department for Industrial engineering, University of Perugia.

Table 13. TGA of spruce wood chips and char (after pyrolysis process)

| Norway spruce – wood chips, TGA	WOOD CHIPS – before pyrolysis (1x dried) (%)	After pyrolysis – CHAR (%)
moisture	6,92	2,34
volatile (db)	90,12	49,75
ash (db)	0,38	1,34
fixed carbon (db)	9,49	48,91

The results from the thermogravimetrical analysis (TGA) indicate that during the pyrolysis process there was no complete decomposition of wood, since there was still 49% volatiles inside char. That could lead to two possible solutions: to increase the temperature inside the reactor or to prolong the residence time for biomass inside the reactor. To increase the temperature inside the reactor we would need to change the electrical heating shells, since the current ones do not allow a further increase in temparature. For a longer residence time of biomass inside the reactor we should reduce the speed of rotation of the rotary kiln reactor. But as the current electric engine works at a constant speed, a new inverter would have to be installed to possibly to reduce the rotation speed when needed. The simplest solution would be to stop the rotation of the rotary kiln reactor for a short time in intervals.

The moisture content of biomass was less than 7% and a limited amount of energy was needed to remove water out of biomass. The rest of the heat was used to degrade wood in the process of pyrolysis.

Gas chromatograph

During the test, two samples of the produced syngas were taken for a gas chromatograph analysis. The samples were collected downstream from the blower where the gas flow was diverted to pass through a condenser to remove any residual tars and was eventually channelled into sampling pockets.

Table 14.   Gas chromatograph analysis of syngas from spruce (16th of January 2009)

	Molecolar weight	Syngas - spruce [% by vol.]	% by weight	LHV (MJ/kg) [39]	LHV - syngas (MJ/kg)
H_2	2	0,84	0,0572	120,78	0,0691
CH_4	16	1,38	0,7522	50,18	0,3775
CO	28	11,42	10,8935	10,1	1,1002
CO_2	44	8,07	12,0968	0	0
O_2	32	11,08	12,0790	0	0
N_2	28	67,22	64,1211	0	0
∑		*100,0*	100		1,5468 MJ/kg

Table 15. Gas chromatograph analysis of syngas from beech (27th of January 2009)

	Molecolar weight	Syngas - beech [% by vol.]	% by weight	LHV (MJ/kg)	LHV - % weight
H_2	2	1,33	0,0868	120,78	0,1048
CH_4	16	4,10	2,1410	50,18	1,0743
CO	28	18,18	16,6110	10,1	1,6777
CO_2	44	19,40	27,8559	0	0
O_2	32	9,43	9,8497	0	0
N_2	28	47,56	43,4554	0	0
∑		100	100		**2,8569 MJ/kg**

The analyzed gas is very rich in nitrogen (67,22 % - spruce, 47,56% - beech) and, therefore, characterized by a lower calorific value (1,55 MJ/kg – spruce, 2,86 MJ/kg - beech). This is because the intake of air from the compressor is much greater than that of the syngas product. As a result of unintentional leaks and loose seals, syngas is mixed with a considerable amount of air. Table 16 presents the calorific value of gas obtained by "normalizing" the amount of CO_2, CO, CH_4 and H_2 gas as if air were not present (ie neglecting O_2 and N_2), which is in accordance with the anaerobic environment that should be present when producing pyrolysis gas.

Table 16. LHV of theoretical syngas produced from beech in anaerobic environment

	Molecolar weight	Syngas - beech [% by vol.]	LHV - % weight
H₂	2	3,0932	3,7360
CH₄	16	9,5337	4,7840
CO	28	42,2672	4,2689
CO₂	44	45,1056	0
∑		100	**12,7891 MJ/kg**

Theoretically, if the anaerobic environment would be achieved inside the micropyrolyser the produced syngas would have the calorific value of 12,79 MJ/kg, a figure that can also be found in literature. To increase the calorific value of continuously produced gas in a micropyrolyser, the sealing system should be improved.

Mass and energy balance

Mass and energy balance were carried out after approximately one and a half hour of continuous working, after the initial transients expired.

Norway spruce biomass, water and char were evaluated through direct weighting of the yield. The gas yield was continuously measured by a flow measuring device (flange). The tar yield was evaluated as the mass difference between biomass and char, gas and water flows.

Table 17. Pyrolysis products from wood chips of Norway spruce

	In	Out	Mass difference (kg)
Biomass (kg)	19,525	8,120 (char)	11,405
Water in the scrubber (kg)	18,700	24,070 (water + light tar)	5,370
		1,20 (heavy tar)	

Table 18. Test results of thermogravimetrical analysis (TGA) of biomass - Norway Spruce (Picea abies (L.) Karst.), before and after pyrolysis.

Norway Spruce – wood chips, TGA	BIOMASS, dried (%)	Correspondent to 19,53 kg of biomass (kg)	After pyrolysis – CHAR (%)	Correspondent to 8,12 kg of char (kg)
moisture	6,92	1,351	2,34	0,190
volatile (db)	90,12	17,596	49,75	4,040
ash (db)	0,38	0,074	1,34	0,109
fixed carbon (db)	9,49	1,853	48,91	3,971

Table 19. End pyrolysis products

Pyrolysis product:	% of weight	End product, correspondent to initial weight (kg)
Tar	25,70	5,02
Char	41,59	8,12
Syngas	37,95	7,40
Water – from biomass	5,95	1,16
ashes	0,38	0,07
∑	<u>111,57</u>	<u>21,77</u>

The pyrolysis test faced many issues.

During the test the leak of air to the internal part of the reactor, to the de-ashing device and to the discharge section of the char caused combustion of char and syngas. The reason for the infiltration of air was the use of glass fibre sealing that was not airtight. That sealing was replaced by special thermoresistant cardboard. In the next pyrolysis test that issue did not occur.

The internal temperature of the reactor was 460°C when biomass was introduced to the reactor. After introducing biomass into the reactor, the internal temperature dropped significantly due to the heating up of biomass and the evaporation of water from biomass. The initial moisture content of biomass (6,92%) is questionable.

According to the TGA analysis, the char consisted of almost 50% volatiles. That could be the result of a low temperature inside the reactor or too short residence time. The residence time of feedstock in the reactor is a very important parameter in the pyrolysis process because it determines the energy received by biomass at a given heating rate. This parameter strongly influences the yield of the products, given the humidity content and the size of biomass [40]. In order to increase the internal temperature inside the reactor new electric heaters should be installed to increase the power provided to the reactor, with improvements to the isolation.

To increase the heat exchange inside the reactor additional mixing flaps could be introduced on the side walls of the reactor to increase the friction factor. For simultaneous adjustment of the rotation speed of the reactor an inverter with an electrical engine should be installed.

According to the previous drying and pyrolysis tests the homogeneous particle size of small dimensions are the key players in a small scale pyrolysis plant, due to the better heat exchange rate. With bigger particles (>20 mm), the internal pyrolysis temperature must be higher or the residence time must be adapted according to the pyrolysis conditions.

After the pyrolysis test, char, heavy tar, light tar and water were weighed to determine the mass output of the system. Syngas was calculated afterwards. The excess of the mass output (+11%) is due to questionable moisture and volatile matter from the TGA analysis. After the test the water scrubber was completely empted of all excess heavy tar from the bottom of the scrubber, which were the remains of the previous tests. Approximation of this heavy tar was not the case in this test. In the future just after the pyrolysis test the water scrubber will be emptied of light and heavy tar, before the sedimentation of tar to the wall of the scrubber

would occur. Tar is an extremely complex compound, insoluble with most detergents and 90% alcohol, but according to literature can be removed by methanol.

Energy balance

Gas LHV is indirectly derived by measuring gas and primary air temperatures and mass flows, and the temperature of exhaust gases; eventually an energy balance at the combustion chamber was carried out assuming no VOC after combustion. Tar and char LHVs were evaluated through chemical analysis.

Table 20. Numerical values of parameters used in energy balance

Parameter	Value	*References*
P (MJ)	24,027	*Experimentally determined*
η	0,68	*Experimentally determined – drying test*
C_B (J/kg*K)	2567	*Fantozzi et al. [41]*
C_T (J/kg*K)	2500	*Fantozzi et al. [41]*
C_G (J/kg*K)	1100	*Fantozzi et al. [41]*
C_C (J/kg*K)	1000	*Fantozzi et al. [41]*

The energy provided by the electrical heaters ($\sum$ 24,027 MJ) was partly used to decompose biomass, partly to heat residual dry biomass and water vapour, and partly to heat the pyrolysis product as described in [41].

$$E_S = E_G + E_T + E_C + Q_G + Q_T + Q_C + Q_B + Q_V$$

where:

E_S = External energy supplied from time equal to pyrolysis retention time

E_G = Energy used up for gas production

E_T = Energy used up for tar production

E_C = Energy used up for char production

Q_G = Energy absorbed to warm up the gas produced

Q_T = Energy absorbed to warm up the tar produced

Q_C = Energy absorbed to warm up the char produced

Q_B = Energy absorbed to warm up the residual dry biomass

Q_V = Energy absorbed to warm up the vapour

The total energy given by the electric heating shells during pyrolysis retention time was 24.027 MJ. First the biomass (wood chips) was heated to 100°C when energy for evaporation was used. The preparation of biomass for pyrolysis took 7.08 MJ in total. Pyrolysis of biomass was at the average temperature of biomass, 300°C. Totally 14, 235 MJ of an initial 24,027 MJ were derived to pyrolysis end products. 5,712 MJ or 23,77% was recorded as a

heat loss during the pyrolysis process. The heat losses can be minimized with additional isolation of the reactor and the discharge section of the plant.

Table 21. Energy balance of the process

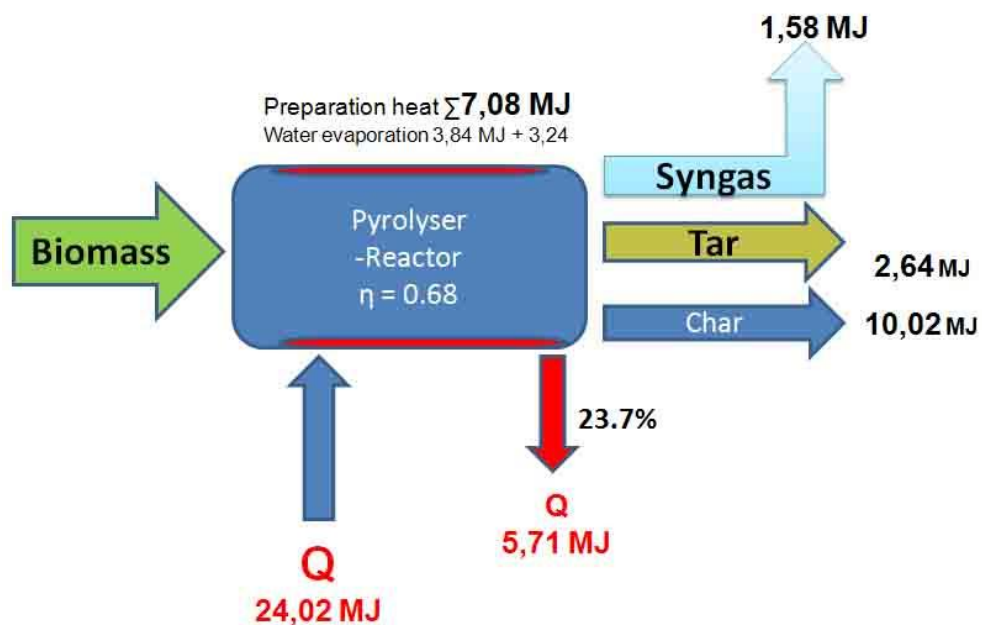|		
E_S	24.027 MJ	
E_G	1.58 MJ	
E_T	2.635 MJ	
E_C	10.02 MJ	
Q_B	3.840 MJ	
Q_V	3.24	
Heat losses	5.71MG	23,7%

Figure 55. Energy balance

7   CONCLUSIONS

The pyrolysis tests carried out on the 16th , and especially the 27th , of January 2009 are very important for the progress of pyrolysis research with a continuous production of syngas in a micro pyrolyser. The results are, without doubt, interpreted in a positive way because not only have they proven the effective combustibility of the gas produced, but they have also highlighted the issues of slow pyrolysis in a rotary kiln reactor, which had to be done to optimize the entire process.

In particular, we could see that the gas sample is mixed with ambient air, leading to a very low calorific value of the gas. That depends on the value of the compressor suction. A reduction in the scale (25 Hz) resulted in an immediate increase in the value of PCI, but further decreasing the frequency of compressor power is quite risky. If the electric motors are working at low frequencies (<30 Hz) they could have problems with overheating and that would require an additional ventilation.

Furthermore, the infiltration of the ambient air into the pyrolyser must be eliminated. Not just because of diluted gas, but also to avoid the phenomena of the internal combustion engine – combustion. To avoid that, a series of actions must be taken:

• improving the sealing of the discharge section of the char with a char collection box;
• replacing the rings sealings rotating between the reactor and the screw conveyor and discharge section for gas and char

Finally a crucial step before reaching the goal of pyrolysis is the usage of homogeneous small biomass particles with low moisture content. To increase the heat exchange inside the reactor, the internal reaction temperature must be higher or with a longer retention time. To lower the heat losses between the electrical heating shells, additional isolation must be added.

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